DEBRE BERHAN UNIVERSITY

COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES

DEPARTMENT OF CHEMISTRY

FIBROUS MANGO PEEL AND SEED ACTIVATED CARBON PREPARED BY $ZnCl_2$ ACTIVATION FOR ADSORPTIVE REMOVAL OF AMOXICILLIN

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POSTGRADUATE STUDIES

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APPROVAL SHEET I

This is to certify that the thesis entitled **"FIBROUS MANGO PEEL AND SEED ACTIVATED CARBON PREPARED BY $ZnCl_2$ ACTIVATION FOR ADSORPTIVE REMOVAL OF AMOXICILLIN"** submitted in partial fulfillment of requirements Degree of Master of Science in Chemistry**,** College of Natural and Computational Science**,** DebreBerhan University and is a faithful record of original research work carried out by Lingerew Ayele Under my guidance and supervision. No part of this thesis has been submitted for any other degree or diploma. It is further certified that the assistance and help received by him from various sources during the course of investigation has been duly acknowledged. Therefore, I recommend that it be accepted as fulfilling the thesis requirements.

Neway Belachew (Ph.D.) _____ _____

Advisor Signature Date

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APPROVAL SHEET II

We, the undersigned members of the board of the examiners of the final open defense by Lingerew Ayele have read and evaluated his thesis entitled **"FIBROUS MANGO PEEL AND SEED ACTIVATED CARBON PREPARED BY $ZnCl_2$ ACTIVATION FOR ADSORPTIVE REMOVAL OF AMOXICILLIN**" and examined the candidates. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirements for the degree of Masters of Science in Chemistry.

Neway Belachew (Ph.D.)	_____	_____
Advisor	Signature	Date
_____	_____	_____
Name of external examiner	Signature	Date
_____	_____	_____
Name of internal examiner	Signature	Date
_____	_____	_____
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DECLARATION

I under signed, declare that this thesis is my original work and has not been presented for degree in any other university and that all source of materials used for the thesis have been duly acknowledged.

Name: Lingerew Ayelew

Department: Chemistry

Signature: _____

Date: _____

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ABBREVIATIONS

AC	Activated carbon
AMX	Amoxicillin
R^2_{Adj}	Adjusted determination coefficient
BOD	Biochemical oxygen demand
Q_e	Equilibrium Adsorption
Ce	Equilibrium concentration
FTIR	Fourier transforms infrared spectroscopy
CO	Initial concentration
pH_{PZC}	Point of zero charge
SD	Standard Deviation
UV	Ultra violet
XRD	X-ray diffraction

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ABSTRACT

When mangoes are consumed or processed, their peels and seeds are generated as waste. Waste is an environmental concern, but it is a natural and renewable resource. In this Thesis, a process was developed to convert mango peel and seeds into carbonized adsorbents. The effectiveness of mango peel and seed-derived activated carbon was prepared for the removal of AMX from an aqueous solution. The formation and composition of the prepared AC were characterized by XRD and FTIR techniques. FTIR analysis identified the presence of O-H, C=C, C-O and C=O on surface of AC adsorbent. The AMX uptake efficiency of AC was investigated at different parameters such as the initial concentration of amoxicillin (10-50mg L^{-1}), contact time (min), and different dosages of activated carbon (0.25-1.25g) through batch adsorption study. The equilibrium information was analyzed using Langmuir, Freundlich and Liu models. The results displayed that the experimental data were well fitted with Langmuir isotherm. Pseudo- first order, pseudo-second-order, as well as Elovichmodels were utilized to analyze experimental kinetics data with a high correlation coefficient for pseudo- second - order model with .obtained with lower SD and higher R^2adj values

Keywords: Adsorption, Activated carbon, Amoxicillin, Isotherm, Mango

1. INTRODUCTION

1.1 Background

Pollution is a discharge of solid, liquid, or gaseous substance or Radiation (energy) into an environment that causes unwanted changes [1]. Pollution causes short term or long term harm that affects the earth's ecological balance and lowers the quality of life in the environment. A pollutant is a substance that changes air, water or any other natural resource in a way that in pairs the use of the resource [1].Water pollution is one of the most undesirable environmental problems in the world and it requires solutions [1].Antibiotics and anti-inflammatory drugs are widely used worldwide for treatments in humans, animals and the agricultural industry. Antibiotics and anti-inflammatory drugs administered are often poorly absorbed and metabolized by humans and animals, and tend to enter water bodies being difficult to recover because of their low concentration and, in large quantities, can cause damage to the ecosystem, degrading water quality [1].In addition, exposure to these and their by-products after transformations in the environment can cause a variety of adverse effects, including acute and chronic toxicity and micro-organisms with antibiotic resistance [2-6].

Amoxicillin is one of the most widely used drugs, 60-70% of which is excreted unaltered, once consumed, it therefore has a negative impact on two levels: during manufacture and during and after use [7, 8].Bio adsorption is a technology that offers the possibility of reducing the concentration of heavy drugs present in liquid effluent, through the use of biomass as adsorbent material. In recent decades, the emphasis of research in this area has been directed towards the research and development of typical and regional biomass, which have excellent adsorbent properties [9, 10]. Activated carbons from biomass and agro-industrial waste provide the products obtained with a high affinity for the removal of substances that wish to be removed from an effluent due to the inherent characteristics of the precursor material and the chemical agent used, This is how activated carbons have multiple applications such as the synthesis of activated carbon from mango peel and seed chemically impregnated with $ZnCl_2$ for the efficient removal of AM from aqueous solutions.

Mangoes are consumed worldwide, and there has been an increasing demand in the past few decades. However, fruits have the highest wastage rate of all foods. A mango's peel and seed consist up to forty percent of its total fruit weight. Since mangoes are abundant in a multitude of countries, a large amount of waste is produced and difficult to dispose of. One possible solution to the agricultural waste and polluted water issues is to convert mango seeds into activated carbon, and use the resulting carbon to remove contaminants from water

Activated carbon (AC) is an amorphous form of carbon that is specially treated to produce a highly developed internal pore structure and a large surface area, thus, producing reasonably cheap and excellent adsorbent [13, 14]. There is a multitude of industrial applications of AC including de colorization, purification and deodorization of vegetable oils and fats, sugar refining and other food industries. Pollution control and wastewater treatment are growing areas to combat environmental pollution through adsorption [13, 15].

Adsorption technology using agro-industrial wastes as an adsorbent in the form of activated carbon is a new emerging option in the treatment of effluents that contain pharmaceuticals like AMX because of its efficiency, ease of operation, and cost effectiveness [11, 12]. Unlike commercially available adsorbents that are expensive [11], activated carbons made from agricultural wastes are cheap, renewable, and abundant [11]. Mango peel and seed coat a by-product of *mango* plantations, is an agro-waste biomass that can be used for activated carbon production. The present study aims at preparing the activated carbon from mango peel and seed for the removal of AMX from aqueous solutions. Effective parameters in the adsorption process including pH, contact time, amount of bio-adsorbent, concentration of pollutant, were studied and the characteristics of prepared bio -adsorbents, isotherms, kinetics and thermodynamics of the adsorption in this investigation were determined.

1.2. Statement of the problem

Pharmaceutical compounds play an essential role in preventing and treating human and animal diseases. Growing population and the search for a cure for new and old diseases have significantly increased. The excessive increase in drug use occurs, an increase in the disposal of these compounds in the environment. These chemical compounds can be released into the environment in a variety of way. After administration; a significant part of the original

pharmaceuticals and its metabolites is excreted through human and animal urine and feces, reaching in domestic sewage, industrial and hospital effluents, soil, and aquatics ecosystems.

The inappropriate disposal of miss used and overpowered pharmaceuticals has contributed to the increase in the incidence of it in the environment. After dispersed to the environment, these chemical compounds can compromise water and soil quality by compromising human and animal health. The presence of pharmaceuticals on domestic and industrial wastewaters was detected in the waters of different countries. Pharmaceuticals are very persistent and poorly biodegradable compounds and may be hazardous in aquatic life even at low concentrations. For this reason, environmental regulatory agencies around the world have given additional attention in monitoring these chemical compounds in waters. There are several treatment methods available that can be employed for the removal of pharmaceutical compounds from aqueous media. Adsorption is considered to be one of the most valuable and effective process to remove various contaminants within wastewater. This method is simple, environmentally friendly and applicable at low cost using mango peel and seed adsorbent materials. In this study, zinc chloride has been extensively used for activating agent due to its ability to produce activated carbon with a high surface area, its distribution of fine pore size under the same conditions, low environmental pollution, less corrosiveness and lower cost and mango peel and seed activated carbon were used for removal of amoxicillin from aqueous water.

1.3. Objective of the Study

1.3.1 General Objective

The general objective of this study is adsorptive removal of amoxicillin using fibrous mango peel and seed activated carbon

1.3.2. Specific objective

The specific objectives of this study were…

- To prepare activated carbon from mango peel and seed using $ZnCl_2$ as activating agent.
- To investigate the surface structure and composition of the prepared activated carbon using XRD, and FTIR instrumentations.
- To examine the adsorption efficiency of the prepared AC for the removal of amoxicillin.

- To study the kinetic and isotherm of the adsorption of amoxicillin onto activated mango peel and seed.

1.4. Significance of the Study

The significance of the current study is introducing an alternative preparation approach for efficient adsorbent for the removal of amoxicillin from waste water by mango peel and seed activating carbon using zinc chloride activating agent which is form high pore structure, low environmental pollution, less corrosiveness and lower cost.

2. LITRATURE REVIEW

2. 1. Adsorption

Water purification or water treatment is the process of removing undesirable chemicals, biological contaminants suspended, solids and gases from water [18]. Purifying water may reduce the concentration of particulate matter including suspended particles, parasites, bacteria, algae, viruses' fungi [19]. Some of the common water purification techniques are sedimentation or settling boiling/distillation, chemicals treatment (precipitation/coagulation/adsorbents), densification and filtration. Sedimentation/settling:-during sedimentation, flocculation settle to the bottom of the water supply due to its weight [18]. Precipitation is also another common technique for removing one or more substances from a solution by adding regents so that insoluble solids appear [18, 19]. This technique is used to for in softening of water as well as to remove impurities like phosphorus, fluoride, arsenic, Ferrocyanide and heavy metals, dyes. Besides, distillation is the most common separation techniques [19, 20]. In this separation technique, the mixed components in water are separated by the application of Heat. It is based on the differences in boiling point of the individual component [20]. Photocatalytic degradation and membrane filtration are the best alternatives currently employed for the advanced water treatment process [21]. Despite, the efficiency of the aforementioned water treatment of techniques, they are not economically wise and some of them are not guaranteed to reduce the pollutants to the minimum permissible limit [29]. Hence, low-cost and environmentally benign water treatment technologies such as adsorption are highly desirable [22]. Adsorption is a process; dissolved contaminants adhere to the porous surface (solid) parts including activated carbon, silica gels, and alumna's zeolites [23]. It is based on the capability of porous materials with large surfaces to selectively retain compounds on the surface of the solid (adsorbent) [37]. There are two types of adsorption; physical and chemical adsorptions

Table 2.1 Differences between physisorption and chemisorptions

Chemical Adsorption	**Physical Adsorption**
Chemical bonding is involved in the interaction between adsorb ate and the surface of the adsorbents	Intermolecular forces are involved in the interaction between adsorbents and the surface of the adsorbents
Highly specific	Nonspecific
Monolayer	Can be both monolayer or multi-layer
Dissolution can occur	No dissociation of adsorbed
Adsorption can occur over a wide temperature range	Occurs at low temperature
Adsorption may be slow and is irreversible	Adsorption is fast and the interaction is reversible
Bonds are formed as a result of electron transfer	No transfer of electrons

Physical adsorption is achieved by Vander Waals forces, dipole interactions, and hydrogen bonding [24]. There is no electron exchange between adsorbent and adsorb ate. Because there is no activation energy required for physical adsorption, the time needed to reach equilibrium is very short. Physical adsorption is a non–specific and reversible process [24, 25].

2.2 Adsorbents from Agro-industrial wastes

Large quantities of agro-industrial waste are generated because of industrial development. A novel attribution of greater added value is given by the application of the residues as adsorbents. Although their removals capacities are usually lower than those of activated carbon, their use in industrial scale is more economically attractive [47]. Besides low cost, higher abundance and availability, the agro-industrial waste adsorbents offer environmental advantages in comparison with conventional adsorbents, including renewable nature and the possibility of partial reduction of the waste. Cellulose is the main contaminant of agro-industrial wastes and the one that most contribute to their adsorption properties. Other important components are hemicellulose, lignin, lipids, proteins, simple sugars, water, hydro-carbons, and starch.

2.3. Activated carbon

Activated carbon is carbon produced from carbonaceous source materials such as bamboo, wood, lignite, coal, and petroleum pitch, etc. It can be produced by one of the following processes:

2.4. Preparative methods of activated carbon

2.4.1 Physical activation

The source material is developed into activated carbons using hot gases. Air is then introduced to burn out the gasses, creating a graded, screened and de-dusted form of activated carbon. This is generally done by using one or a combination of the following processes: Carbonization: Material with carbon content is pyrolyzed at temperatures in the range 600–900 °C, usually in inert atmosphere with gases like argon or nitrogen Activation/Oxidation: Raw material or carbonized material is exposed to oxidizing atmospheres (oxygen or steam) at temperatures above 250 °C, usually in the temperature range of600–1200°C.

2.4.2 Chemical activation

Prior to carbonization, the raw material is impregnated with certain chemicals. The chemical is typically an acid, strong base or a salt [16] (phosphoric acid, potassium hydroxide, and sodium hydroxide, calcium chloride, and zinc chloride). Then, the raw material is carbonized at lower temperatures (450– 900 °C). It is believed that the carbonization / activation step proceeds simultaneously [17] with the chemical activation. Chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating. Activated carbons are complex products which are difficult to classify based on their behavior, surface characteristics and other fundamental criteria. However, some broad classification is made for general purpose based on their size, preparation methods, and industrial applications [17]. Natural materials which are available in large quantities, or certain waste products from industries or agricultural operations, may have potential as inexpensive adsorbents. Generally, an adsorbent can be assumed as low cost if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry. Of course, improved adsorption capacity may compensate the cost of additional processing. Research has already been conducted on a

wide variety of adsorbents. They include walnut shell, waste tea, Turkish coffee, nut shell, exhausted, rice bran carbon have been investigated to remove nickel (II)from wastewater. Reports have appeared on preparation of activated carbon from biomass like soya bean, peanut, pecan and walnut shell. In this study the activated carbon prepared from mango peel and seed was used.

2. 5 Activators in the chemical activation process

2.5.1 Activated carbon preparation through activation with phosphoric acid

Among the activating agents, phosphoric acid with the chemical formula H_3PO_4 is widely used in the activation of various lingo-cellulosic materials [39]. In the reaction of phosphoric acid with lingo cellulose since cellulose is resistant to hydrolysis of acid, at the beginning of the mixing of the compounds the acid first reacts with the cellulose and lignin. Activation with phosphoric acid is used in the preparation of activated carbon from various forms of biomass. Acidic groups are the most derivative of the reaction between phosphoric acid and activated carbon precursor. Activation with phosphoric acid leads to the composition of the phosphorus element in the carbon structure [40]. Phosphoric acid is the most commonly used chemical activator, can produce high porous activated carbon from raw materials and has fewer environmental and toxicological contaminants than potassium hydroxide and zinc chloride. Moreover, phosphoric acid requires a lower activation is not volatile and can form a large number of alkaline or acid-soluble phosphates with elements such as iron, nickel and boron and others that can be incorporated into carbon precursors.

2.5.2Activated carbon preparation through activation with potassium hydroxide

The chemical activation of phosphoric acid and zinc chloride is used to activate lingo-cellulosic materials that have not previously been carbonized, while metal compounds such as potassium hydroxide are used to activate the precursors of coal [41]. Several reports have been presented on the effectiveness of KOH-activated carbon in the adsorption of various organic chemicals such as phenol, dyes, heavy metals and pesticides. OH activator is an activating agent rapidly saturated with precursors and does not evaporate completely, so its activation temperature is generally lower than the boiling point of KOH. KOH-activated carbon has a higher surface area

and pore volume, but typically has lower yield (10–40%) compared to other activators such as $ZnCl_2$ and H_3PO_4 [42].

2.5.3 Activated carbon preparation through activation with sodium hydroxide

Studies show that chemical activation using alkaline materials such as sodium hydroxide and potassium hydroxide produces large amounts of microspores on the activated carbon surface [43]. Sodium hydroxide is widely known as an effective activating agent for the production of activated carbon. The proposed reactions during activation by NaOH are presented in the following equation

$$6NaOH + 2C \rightarrow 2Na + 2Na_2CO_3 + 3H_2 \text{----------1}$$

$$Na_2CO_3 \rightarrow Na_2O + CO_2 \text{----------2}$$

$$2Na + CO_2 \rightarrow Na_2O + CO \text{----------3}$$

The possible reactions between active substances and the surface of the organic precursor result in the creation of micro pores on the activated carbon surface due to: i) the release of CO, CO_2, H_2 gases Esq.[1]– [3], which are produced by Na_2CO_3 decomposition at high temperature and hydroxyl reduction, respectively, and ii) alkali metal intercalation into the carbon structure.. As a result, the evaporation of sodium hydroxide and other compounds derived from activated carbon gives rise to a rugged surface with different pore sizes, indicating that the porous structure is well developed and that these canals are suitable channels for adsorbent materials to penetrate the surface of the activated carbon.

2.5.4 Activated carbon preparation through activation with zinc chloride

Among the activating reagents, zinc chloride is widely used to produce activated carbon, especially lignocelluloses and cellulosic precursors [44]. Zinc chloride acts as a dampening agent for samples impregnated with this material during activation. Movement of volatile substances through zinc chloride-saturated pores is not disrupted, and after that, during the activation process, volatile substances are released from the surface of activated carbon. Increasing the mass ratio of zinc chloride causes easier release of volatile substances, so the absorption of nitrogen increases on the activated carbon ([44].During the activation process, lingo cellulosic

materials are converted into carbon, and hydrogen atoms, oxygen, carbon monoxide, carbon dioxide, aldehydes are liberated, and diatomaceous distillates are produced. Zinc chloride prevents the formation of bitumen and other fluids that block the surface of carbon monoxide and prevent the movement of volatile substances, and volatile substances are subsequently released from the surface of activated carbon [45] Since zinc chloride does not react with carbon, the obtained activated carbon has a higher yield than activated carbon produced with potassium hydroxide In recent years, ZnCl2 have been widely used in the production of low-cost activated carbon [46]. Among the various activators, zinc chloride has been extensively used, due to its ability to produce activated carbon with a high surface area, its distribution of fine pore size under the same conditions, low environmental pollution, less corrosiveness and lower cost.

2.6. Amoxicillin

Pharmaceutical compounds belong to the class of emerging contaminants that have been identified in low concentrations in the environment and that can negatively affect human health and/or ecosystems. Pharmaceuticals especially antibiotics are among the numerous emerging pollutants that have been detected in different water systems. Studies have shown that most antibiotics cannot be absorbed and digested well by living organisms. In general, antibiotics reach water systems through the discharge of poorly treated wastewaters and effluents discharges. The presence of antibiotics in aquatic systems is of concern because of their toxicity to aquatic life and other organisms. Their toxicity may cause a long-term effect on ecological sustainability even if they are present in trace levels. Besides, antibiotics are known to have adverse effects such as the emergence of multi-resistant bacteria, acute and chronic toxicity in humans and animals.

Among other antibiotics, amoxicillin (AMX) is the most widely used drug for the treatment of bacterial infections such as ear, nose, throat, skin, and lower respiratory tract [48]. It has been reported that over 80% of oral administration of AMX in humans is excreted through urine after 2 h of consumption [3, 11]. Recently, the presence of AMX in concentration ranges of ng L^{-1} to mg L^{-1} in surface water, domestic and industrial wastewater and hospital waste has been reported. Hence, it is highly desirable to remove AMX before discharging to the environment.

3. MATERIALS AND METHODS

3.1 Materials

Amoxicillin ($C_{16}H19N_3O_3S$) (Figure 3.1) was purchased from an Ethiopian pharmaceutical agency NaOH was purchased from the alnhax chemical industry (India), HCl was purchased from alpha chemical industry (India)NaCl purchased from the loba chemical industry (India. $ZncL_2$ (97%)purchased from UMI chem^R chemical reagent (India) Mango peel and the seed wastes were collected from Debre Berehan town .Distilled water was used throughout the whole experiment. All the remaining reagents used in the experiments were of analytical graded.

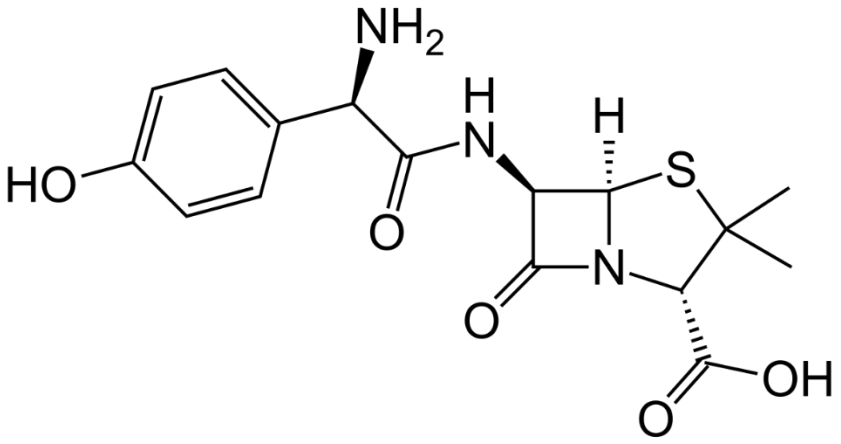

Figure 3.1Structure of AMX

3.2. Preparation of mango peel and seed activated carbon

Collected mango peel and seedwere cut into small pieces about (1-2 cm). The peel and seed were washed several times with tap water and followed by distilled water. The washed materials were allowed to sun-dried for 12 hours and followed by oven-dried at 105 C^0 for 12 hours to remove the moisture contents from the peel and seed. The dried material was finely grounded and screened through the sieves of different mesh sizes (250,90mm). After sieves 10g of powder was measured, and soaked with 20 mL of $ZnCl_2$ (97%) for1:2 ratio in a Beaker, stirring for 10 min until the powder was dissolved with acid and put for 24 hours. Then washing with distilled water until the pH is in the range of 6-7using a pH meter (209 Hannah pH meter). Then, the black

residue was dried in a muffle furnace at 500 ^{o}C for 1 hour for further activation purpose [36]. Finally, the activated carbon powder was obtained. The overall schematic diagram for preparation activated is presented in Figure 3.2.

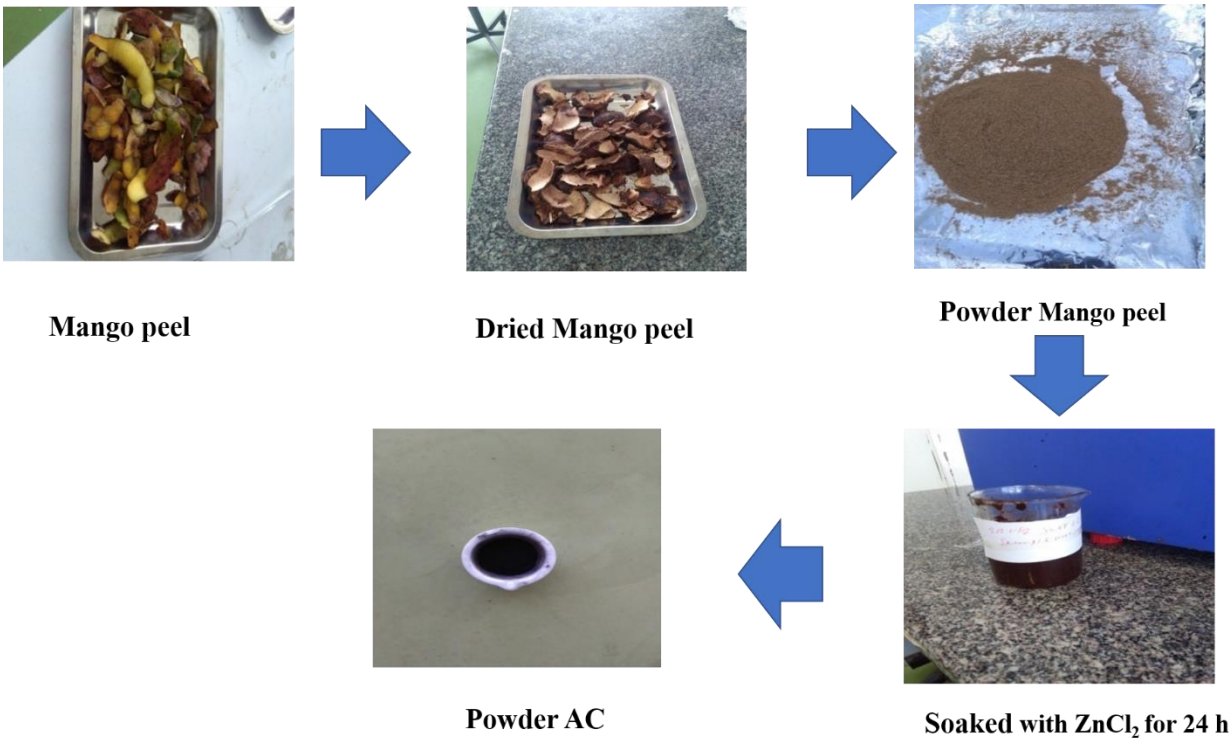

Figure 3.2. Preparation of mango peel and seed activated carbon powder.

3.3. Adsorption study

The Stock solution of amoxicillin of Concentration 250 ppm (250 mg/L) was prepared by dissolving (0.25) g of amoxicillin in a 250 mL volumetric flask by using a magnetic stirrer .The batch experiments were performed by adding the desired amount of the stock solution in 250 mL of volumetric flask at the designated adsorbent dose, pH, and temperature. The solution was shaken using a mechanical Gemmy orbit shaker (model: VRN-480, USA) for a definite period. Adsorbent dose, contact time, initial concentration and pH were optimized by continuous variation method (studying one, keeping the other parameters constant). After equilibrating, the system was allowed to settle for 20-30 min, filtered and analyzed for AMX. The pH of the original solution and the filtrate solution was determined using HANNA instruments pH meter (pH 209 models, Portugal).Batch experiments were carried out in a 250-

mL glass beaker containing 50mL of AMX solution of known concentration, pH, and AC dosage. The removal of AMX from aqueous solution was investigated using four operating variables: pH (2,4,6,8 and 10), initial AMX concentration (10, 20,30,40 and50 mg L-1), contact time (30,60,90,120,150 and180min), and AMX dosage (0.25, 0.5, 0.75, 1.0, and 1.25 g). The pH of the solution was adjusted using 0.01M of $NaOH$ and HCL [16]. Each run was conducted at room temperature using a magnetic stirrer. The percent removal of AMX can be calculated by using the formula.

$$\%\text{removal} = \frac{(\text{Co} - \text{Ce})100}{\text{Co}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

$$qe = \frac{(\text{Co} - \text{Ce})\text{v}}{\text{m}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5$$

The equilibrium concentration for each solution was calculated from the absorbance using the Calibration Curve equation where C0 (mg/L) represents the concentration before the adsorption, whileCe (mg/L) represents the concentration after adsorption, m (g) represents mass of carbon, (qe) equilibrium amount of AMX adsorbed per unit mass of carbon and V (L) represents the volume of AMX solution

3.3.1. Effect of pH

Samples with initial pH values of 2–10 with a fixed concentration of AMX (10 mg L^{-1}) and the adsorbent dose of 0.25g L^{-1} were prepared in order to determine the optimum PH. The concentration of AMX was measured after the retention time of 180 min and the optimum pH was determined given the removal efficiency. To adjust the pH of the solution, 0.01 M HCl and NaOH were applied.

3.3.2. Effect of initial AMX concentration:

The effect of initial AMX concentration was estimated for every30 min. by contacting 0.25 g of mango peel and seed powder with 50 ml of AMX at different initial concentrations ranging from 10 to 50 mg/L for 120 min. For every 30 min, we measured the absorbance in order to optimize the initial concentration of AMX.

3.3.3. Effect of contact time

Samples of AMX with a fixed concentration of fife 50ml of beaker each 10mgL^{-1},0.25 g of adsorbent at optimum PH were prepared different time intervals of 0–180 min and their concentration was measured.

3.3.4. Effect of the amount of adsorbent

In this stage, samples with fixed concentrations (10 mg L^{-1}) were prepared and the adsorbent dose was changed from 0.25 to 1.25 g and the samples were analyzed at optimum contact time and optimum pH according to previous stages in order to study the effect of the amount of adsorbent on the adsorption process.

3.4. Characterizations

3.4.1. Fourier transforms infrared (FTIR)

FTIR analysis was performed to identify functional group of adsorbents before and after adsorption. For FTIR analysis of activated carbon prepared from mango peel and seed stem, a small amount of powdered adsorbent sample was mixed with dry AMX and ground. After pressure was applied, the sample was scanned over a wave length of 4,000 – 400 cm^{-1} by attenuated total reflection FTIR [28] and the results were presented in form of graphs.

3.4.2. Powder X-ray diffraction (XRD)

Powder X-ray diffraction was employed to investigate the crystal structure of AC, and AC-AMX composite materials. Identification of the impurity phase and unit cell parameters was calculated from the diffraction pattern of the so-synthesized materials. The crystallite size of the as-synthesized AC was calculated using Scherer equation.

$$\text{Particle Size (D)} = \frac{\mathbf{0.9 \times \lambda}}{\boldsymbol{B \cos \theta}} \quad \mathbf{-----------6}$$

Where; B is the averaged dimension of crystallites; K (0.9) is the Scherer constant, λ is the wavelength of X-ray; and B is the integral breadth of a reflection (in radians 2θ) located at 2θ.

In the present work, the interlayer structural investigation of AC And AC-AMX were determined by performing X-ray diffraction analyses using Philips X' Pert-PRO PMRD system operating at 2θ values of 2-50°. The operating conditions were 50 kV and 100mA in continuous scan mode.

3.4.3. Point of zero charge

The pH of the aqueous solution at which the sum of all the surface positive charge balances the sum of all the surface negative charges is called the *point of zero charge*. Take 0.01M$NaCl$solutions in 500mL of the conical flask were prepared. Take 50 ml of the above solution into fife beakers. Then the pH was adjusted for 2,4,6,8 and 10 by using the pH-meter use 0.01M $NaOH$ and HCl. Then, 0.25g of adsorbent was added in contact with 50ml of each solution and keep for shaking for 24 hours. After, 24 hours shaking, filter and measure the pH for each set. Then, draw a line where Δ pH (final pH-initial pH) via initial pH.The resulting pH = 0 is taken as the pH_{PZC}.

3.5. Kinetics of the reaction

Kinetics of adsorption is one of the major characteristics defining the efficiency of adsorption. The kinetic models have been used to elucidate the mechanism and designing the adsorption of AMX molecules. The rate and mechanism of adsorption are controlled by various factors like physical and/or chemical properties of adsorbent as well as a mass transfer process. Hence, these kinetic models are useful for the design and optimization of effluent treatment in the practical application. The pseudo-first-order, pseudo-second-order models and as well as Elovich models were used in this stage and the results obtained from the effect of contact time on the kinetics of the reactions were studied and in the end, the best kinetic model of the process was determined based on the correlation coefficient. Pseudo first-order, pseudo-second-order, and Elovich models were used to fit the kinetic data [33].

The kinetic and equilibrium data fitness was carried out with nonlinear methods, which were evaluated using the Simplex method and the Levenberg–Marquardt algorithm using the fitting facilities of the Origin 2018 software [35]. The adequacy of the equilibrium and kinetic models was evaluated using the determination coefficient (R2), the adjusted determination coefficient (R2adj), and the standard deviation of residues (SD) [35].The Lagergren pseudo first order model is one of the most widely used rate equation for the adsorption of adsorb ate from aqueous solution. It was found that well represented the experimental kinetic data where the adsorb ate interactions were expected to be negligible The main assumptions of pseudo-second-order

kinetics model are the adsorption may be second-order, and the rate-limiting step could be chemical adsorption involving valent forces through sharing or the exchange of electrons between the adsorbent and adsorb at. The mathematical equations of these respective models are shown in

$$q_t = q_t x[1 - \exp(-k_1 x t)] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 7$$

$$q_t = \frac{{q_e}^2 k_2 t}{[k_2(q_e)xt + 1]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . 8$$

$$q_t = \frac{1}{a}\ln\left(1 + (a * b * t)\right) ’’’ 9$$

Where k1 is the pseudo-first-order rate constant (min-1), K2is the pseudo-second-order rate constant (g mg^{-1} min^{-1}), t is contact time (min), qt and qe are the amounts of adsorb ate adsorbed at time t and the equilibrium (mg g^{-1}). “b” is the desorption constant of the Elovich model (g mg^{-1}).

3.6. Adsorption Isotherm

The adsorption isotherm was significant for the explanation of how the adsorbent interact with adsorb ate and give an idea of adsorption capacity. The adsorption isotherms give further insight into the adsorption mechanism and quantitatively describe adsorption capacities of the adsorbent. The adsorption phenomenon between the AMX and adsorbent were described by fitting experimental isotherm data collected at a different concentration, pH, and temperatures, to the adsorption isotherms, i.e. Langmuir, Freundlich, and Liu [29] adsorption isotherm models.

The isotherm models of Freund lich, Langmuir and Liu were studied in this investigation. The Freundlich model is an equation assuming that the adsorption process takes place on heterogeneous surfaces. Whereas in the Langmuir theory basic assumption is that the adsorption takes place at specific homogeneous sites within the adsorbent. Langmuir, Freund lich, and Liu’s models were employed for analysis of equilibrium data.Equations10, 11and 12show the corresponding Langmuir, Freund lich, and Liu models respectively [33].

$$q_e = \frac{Q_{max} x K_L x C_e}{1 + K_L x C_e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 10$$

$$q_e = K_F x C_e^{1/nF} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 11$$

$$q_e = \frac{Q_{max} x (K_g x C_e)^{nL}}{1 + (K_g x C_e)^{nL}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 12$$

Where qe is the adsorb ate amount adsorbed at equilibrium (mg g-1); Ce is the adsorb ate concentration at equilibrium (mg L^{-1}); $Qmax$ is the maximum sorption capacity of the adsorbent (mg g-1); KL is the Langmuir equilibrium constant (L mg^{-1}); KF is the Freundlich equilibrium constant (mg g-1.(mg L^{-1})-1/nF); Kg is the Liu equilibrium constant (L mg^{-1}); nF and nL are the exponents of Freundlich and Liu model, respectively,[27] (nF and nL are dimensionless).

4. RESULTS AND DISCUSSION

4.1. Characterizations study

4.1.1. FTIR analysis

The FTIR technique is an important tool to identify important functional groups present on the surface of materials which are capable of adsorbing organic pollutants. The different functional groups were found in activated carbon like carboxylic group, ketone group, aldehydes, hydroxyl group, ester group, alkenes etc. The presences of this functional group in the activated carbon were responsible for adsorption of AMX from aqueous solution.Figure 4.1 shows thatFTIR peaks detected in the modified AC Spectrums of 3,369 cm^{-1} are related to stretching area functional groups of O–H [32]. The peak at 1,671 cm^{-1} are related to stretching area of alkenes(C=C), ~ 1540 (C=O), 1128 alcohol (C-O) and 1462 (ketone/phenol) are identified.

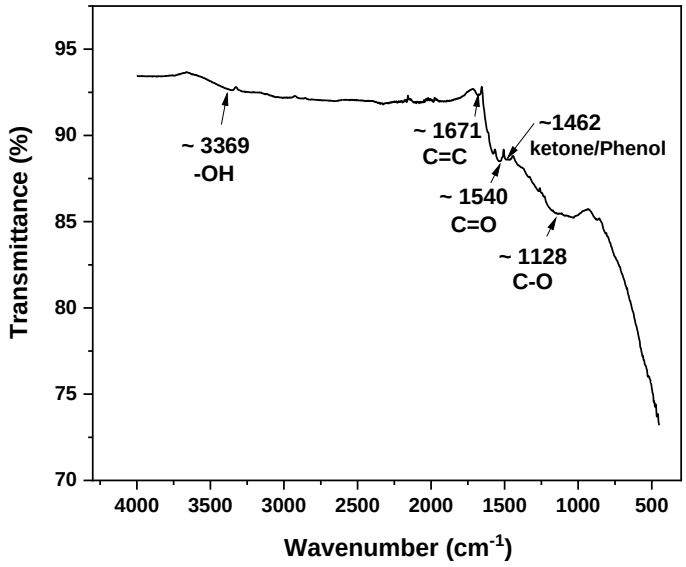

Figure 4.1FTIR Spectrum of AC prepared from Mango peel and seed

4.1.2. Powder XRD (XRD)

The powder XRD pattern of activated carbon prepared from mango peel and seed is presented in Fig.4.2. As shown in Figure 4.2, the strong and weak diffraction peaks emerged at 2θ = 25◦ and

2θ = 44°respectively. This result indicates the existence of graphite crystallite in mango peel and seed active carbon.

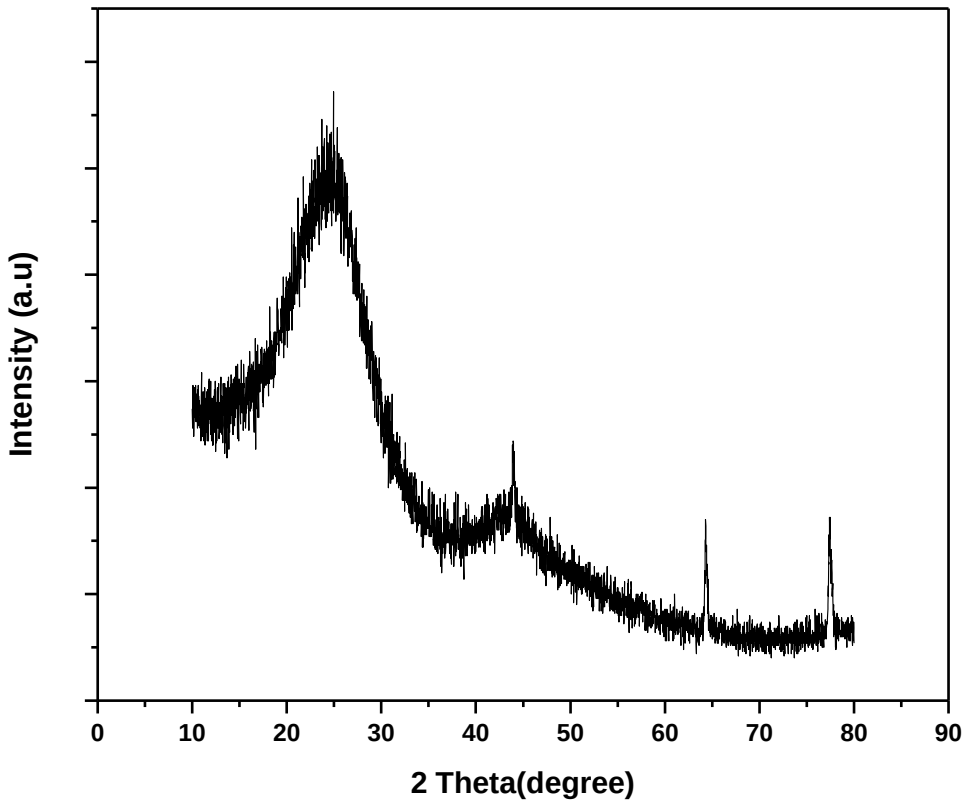

Figure 4.2 The powder XRD pattern of AC.

4.2. Adsorption study

4.2.1. Effect pH of the solution and Point of zero charge

The pH influences adsorption capacity and the surface charge of the adsorbent and leads to ionization of substance in the solution and separation of functional groups on the active sites of the bio adsorbent. The pH of zero-point charge (pH_{PZC}) of AC was determined (Figure 4.5). The pH at 5 was found to be a point of zero charge, the value of pH at which the surface became neutral. For the pH below 5 a cationic surface is obtained. This is due to the proto nation of the surface in acidic medium. In basic medium at pH above the source became anionic due to OH^- ions dominates on the surface of the adsorbent. Hence, the maximum AMX removal

(95.5%) was obtained at pH = 6. So, the pH 6.00 was selected as optimum pH for adsorption of AMX. Amoxicillin has positive and negative charge due to the proto nation of amoxicillin carboxyl and amine groups by the presence of free H^+ ions in the solution. For carboxyl and amine groups the proto nation took place as follows but phenol groups were not protonated on amoxicillin [34].

$$COO^- + H^+ \longrightarrow COOH \text{ When } pH < 2.68$$

$$NH_2 + H^+ \longrightarrow NH3^+ \text{ When } pH < 7.49$$

In the present study, the pH values for the zero point charge for AC is pH = 5. Therefore, at low pH (pH>5), the adsorbent surface has a negative charge and adsorbs the AMX (cationic) Hence, the maximum AMX removal (95.5%) was obtained at pH = 6 (Fig 4.4). via electrostatic attraction.

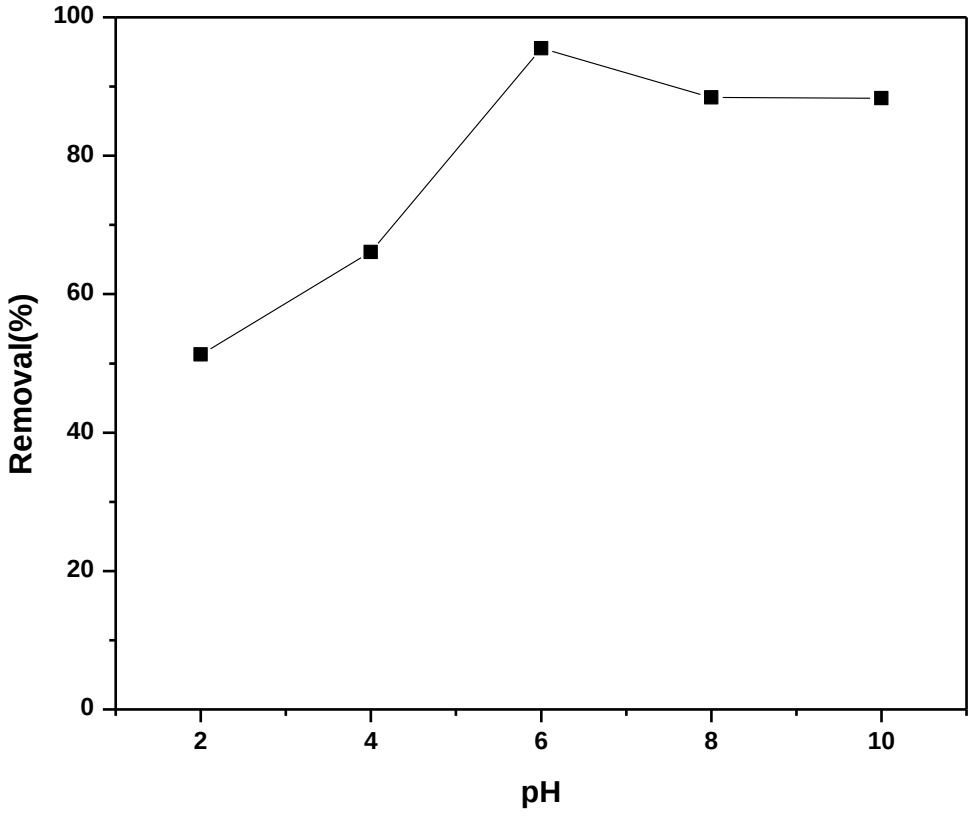

Figure 4.3:Effect of pH on adsorption of AMX onto the AC material.

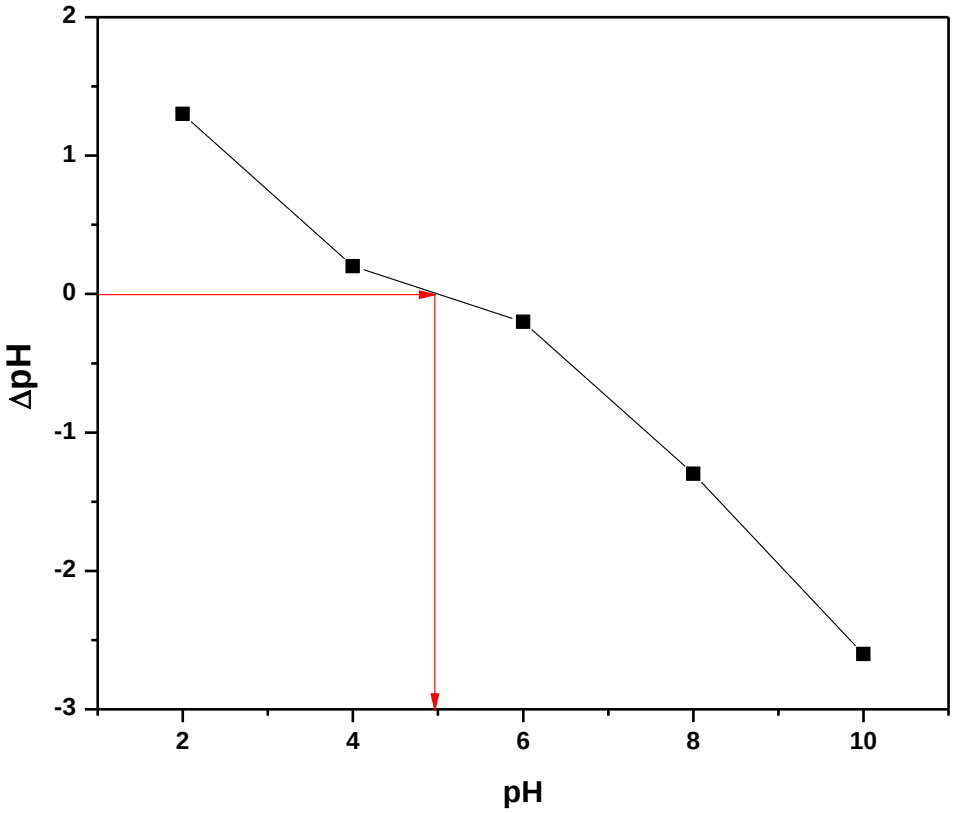

Figure 4.4: Point of zero charge analysis of AMX adsorption on to AC material.

4.2.2. Effects of the initial AMX concentration

The effects of the initial AMX amount on the removal of AMX were studied by varying the AMX amount (10–50 mg L^{-1}) and the results were presented in Figure 4.6. The results show that by increasing the AMX concentration, the removal AMX efficiency decreased. Due to an increase in the number of AMX ions for a fixed amount of adsorbent i.e. the limited number of surface binding sites. The highest removal efficiency was obtained in amoxicillin concentration of 10mg L^{-1}(95.9%).

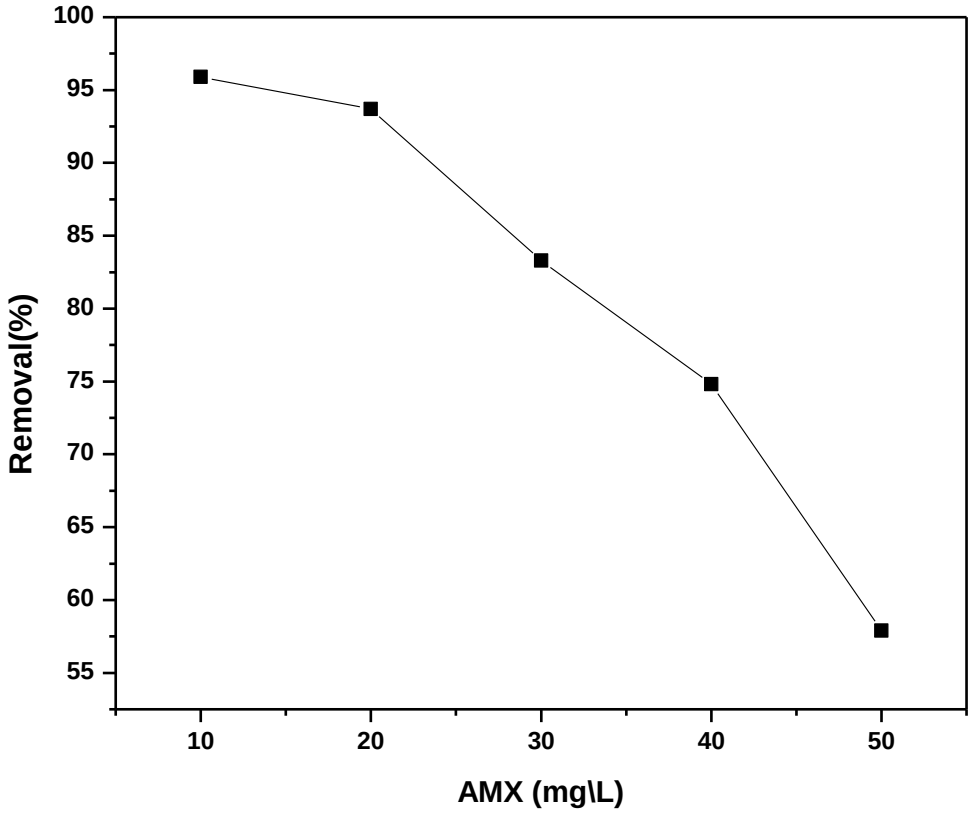

Figure 4.5Effects of the initial AMX concentration [pH=6, Time=120min, Con=10, 20, 30, 40,50ppm].

4.2.3. Effect of contact time

Contact time is one of the effective factors in the adsorption process. The results associated with the effect of contact time on the adsorption rate of AMX are shown in Figure 4.7. The adsorption removal of AMX increased as time progressed and the maximum adsorption was achieved at 120 min. The removal of AMX beyond 120 min became constant and this indicates all free adsorption sites are occupied i.e. after equilibrium time, adsorption is nearly constant and the AMX uptake does not display any considerable results. This is fundamentally due to in the initial time of adsorption, empty surface sites are available, once equilibrium is attained; the remaining vacant sites are difficult to be occupied and also this is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after

a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases[30].

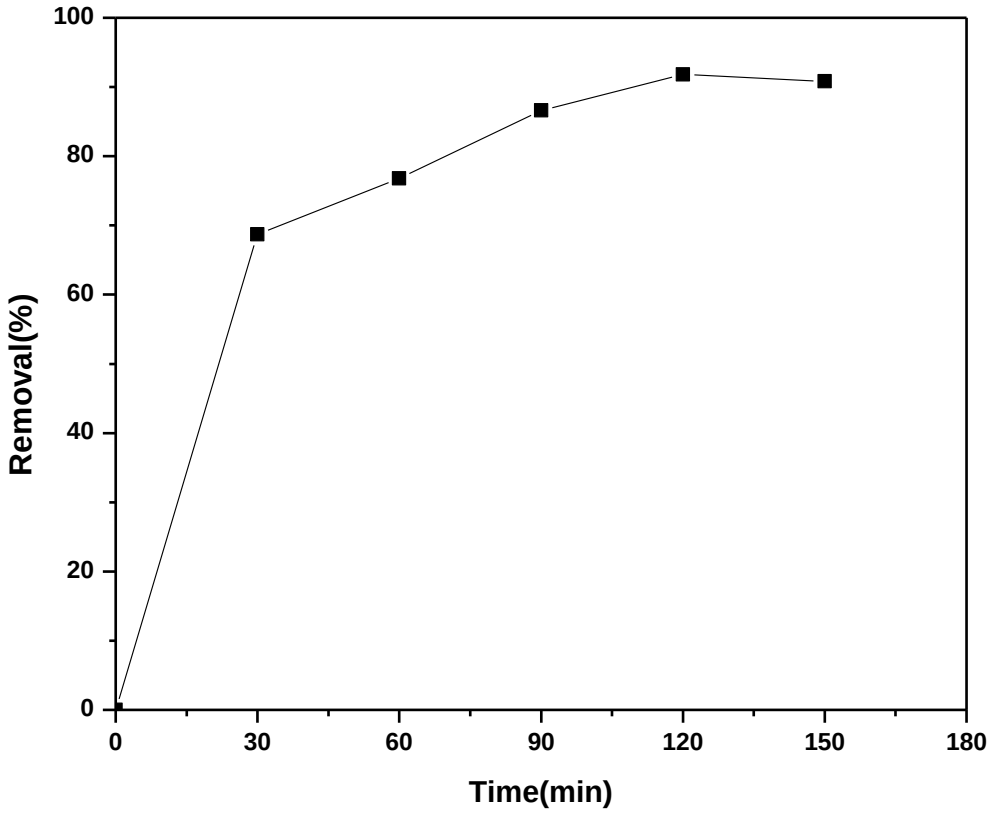

Figure 4.6 The Effect of contact time on adsorption of AMX .

4.2.4. Effect of adsorbent dose

Adsorbent dose study was performed ranges from 0.25 to1.25 g of AC mass represented in Figure 4.8. As the amount of adsorbent dose increased, the percentage of AMX adsorbed increased. This indicates the increase in available binding sites and also increase in the contact surface of the adsorbent which in turn results in an increase in active sites that leads to the adsorption of antibiotic onto the adsorbent[31, 32].

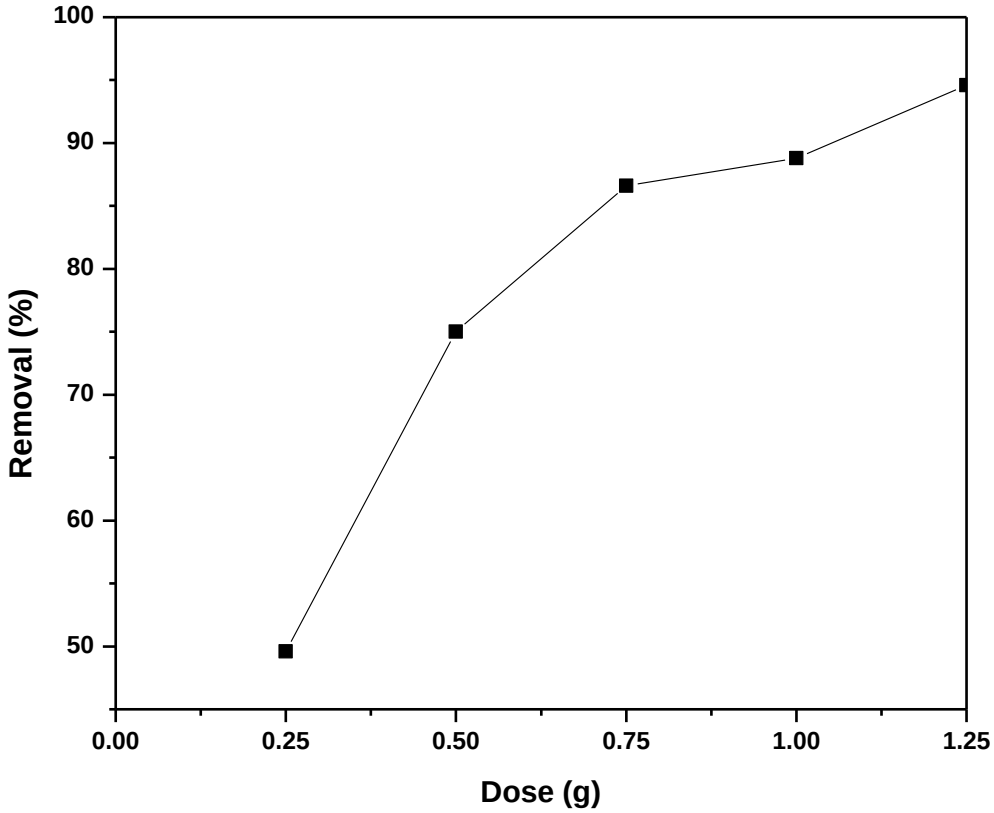

Figure 4.7 The effect of adsorbent dose (from 0.25-1.25, Co=10ppm, pH=6, Time.

4.3. Adsorption Kinetic study

The kinetic adsorption data were processed to understand the dynamics of adsorption process in terms of the rate constant order. The kinetics of AMX adsorption onto activated carbon prepared from mango peel and seed was analyzed using pseudo-first-order, pseudo-second and Elovich kinetic order kinetic models. The data of kinetics of adsorption of the AMX onto AC adsorbent were assessed using the nonlinear kinetic models of the Elovich, pseudo-first-order, and pseudo-second-order [35]. The kinetic adsorption curves and the parameters of the kinetic model are depicted in Figure 4.8 and Table 4.1. The standard deviation (SD) and the adjusted determination coefficient (R^2adj) were used to statistically evaluate the fitting of the kinetic data. The smaller discrepancy between the theoretical (calculated by the models) and experimental ‘q’ values are

obtained with lower SD and higher R^2adj values. The kinetic parameters, SD, and R^2adj are shown in Table 4.1. According to the results shown in Table 4.1, the best fitted kinetic model was found to be the *Pseudo* second order. The *Pseudo* second order exhibited lower SD value 0.03947 and highest R^2adj values 0.951. This indicates that the adsorption of AMX proceeds via chemisorptions process.

Table.4. 1 *Pseudo* first order, Pseudo second order and Elovich kinetic parameter

Pseudo first order	Pseudo second order	Elovich model
k_1 (min^{-1}) = 0.0451	k_2 (g mg^{-1} min^{-1}) = 0.03792	a (g mg^{-1})= 3.786
q_e (mg g^{-1}) = 1.8	q_e (mg g^{-1}) = 1.985	b (mg g^{-1} min^{-1}) = 1.822
R^2_{adj}= 0.865	R^2_{adj}= 0.951	R^2_{adj}=0.940
SD (mg g^{-1}) = 0.07332	SD (mg g^{-1}) = 0.03947	SD (mg g^{-1}) = 0.04355

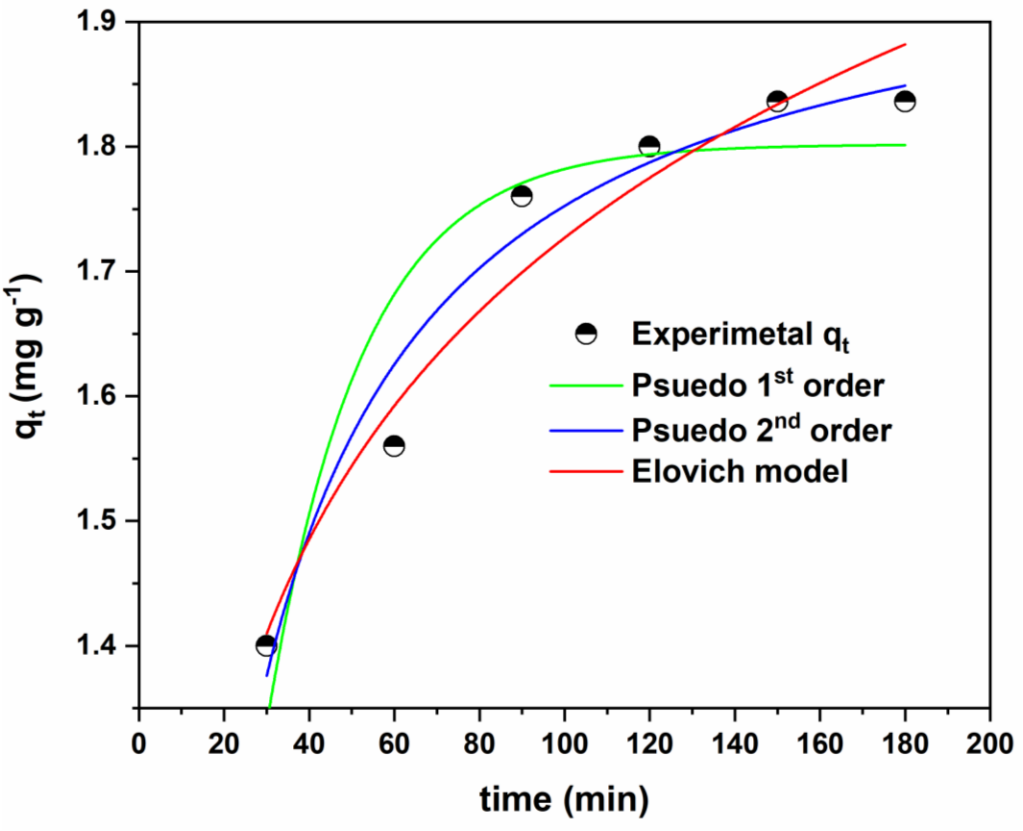

Figure 4.8The kinetics plot of AMX adsorption onto AC analyzed by Pseudo first, Pseudo second and Elovich kinetic models.

4.4. Adsorption Isotherm

The Freund lich, Langmuir, and Liu isotherm models were employed to explore the equilibrium adsorption data. The experimental studies were done employing the best adsorption conditions previously obtained, 120 min of contact time, the temperature of 25 °C, amass of adsorbent 0.25g and pH 6 .Equilibrium adsorption studies were performed to determine the maximum amoxicillin adsorption capacities of AC. The Langmuir model assumes that the adsorptions occur at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes [40]. The Freund lich model endorses the heterogeneity of the surface and assumes that the adsorption occurs at sites with different energy levels of adsorption [38].The applicability of the isotherm equation is compared by judging the correlation coefficients. It can be seen from table 4.2.The Langmuir isotherm presented R^2adj closer to 1.0 and lower SD values (see Table 4.2), suggesting being the best fitted isotherm model. The maximum sorption capacities (Q_{max}) obtained by the Langmuir model was6.166mg g^{-1} AMX.

Table 4.2 Langmuir Freundlich and Liu adsorption isotherms parameter

Langmuir	Freundlich	Liu
Q_{max} (mg g^{-1}) = 6.166	K_F (mg g^{-1} (mgL^{-1})$^{-1/nF)}$ = 3.298	Q_{max} (mg g^{-1}) = 6.274
K_L (L $mg^{-1)}$ = 1.2	n_F = 4.57	K_g (L $mg^{-1)}$ = 1.152
R^2adj = 0.973 SD (mg g^{-1}) = 0.27	R^2adj = 0.854 SD (mg g^{-1}) = 0.6297	n = 0.933 R^2adj = 0.96 SD (mg g^{-1}) = 0.3266

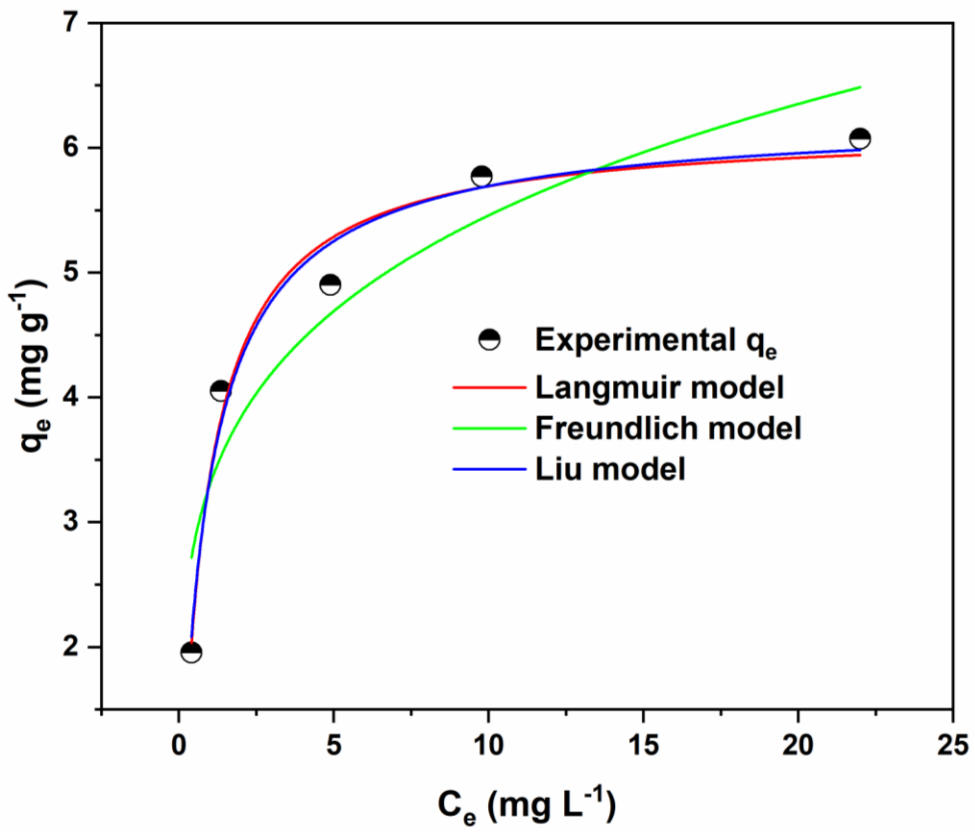

Figure 4.9 The graph for Langmuir, Frindlich and Liu isotherm models.

4.5. Plausible mechanism of AMX adsorption and stability analysis

FTIR analysis was used to determine the functional groups present on the surface of activated carbon. FTIR peaks of figure4.10 detected inthemodifiedACbeforeandafterAMXadsorption, indicating the shifting and disappearance of some peaks were observed. These changes observed in the spectrum indicated the involvement of specific functional groups during AMX adsorption. Before and after adsorption the activated carbon surface show the same feature indicates stability.

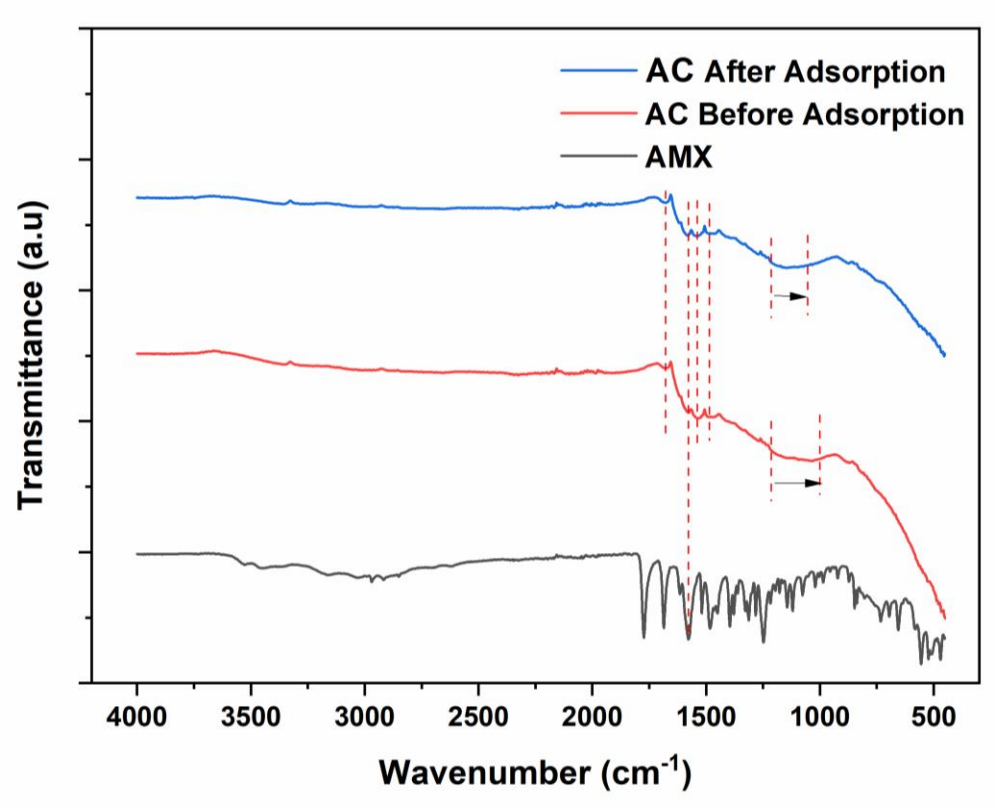

Figure 4.10 : The FTIR spectra of AC before and after adsorption of AMC.

5. CONCLUSIONS

In this work, an efficient and new activated carbon was produced from mango peel and seed by activating$ZnCl_2$.The removal of AMX from wastewater is primarily controlled by the AMX concentration in the wastewater, the adsorbent concentration, the pH of the wastewater. The percentage of AMX removal was found to increase with an increase contact time, and adsorbent concentration and found to decrease with an increase in initial AMX concentration. The percentage of AMX removal increased with increasing PH and decreases as PH increase. The maximum adsorption was obtained at pH 6.It was found that the sorption of the AMX was increased by the presence of cationic surfactant, and on the other hand was decreased by the presence of cationic and nonionic surfactant. FTIR analysis identified the presence of O-H, C=C, C-O and C=O functional groups on surface of AC adsorbent. The isothermal analysis show Langmuir isotherm presented R^2adj closer to 1.000 and lower SD values suggesting being the best fitted isotherm model from Frindlich and Liu models.. The results of the kinetic equations also confirmed that the adsorption behavior of AMX per unit time follows a pseudo-second-order kinetic model. The *Pseudo* second order exhibited lower SD value 0.03947 and highest R^2adj values 0.951 from other models.. This indicates that the adsorption of AMX By second-order model to study the mechanism of adsorption, calculated qe value agreed with the qe experimental value. According to the results, the *mango peel and seed* bio adsorbent, as the cost-effective adsorbent, in comparison with other natural adsorbents, can be used in the removal of AMX antibiotic.

6. REFERENCES

1. Fu, H., Li, X., Wang, J., Lin, P., Chen, C., Zhang, X., Suffer, I. M. “Activated carbon adsorption of quinolone antibiotics in water: Performance, mechanism, and modeling”, *Journalof Environmental Sciences, vol.* 56, pp. 145-152, 2017.

2. Tejada, C., Quiñonez, E. “Contaminants emergences en agues metabolites de fármacos. Unarevisión”,Facultad de CienciasBásicas, pp. 80-101, 2014.

3. Chao, Y., Zhu, W., Ye, Z., Wu, P., Wei, N., Wu, X., Li, H. “Preparation of metal ions impregnatedpolystyrene resins for adsorption of antibiotics contaminants in aquatic environment. Appl. Polym. Sci., vol. 132, no. 15, pp. 1-9. DOI: 10.1002/APP.41803, 2015.

4. Tong, L., Huang, S., Wang, Y., Liu, H., Li, M. “Occurrence of antibiotics in the aquatic environment of Jianghan Plain, central China”,Science of the Total Environment,vol. 497, pp. 180-187, 2014.

5. Ebele, A. J., Abdallah, M. A. E., Harrad, S. “Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment”, Emerging Contaminants, vol. 3, no. 1, pp. 1-16, 2017.

6. Rodriguez-Mozaz, S., Chamorro, S., Marti, E., Huerta, B., Gros, M., Sànchez-Melsió, A., Borrego, C.M., Barceló, D., Balcázar, J.L, “Occurrence of antibiotics and antibiotic resistance genes in hospital and urban wastewaters and their impact on the receiving river”,WaterResearch,vol. 69, pp. 234-242, 2015.

7. Aubakirova, B., Beisenova, R., Boxall, A.B.A. Prioritization of pharmaceuticals based on risks to aquatic environments in Kazakhstan. Integr. Environ. Assess. Manag, vol. 13, no. 5, pp. 832-839, 2017, DOI: 10.1002/ieam.1895.

8. Matozzo, V., Bertin, V., Battistara, M., Guidolin, A., Masiero, L., Marisa, I., Orseti, A, “Does the antibiotic amoxicillin affect haemocyte parameters in non-target aquatic invertebrates? The clam Ruditapesphilippinarum and the mussel Mytilusgalloprovincialis as model organisms”, Marine Environmental Research,vol. 119,pp. 51-58, 2016.

9. Limousy, L., Ghouma, I., Ouederni, A., Jeguirim, M. “Amoxicillin removal from aqueous solution using activated carbon prepared by chemical activation of olive stone “Environmental Science and Pollution Research, vol. 24, no. 11, pp. 9993-10004, 2017.
10. Seconds, M.F.N., Naddeo, V., Ballesteros, F. Jr., Belgiorno, V. “Adsorption of emerging contaminants enhanced by ultrasound irradiation, Sustain”,Environ. Res,vol. 24, no. 5, pp. 349–355, 2014

11. M.G.D. de Luna, E.D. Flores, D.A.D. Genuino, C.M. Futalan, M.W. Wan, Adsorption of Eriochrome Black T (EBT) dye using activated carbon prepared from wastericehull Optimization, isotherm and kinetic studies, *J. Taiwan Inst. Chem. Eng. 44* (2013) 646–653.
doi:10.1016/j.jtice.2013.01.010.

12. R. Baccar, M. Sarra, J. Bouzid, M. Feki, P. Blanquez, Removal of pharmaceutical compounds by activated carbon prepared from agricultural by-product, Chem. Eng. J. 211–212 (2012)310–317.doi:10.1016/j.cej.2012.09.099.

13. Hassler, John, W., "Purification with Activated Carbon: Industrial, Commercial and Environmental", Chemical Publishing Company Inc., New York, N.Y. (1974).
14. Derbyshire, F, Jagtoyen, M. and Thwaites, M., Activated Carbons-Production and
15. Stenzel, Mark, H "Remove Organics by Activated Carbon Adsorption", Chemical EngineeringProgress, 89:4(1993).

16.Romanos, J., M. Beckner, T. Rash, L. Firlej, B. Kuchta, P. Yu, G. Suppes, C. Wexler, a P. Pfeifer. 2012. “Nano space Engineering of KOH Activated Carbon.” *Nanotechnology* 23(1):015401.

17. Diao, Yulu, W. P. Walawender, and L. T. Fan. 2002. “Activated Carbons Prepared from Phosphoric Acid Activation of Grain Sorghum.” *Bioresource Technology* 81(1):45–52.

18. Annadurai, G., R.-S. Juang,& D.-J. Lee. (2002) Use of cellulose based waste for adsorption of dye from aqueous solutions. Journal of Hazardous Materials 92: 263-274.
19. Rubenowitz E, Axelsson G, Rylander R. (1999). "Magnesium and calcium in drinking water and death from acute myocardial infarction in women" Epidemiology 10 (1): 31–6.

20. Stitt, F., D. Clayton, et al. (1973). "Clinical and biochemical indicators of cardiovascular disease among men living in hard and soft water areas."*The Lancet 301*(7795): 122-126.

21.MarqueS,Jacqmin-Gadda H, Dartigues JF, Commenges D. (2003)."Cardiovascular mortality calcium and magnesium in drinking water an ecological study in elderly people"(PDF). Eur. J. Epidemiol. 18 (4): 305–9.

22. Hossain, M., H. Ngo, W. Guo, & T. Nguyen, (2012). Biosorption of Cu (II) from water by banana peel based biosorbent: experiments and models of adsorption and desorption. Journal of WaterSustainability2: 87-104.

23. Haimour N.M., Emeish S. (2006). Utilization of date stones for production of activated carbon using phosphoric acid. Waste Manage, 26: 651– 660.

24. Ferrari, L.; Kaufmann, J.; Winnefeld, F.; Plank, J, 2010. "Interaction of cement model systems with super plasticizers investigated by atomic force microscopy, zeta potential, and adsorption measurements". *J. Colloid Interface Sci*. 347 (1): 15–24.

25 Vidali, Gianfranco, Ihm, G, Kim, Hye-Young, Cole, Milton W (1991).Potentials of Physical adsorption, Surface Science Report.12:135-181.

26. APHA. 1998. "Standard Methods for the Examination of Water and Wastewater.American Public Healt Association." *American Water works Association; Water Environment Federation, Washington, DC.*

27. Kumar, S., Ramalingam, S., Senthamarai, C., Niranjanaa, M., Vijayalakshmi, P. &Sivanesan, S. (2010). Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions. *Desalination,* 261, 52-60.

28 A.A. Matin, M.A. Farajzadeh, A. Jouyban, A simple spectrophotometric method for determination of sodium diclofenac in pharmaceutical formulations, Farm.60 (2005) 855–858.
doi:10.1016/j.farmac.2005.05.011.

29. Samer, Mohamed. 2015. "Biological and Chemical Wastewater Treatment Processes.*Waste waste Treatment Engineering* 1–50.

30. Adamu A., (2008), Adsorptive removal of reactive azo dyes using industrial residue, M.Sc Thesis, Addis Ababa University.

31. Balarak D, Azarpira H, Mostafapour FK. Thermodynamics of removal of cadmium by adsorption on Barley husk biomass. DerPharmaChemica, 2016,8(10):243-47.
32. Diyanati RA, Yousefi Z, Cherati JY, Balarak D. Investigating phenol absorption from
aqueous solution by dried azolla.JournalMazandaran University of Medical Science. 2013; 22(2); 13-21

33.Lima EC, Adebayo MA, Machado FM (2012-5) Chapter 3-kinetic and equilibrium models of adsorption, in Carbon nano materials as adsorbents for environmental and biological applications, ed. by C.P. Bergmann, F.M. Machado (Springer, Berlin, 2015), pp. 33–69

*34.*Andreozzi, R., Canterino, M., Marotta, R., Paxeus, N. 2005. Antibiotic removal from wastewaters: the ozonation of amoxicillin. *J. Hazard. Mate* 122(3), 243-250.

35.Lima EC, Adebayo MA, Machado FM (2012-5) Chapter 3-kinetic and equilibrium models of adsorption, in Carbon nanomaterials as adsorbents for environmental and biological applications, ed. by C.P. Bergmann, F.M. Machado (Springer, Berlin, 2015), pp. 33–69

36. Thue PS, Adebayo MA, Lima EC, Sieliechi JM, Machado FM, Dotto GL, Vaghetti JCP, Dias SLP (2016) Preparation, characterization, and application of microwave-assisted activated carbons from wood chips for removal of phenol from aqueous solution. *J MolLiq* 223:1067–1080

37.Ertaş M, Acemioğlu B, Alma MH, Usta M (2010) Removal of methylene blue from aqueous solution using cotton stalk, cotton waste and cotton dust. *J. Haz. Mater* 183(1–3):421–427

38. H. Freundlich, “Uber Die Adsorption in Losungen,” *The Journal of Physical Chemistry*, vol. 57, pp

39. Yahya MA, Al-Qodah Z, Ngah CZ (2015) Agricultural bio-waste materials as potential sustainable precursors used for activated carbonproduction: a review. Renew Sustain Energy Rev 46:218–235

40.Baccar R, Bouzid J, Feki M, Montiel A (2009) Preparation of activated carbon from Tunisian olive-waste cakes and its application for adsorption of heavy metal ions. *J Hazard Mater* 162:1522–1529.

41. Yakout S, El-Deen GS (2016) Characterization of activated carbon prepared by phosphoric acid activation of olive stones. *Arab J Chem9*:S1155–S1162

42. Ahmed MJ, Theydan SK (2014) Optimization of microwave preparation conditions for activated carbon from Albizialebbeck seedpods for methylene blue dye adsorption. *J Anal Appl Pyrolysis*105:199–208

43.Martins AC, Pezoti O, Cazetta AL et al (2015) Removal of tetracycline by NaOH-activated carbon produced from macadamia nut shells:kinetic and equilibrium studies. ChemEng J 260:291–299.

44.Arami-Niya A, Daud WMAW, Mjalli FS (2010) Using granular activated carbon prepared from oil palm shell by ZnCl2 and physical activation for methane adsorption. *J Anal Appl Pyrolysis*

45.Deng H, Yang L, Tao G, Dai J (2009) Preparation and characterization of activated carbon from cotton stalk by microwave assistedchemical activation—application in methylene blue adsorptionfrom aqueous solution. *J Hazard Mater* 166:1514–152189:197–203

46. Hui TS, Zaini MAA (2015) Potassium hydroxide activation of activated carbon: a commentary. Carbon Lett 16:275–280

47. Contreras, E.; Sepúlveda, L.; Palma, C., Valorization of Agroindustrial Wastes as Biosorbent for the Removal of Textile Dyes from Aqueous Solutions.*International Journal*
of Chemical Engineering **2012,** 2012, 9.

48. Portinho, R.; Zanella, Osss.;Féris, L. A., Grape stalk application for caffeine removal through adsorption. *J. Environ. Manage.* **2017,** 202, 178-187