CHAPTER 1

1. INTRODUCTION

1.1 Background

Nanotechnology is currently becoming one of the most dynamic and rapidly developed areas of interdisciplinary research, which is believed to have the potential to revolutionize a wide range of science related technological fields. Nanoscience and nanotechnology are at the cutting edge of today's scientific research. Recent developments that have been made in this field are highly advantageous to the human society [1, 2, 3].

Porous materials especially the meso- and microporous, belong to typical class of nanotechnology research. Activated carbons, the amorphous solids with large internal surface area and pore volumes usually prepared from carbonaceous raw materials using chemical and physical activation method are of great interest in recent years. The presence of unique pore structures in them play an important role in many different liquid and gas phase applications because of their versatile adsorptive capacity [4,5].The porosity is classified by IUPAC into three different groups of pore sizes, viz, micropores (8 to 100 Å), mesopores (100 to 500 Å) and macropores (500 to 20000 Å). The most widely used commercial activated carbon from coconut shell have a specific surface area varying from 1050 to 1200 m^2/gm, as determined by nitrogen gas adsorption and desorption method using BET equation [6].

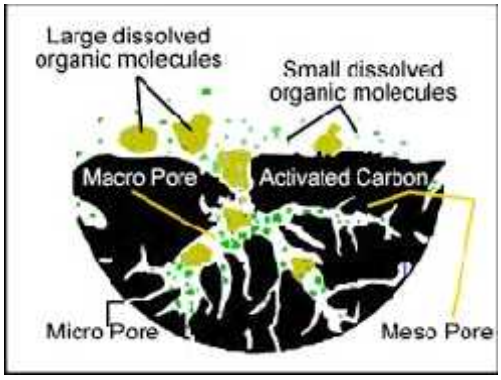


Figure 1: Different pore sizes in activated carbon

The functioning of activated carbon mainly depends on the adsorption process which further depends on the availability of the surface area for adsorption. Organic materials are more preferred than the polar inorganic species for adsorption due to non-polar character of carbon. Simple mechanisms such as hydrogen bonding, Van der Waal's force between carbon surface and organic compounds are involved in the adsorption process. The organic adsorbates have the properties such as high molecular mass, low polarity and low degree of ionization, due to which they show very low solubility in aqueous phase. It is one of the most important factor that enhances adsorption on to the carbon surface [6].

The application of activated carbon in adsorption process mainly depends on the surface chemistry and pore structure of activated carbon as stated earlier. Its use for different purposes has been since several thousands of years. It is widely used in the medical fields and as purifying agents [7]. The activated carbon has high ability to adsorb to other substances. Treatment of intestinal disorders such as intestinal gas, constipation, diarrhoea is also done by the use of activated carbon. It can be effectively used to clean skin wounds too [8].

Activated carbon can not only be used for whitening the teeth, but also for promoting the oral health since it prevents cavities, bad breadth and gum diseases and is also highly effective in treating body odour, acne etc. Application of mixture of activated carbon with coconut oil on the affected area can help in mitigating the problems due to insects and snake bites.

Aging is a natural life process, but due to over exposure to toxic substances, premature aging is one of the major problem of present day situation. Consumption of activated carbon in controlled amount in daily basis supports better cognitive functions, reduces brain fog and promotes healthier kidney, liver function and digestive tracts [9]. Also, pharmaceuticals and food industries employ activated carbon as the most effective decolorizing agent during the purification process.

The treatment of industrial and domestic waste water for the removal of undesirable color, odour, taste and organic impurities can also be done by the use of activated carbon as an adsorbent. Besides the above mentioned areas, application of activated carbon has also been seen in the field of hydrometallurgy for the recovery of heavy metals such as gold, silver etc [6]. Even the cigarette industries produce high quality goods by using activated carbon in the filters of

cigarette to minimize the consumption of cancer causing agents [6]. Biomedical engineering have employed activated carbon for the storage of hydrogen as the alternative source of energy instead of gasoline and diesel fuel for future use [3].

1.2 Statement of Problems

During the last years, trace organic pollutants have increasingly gathered scientific attention. The chemical dyes are toxic. Toxic chemical dyes cause several environmental problems to our ecosystem. There is a chance to enter it into the food chain. These are the persistent organic pollutants and are of great concern due to their toxicity, persistence, long range transport ability and bioaccumulation in water.

In Nepal, most of the carpet and dying industries are near the water sources and all the waste produced (liquid as well as the solid) from the industries are dumped directly to water resources without treatment. The wastes from carpet industries usually contain dyes which may change the color as well as the odour of the water. Presence of these coloring substances reduces the amount of light penetrating the water bodies which effects the photosynthesis in aquatic plants imposing ecological risks. When the aquatic animals exposed to such water bodies are consumed by humans, major problems such as dysfunctioning of kidney, reproductive system, liver, brain etc are detected in humans [10]. Due to the high rate of population growth, problem of drinking water supply is increasing day by day. Therefore, the treatment of waste water has become one of the important issue in current situation.

The trend of excessive use of insecticides, pesticides and inorganic fertilizers in the agricultural sectors to increase the crop yield has caused the amount of toxic chemicals to increase in food products. Consumption of these vegetables and fruits causes toxicity in the body. Being over exposed to the atmosphere containing toxic substances either in the factories or in the outer polluted environment also increases the toxic load in the human body. This causes several problems especially in the digestive tract [9].

Other problems of great concern are the drug over dosage and poisoning. It is estimated that one million children accidently overdose on drugs mistakenly as candies or eat, drink or inhale poisonous household products each year such as disinfectants, room freshener etc. Infants and toddlers are in greatest risk for because of accidental poisoning of its. In adults and old aged people the drug over dosage may observe due to mental tension, forgetfulness etc. Some of the

antipyretic and anti- analgesic medicines are easily available in the markets which are frequently consumed by the people even in minor cases. This leads to medicine over dosage and poisoning as well as fatal for life (cause death).

Now a days, due to luxurious cuisines, life styles and replacement of homemade food by the fast food and soft drinks, several health problems are seen in modern day people. One of the major problem is diabetes. In context of Nepal, as carbohydrate is one of the major source of energy, its consumption is very high. This increases the chance that the people suffer from diabetes and it is a hereditary disease too. To control the amount of sugar in the body, one of the mostly used anti-diabetic medicine is glimepiride. Now a days, this disease is even seen in young people. Regular consumption of this medicine, people suffer from mental tension, tiredness, forgetfulness and sometimes even overdose is caused which may lead to death.

Therefore, to overcome these types of problems, activated carbons can be one of the solutions. Since, very few works have been done in the field of treatment of waste water before letting them into the water resources and in the medical field for treating the medicinal overdose and toxicity problems using activated carbon from *Areca catechu* nuts, this research is necessary to find the way for the solution of such problems.

1.3 Precursor for Activated Carbon

It is essential to know that the effectiveness of the use of activated carbon depends upon the choice of the precursor as well as the methods employed for its manufacture. Activated carbons can be produced by carbonization of any material containing high percentage of carbon including coal, wood, coconut shells, fruit stones, olive stones, cherry stones and different agricultural wastes. These materials are usually lignocellulosic in nature. Lignocellulosic material contains cellulose, hemicelluloses and lignin bonded together differently as shown in Figure 2, 3 and 4 [11].

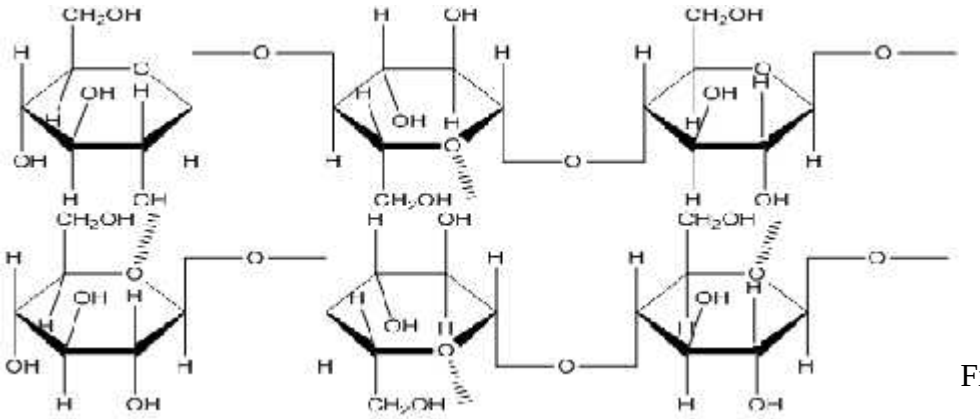


Figure 2: Cellulose [11]

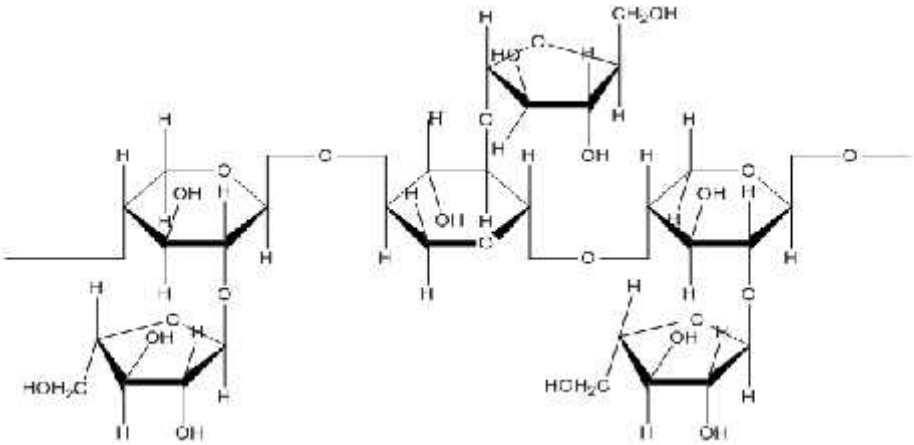
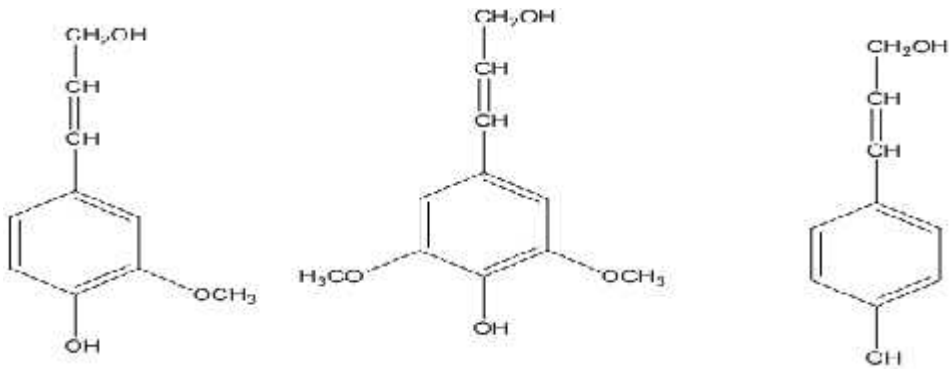


Figure 3: Hemicellulose [11]



Coniferyl alcohol Sinapyl alcohol *p*-coumaryl alcohol

Figure 4: Lignin [11]

The selection of precursor for the preparation of activated carbon depends upon availability, carbon content, cost and ease of activation.

Areca catechu nuts, locally known as Supari in countries like Nepal and India is a name given to the seed of *Areca catechu* tree of Arecaceae family more commonly referred to as the palm family. This family consist of over 200 genera and 2600 species, almost all of which grow in the warm tropical and sub- tropical areas [12]. In Nepal, every year tons of *Areca catechu* nuts are produced, especially in the Terai region. Mainly the eastern districts such as Jhapa, Morang are the largest producer of *Areca catechu* nuts in Nepal. Large amount of *Areca catechu* nuts are exported each year to India from eastern boarders as a source of income to the country. In the year 2006/07, total production of *Areca catechu* nuts in Nepal was 3,922 metric tons. During the year 2006/07 to 2009/10, the total production was in general increasing trends. In the year2009/10 total production was 4,266 metric tons, as compared to previous (2008/09) the production was increased by 7.27 %. In the fiscal year 2012-13, the production stood at 8,914 tonnes in Jhapa and 2041 tonnes in Morang [13]. Since *Areca catechu* nuts are rich in lignocellulosic materials, it can be used as the precursor for preparing activated carbon. It is edible and the extract of *Areca catechu* nuts shows antimicrobial activities against several microorganisms [14]. Therefore, the activated carbon from *Areca catechu* nuts can be used as antidote too. Hence, the activated carbon derived from it can be used in several cosmetic products and medicines to treat acne and pimples. The images of *Areca catechu* nuts are given in the Figure 5,6 and 7.

Figure 5: *A. catechu* nuts hanging from the palm

Figure 6: A ripe *A. catechu* nut

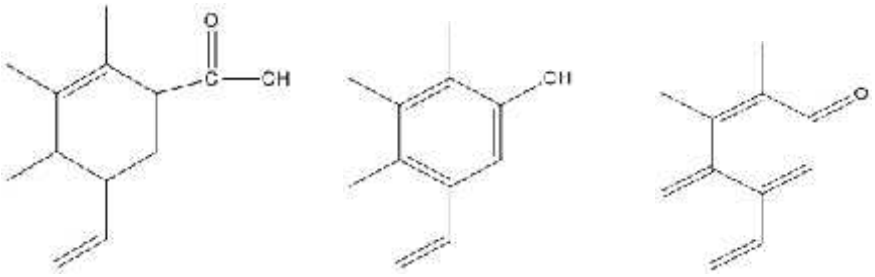
Figure 7: Dried *A. catechu* nuts

1.4 Preparation and Activation of Precursor

The precursor for activated carbon is first washed, dried and grinded to small particle size. It is then sieved to mesh size less than 2 mm. The precursor can be activated either by physical or chemical activation process.

In physical activation the carbonized material is exposed to carbondioxide, oxygen or steam at high temperature from 800°C to 1100°C in order to remove tar and create sufficient micro and mesopores along with surface oxygen functional group [11].

In chemical activation, the raw materials are first impregnated with certain activating agents which may be acids such as conc. HCl, conc. H_2SO_4, conc. HNO_3, H_3PO_4 etc, bases such as KOH, NaOH, $Ca(OH)_2$ etc or salt such as $ZnCl_2$. The most extensively used activating agents to produce activated carbon with desired pore size distribution at low temperature are phosphoric acid and zinc chloride [15,16]. Chemical activation is preferred to the physical activation. Usually the surface groups depend upon the conditions during and after the preparation of activated carbon. Some of the structures of surface functional groups are shown in Figure 8 [6].



(a) (b) (c)

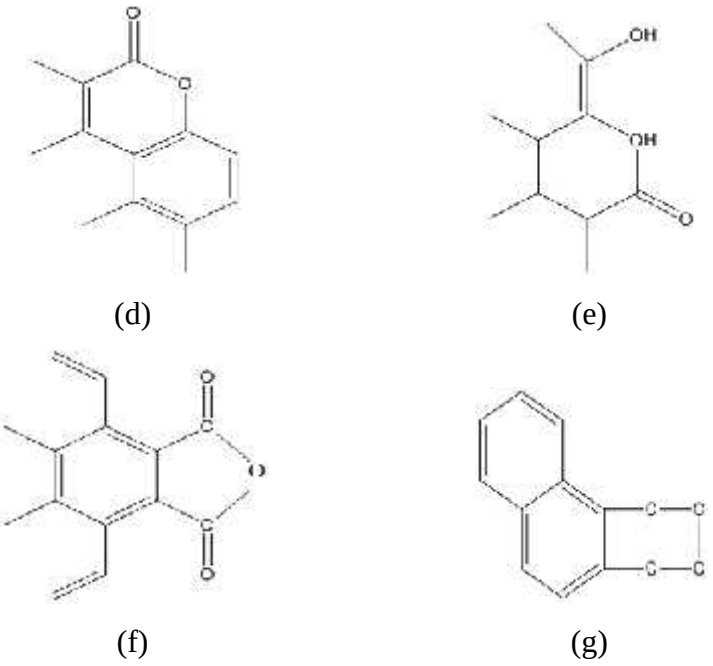


Figure 8: Structures of some surface oxides: (a) Carboxylic acid (b) Phenolic hydroxyl (c) Quinone- type carbonyl group (d) Normal lactone (e) Fluorescein-type lactones (f) Carboxylic acid anhydrides (g) Cyclic peroxides

1.5 Characterization of Activated Carbon

1.5.1 Moisture and Ash content of Precursor:

Proximate analysis of the adsorbent is done to determine the percentage of ash, percentage of moisture in the precursor. Adsorbent with the low ash and moisture content is regarded as the good adsorbent because it has the high percentage of carbon. The percentage of ash and moisture content is determined by the formula [5]:

Ash content/Moisture content (%) = ... (1)

Where,

W_1= weight of sample before heating (in gm)

W_2= weight of sample after heating (in gm)

Ash quantity = (W_1-W_2) gm

1.5.2 Methylene Blue Number

The methylene blue number is defined as the maximum number amount of adsorbate adsorbed on 1.0 gm of the adsorbent. It gives the estimation of the mesopore content of the activated carbon. The methylene blue solution is analyzed for the residual concentration using spectrophotometer, after it has been agitated with 0.1 gm of activated carbon for 24 hours. The value of the absorbance for the solution after the adsorption is applied to the equation obtained from calibration curve for obtaining the final concentration [17].

The amount of methylene blue adsorbed (q_t), uptake per unit mass of the adsorbent (mg/gm) at time 't' is given by the equation:

.....(2)

Where, C_o and C_t are the initial concentration of the solution in mg/L and at time t, respectively. V is the volume of the test solution in liter and M is the mass of the dry adsorbent in gram.

1.5.3 Iodine Number

The amount of iodine (mg) adsorbed by 1gm of adsorbent is called iodine number [ASTM D4607-94], [18]. It is the most fundamental parameter used to characterize the activated carbon performance. It is a measure of activity level often reported in mg/gm. Higher values of iodine number indicate the higher degree of activation due to the increase in nanoporosity with high surface area. It measures the micropore content of the activated carbon by adsorption of iodine from solution [17, 18].

1.5.4 Surface Area

The adsorption capacity of an adsorbent depends upon the surface area of the adsorbent. The more the surface area higher is the extent of adsorption. BET single point method using nitrogen is one of the mostly recommended methods for the determination of surface area of the adsorbent. But surface area also can be determined by the chemical or dye adsorption method. The formula for the determination of surface area by methylene blue adsorption is [19]:

.....(3)

Where,

S_{MB} is the specific surface area in $10^{-3}km^2kg^{-1}$; q_e is the number of molecules of methylene blue adsorbed at the monolayer of adsorbent in $mggm^{-1}$; a_{MB} is the occupied surface area of one molecule of methylene blue (197.2 Å); N_A is the avogadro's number (6.023×10^{23} mol^{-1}) and M_{MB} is the molecular weight of methylene blue (373.99 gm mol^{-1}).

1.5.5 Surface Functional Group

The oxygen containing functional groups are present in the surface of the activated carbon which are formed during the treatment of sample with phosphoric acid. This makes the surface slightly acidic. Usually the oxygen containing functional groups are carboxylic, lactones and phenols. Besides the acidic groups, the activated carbons also possess basic property which is associated with the Pi-sites of the basal plane. The Lewis base property of activated carbon originates because of the Pi-electron system present in the basal plane which can be donated to any reactive electron functional group in the aqueous solution [20].

Boehm titration is a method for the characterization of acid-base properties of the activated carbon. The method is based on the principle that strong acids and bases will react with all the bases and acids respectively, whereas the conjugate bases of weak acid will accept protons only form stronger acid (i.e acids with lower P^{Ka} values). In this process, the neutralization of surface oxides (acidic groups) with bases such as sodium hydroxide (NaOH), sodium bicarbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3) occurs whereas the neutralization of basic functional group occurs with the acids such as hydrochloric acid (HCl). The acidic constant of the acidic groups like carboxylic, lactones and phenols differ over several orders of magnitude and it is possible to distinguish the acidic group on the basis of their neutralization behavior. The various free acidic groups are measured using the assumption made by Boehm that $NaHCO_3$ (P^{Ka}=6.37) neutralizes carboxylic group only, Na_2CO_3 (P^{Ka}=10.25) neutralizes carboxylic group including lactones group and NaOH (P^{Ka}=15.74) neutralizes carboxylic, lactones as well as phenol group [21]. The neutralization reaction in aqueous solution of Boehm titration is given as:

$R\text{-}COOH\ (aq) + NaOH\ (aq) \quad R\text{-}COONa\ (aq) + H_2O\ (l)$

$2R\text{-}COOH\ (aq) + Na_2CO_3\ (aq) \quad 2R\text{-}COONa\ (aq) + CO_2\ (g) + H_2O\ (l)$

$R\text{-}COOH\ (aq) + NaHCO_3\ (aq) \quad 2R\text{-}COONa\ (aq) + CO_2\ (g) + H_2O\ (l)$

Where, R is a generalized representation for the surface bound carbon atom.

The total amount of carboxylic group can be calculated by the amount of $NaHCO_3$ consumed; the amount of lactones group is calculated by neutralization difference between Na_2CO_3 and $NaHCO_3$ and finally phenol group can be measured by neutralization difference between NaOH, Na_2CO_3 and $NaHCO_3$. The total amount of basic sites can be calculated from the amount of HCl consumed by carbon in neutralization reaction between carbon surface and HCl.

1.5.6 Fourier Transform-Infrared Spectroscopy (FT-IR)

FT-IR analysis is carried out to find out the functional group present on the surface of the adsorbent. The spectra from the FT-IR analysis reveal the IR wavelength in which the absorption occurs. Absorption occurs when the frequency of the radiation i.e IR is equal to the vibrational frequency of the covalent bond in the molecule. The sample with the few IR active bonds and high purity gives the simple spectra whereas that of the sample with more complex structure lead to more adsorption resulting more complex spectra [22, 23].

1.5.7 Scanning Electron Microscopy (SEM)

SEM images are used to characterize the surface morphology of the adsorbent. It shows the surface texture and nature of the surface of the adsorbent. In general, the adsorbent possessing more pores and irregular surface is considered to have high surface areas and good adsorption capacity [10,16].

1.5.8 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) technique is one of the family of non-destructive analytical techniques which reveals information about the crystallographic structural, chemical composition, and phases of materials.

It also determines the orientation in polycrystalline or powdered solid samples. It is commonly used to identify unknown substances and may also be used to characterize heterogeneous solid mixture to determine the relative abundance of crystalline compounds [24].

1.6 Adsorption Study

1.6.1 Spectrophotometric Method for the Determination of Adsorption of Dyes and Medicines

The theoretical aspects of spectrophotometric analysis is based on Lambert- Beer's law 25, 26]. Mathematically,

..... (4)

Where,

A = absorbance or optical density

b = path length of the absorbing medium and

c= concentration of the absorbing species

Absorbance (A) can be defined as:

..... (5)

Where,

I_o = intensity of the incident radiation

I_t = intensity of transmitted radiation

The quantity 'a' of the equation (4) is called absorptivity when the concentration 'c' of the solution is express in grams per liter. When 'c' is expressed in mole per liter, the Lamberts-Beer's law is usually written as:

..... (6)

Where, ε is called molar extinction coefficient.

A plot of absorbance (A) versus concentration (c) will give a straight line passing through the origin as shown in Figure 9.

Absorbance

Concentration (ppm)

Figure 9: Absorbance vs. concentration plot

1.6.2 Adsorption Isotherm

Adsorption is a surface phenomenon that occurs when a gas or liquid solute accumulate on the surface of the solid or liquid forming molecular or atomic film. Adsorption by solid is not a very important process unless the solid has a very large surface area compared to its mass. Adsorption of solid or liquid to the adsorbent mainly fall into two board categories i.e physiosorption and chemiosorption. In physiosorption the adsorbate binds loosely to the adsorbent surface via vander Waals' type interaction and therefore, multilayer adsorption is possible but easily disrupted by increasing the temperature. Chemiosorption involves the adsorption of adsorbate to the adsorbent by a process that is more akin to a chemical reaction and hence, only monolayer adsorption is possible. Adsorption isotherm is a curve between the amount of substance adsorbed by a given adsorbent and the concentration of the substance at equilibrium at a given temperature. Freunlich and Langmuir adsorption isotherms are the two commonly accepted models used to analyze the adsorptive behavior of adsorbate on adsorbent.

1.6.2.1 Langmuir Adsorption Isotherm

Among the number of adsorption isotherm models, Langmuir adsorption isotherm is the most commonly used isotherm for the adsorption of the adsorbate from the solution. Langmuir's isotherm describing the adsorption of adsorbate onto the surface of the adsorbent requires three assumptions:

- The surface of the adsorbent is in contact with the solution containing an adsorbate which is strongly attached to the surface.
- The surface has a specific number of sites where the solute molecules can be adsorbed.
- The adsorption involves the attachment of only one layer of molecules to the surface, i.e. monolayer adsorption.

The basic form of the equation developed by Langmuir can be written as:

.....(7)

Where, q_e is the amount of adsorbate adsorbed (mg) per unit mass of the adsorbent (gm)

q_m is the amount of adsorbate adsorbed (mg) per unit mass of the adsorbent (gm) on complete monolayer formation, which is constant at fixed temperature. It is determined solely by the nature of the adsorbent.

b= the adsorption constant (L/mg) related to the energy of adsorption or net enthalpy of adsorption. The higher value indicates that the system attends the equilibrium quickly.

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

To analyze the validity of the Langmuir adsorption isotherm the Langmuir equation is linearized as follows:

.....(8)

From the experimental value of Ce and q_e, a plot of Ce / q_e against C_e can be drawn from which Langmuir parameters q_m and b can be calculated. The values so obtain provide the information of quality of adsorbent. The adsorbent with the high value of q_m is preferred since its adsorption capacity is high.

1.6.2.2 Freundlich Adsorption Isotherm

An alternate isotherm to Langmuir isotherm developed by H. F. Freundlich frequently describes the data better [27]. The Freundlich adsorption isotherm is:

.....(9)

Where, q_e is the number of miligrams of the adsorbate adsorbed per unit gram of adsorbent.

C_e is the equilibrium concentration of the adsorbent (mg/L), K (or K_F) and n are the Freundlich constants related to the adsorbent capacity and adsorbent intensity of the given adsorbent.

To test the validity of Freundlich equation, the linear form of equation is obtained by taking the logarithm on both sides of the equation 9.

k+ ..... (10)

Thus a plot of log q_e against log C_e should give a straight line with slope equal to 1/n and the intercept on the y-axis equal to log K.

The value of 1/n less than 1 indicates that the adsorbent is favorable for the adsorption of the given species.

Apart from the homologous surface adsorption, the Freundlich isotherm is also suitable for a highly non ideal sorption that involves heterogeneous surface and an adsorption isotherm lacking a pleatue, indicating a multilayer adsorption.

1.6.3 Kinetics of Adsorption

The rate of solute uptake by the adsorbent from the solution is perfectly described by the adsorption dynamics. The adsorption dynamics greatly governs the mechanism of adsorption. The kinetics of dye and medicine adsorption on the activated carbon was analyzed using pseudo-first order and pseudo-second order model.

The conformity between experimental data and the model predicted values is expressed by the correlation coefficients (R^2, values closer or equal to 1). A relatively high R^2 value indicates that the model successfully describes the kinetics of dye and the medicine adsorption.

1.6.3.1 The Pseudo-First Order Equation

The pseudo-first order equation according to Lagergren (1898), is generally expressed as follows [28, 29]:

..... (11)

Where, q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/gm); k_1 is the rate constant of pseudo-first order adsorption (L/min).

After integration and applying the boundary conditions t=0 to t= t and q_t=0 to q_t= q_t,

..... (12)

The values of log (q_e –q_t) is linearly correlated with t. The plot of log (q_e – q_t) vs. t gives a linear relationship from which k_1 and q_e can be determined from slope and intercept of the plot, respectively.

1.6.3.2 The Pseudo-Second Order Equation

The pseudo-second order adsorption kinetic rate equation is expressed as (Ho et al., 2000) [28, 29]:

..... (13)

Where, k_2 is the rate constant of pseudo second order adsorption (gm/mg min).
For the boundary conditions t=0 to t=t and q_t =q_t, the integrated form becomes:

..... (14)

Which is the integrated rate law for a pseudo second- order reaction. This equation can be rearranged to obtain a linear form:

..... (15)

If the initial adsorption rate, h (mg/gm min) is:

Then,

..... (16)

The plot of (t/ q_t) and t gives a linear relationship from which q_e and k_2 can be determined from the slope and the intercept of the plot, respectively.

CHAPTER 2

2.1 LITERATURE REVIEW

Studies have shown that different types of medicines and dyes in general can be removed from waste water using activated carbons by the process of adsorption. Once the activated carbon has been used for the treatment of waste water it becomes exhausted and is no longer capable of further adsorption without treatment. Number of raw material such as coconut shells, peach stones, olive stones, lapsi stones etc. have been used as the precursor for the preparation of activated carbon. But not much work has been done using *Areca catechu* nuts as the precursor for the preparation of activated carbon.

Ayranci and Hoda (2005) studied the adsorption of pesticides such as ametryn, diuron, dinose and aldicrab from aqueous solution into high specific area activated carbon-cloth adsorbent and found that the maximum adsorption capacity for ametryn, diuron, dinose and aldicrab were 354.61, 421.58, 301.84, 213.06 mg/gm, respectively [30].

Asadullah et al. (2007) studied the adsorption of carbon tetrachloride and benzene on the activated carbon prepared from jute stick char derived from the pyrolysis process for the bio-oil production. The char was thermally activated using steam at the temperature of 700-850 °C. Effect of activation temperature on the yield of activated carbon showed that as the temperature increased the amount of yield decreased. Whereas, increase in the contact time for the adsorption of both the carbon tetrachloride and benzene the amount of adsorption increased [31].

R.A. Shawabkeh et al. (2007) prepared activated carbon from Pecan shells using phosphoric acid as an activating agent and the activation was followed by treatment with sodium dodecyl sulfate. Thus treated activated carbon showed a great ability for methylene blue adsorption of 410 mg/gm at pH 9 and moderate adsorption for phenol of 18 mg/gm at pH 11 with same concentration for both the solutions [32].

Hamdaoui et al. (2007), studied and modeled the adsorption equilibrium isotherms of five phenolic compounds (toxic organic pollutants) from aqueous solution into granular activated carbon. The five compounds selected were phenol, 2-chlorophenol, 4-chlorophenol, 2,4-

dichlorophenol and 2,4,6-trichlorophenol. It was observed that the interaction of phenolic compounds with activated carbon surface occurred in localized monolayer adsorption type, i.e adsorbed molecules are adsorbed at definite, localized sites [33].

Ip et al. (2008) studied the production of series of activated carbon from bamboo using phosphoric acid as an activating agent in different ratios. The sample activated with the impregnation ratio of 2:1, at 600°C for 4 hours with the rate of 1°C/min showed the highest surface area of 2123 m^2/g [34].

Patnukao et al. (2008) studied the preparation of powdered activated carbon using phosphoric acid as an activating agent. The adsorption capacity of the activated carbon was found to be significantly affected by the carbonization temperature and the weight ratio between the raw material and phosphoric acid. The best result was obtained for the carbon activated with an impregnation ratio of 1:1, and carbonization temperature of 500 °C for 1 hour. The iodine number, methylene blue number and the BET surface area were determined to be 1043 mg/gm, 427 mg/gm and 1239 m^2/gm respectively [35].

Amin (2008) studied the preparation of activated carbon from sugarcane baggase pith by chemical activation with 28% H_3PO_4, 50% $ZnCl_2$ followed by pyrolysis at 600°C. Study was based on the removal of reactive orange dye from aqueous solution using different activated carbon. Batch adsorption experiments were performed as a function of initial dye concentration, contact time, adsorbent dose and pH. Langmuir and Freundlich adsorption isotherms were used to analyze the data. Kinetics studies showed that the adsorption followed pseudo-second order kinetics [36].

K. Tahvildari et al. (2009) manufactured activated carbon using peach stones. The activation of samples of varying sizes was done with phosphoric acid solution in different ratio and carbonized for different periods of time. The sample with the size of 0.25 mm and carbonized time of 1.5 hours gave the best result for methylene blue test with the least absorbent number (A=0.0470). Similarly, the result of Iodine value test was in the range of 1697.03 to 1759.24 mg/gm [37].

Ekpete O.A. and Horsfall M. JNR (2011) prepared activated carbon from fluted pumpkin waste by carbonizing it at 350 °C for two hours and allowing it to cool at room temperature for another three hours before activating it with 0.3 M H_3PO_4 and heating to 300 °C for thirty minutes. Carbonization above 350 °C converted the sample completely into ashes. The value of iodine number for the activated carbon by above process was found to be 224.90 mg/gm. Comparisons were done with the commercially available activated carbon on the basis of iodine number, porosity and pH by analyzing the data obtained statistically [5].

Wang et al. (2013) prepared mesoporous activated carbon from coconut shells by the method of chemical activation with phosphoric acid. The surface area for the activated carbon was 891 m^2/gm as determined by BET method. The methylene blue adsorption was 21.5 ml/0.1gm and iodine number was found to be 889.36 mg/gm [38].

M. Stoykova et al. (2013), studied the adsorption of carbamazepine, an antiepileptic drug from aqueous solution using the steam activated beech charcoal. The uptake of the adsorbent was directly proportional to their specific surface area. The adsorbents, activated at higher temperature > 700 °C had a higher adsorption capacity than those activated at lower temperature < 500 °C [39].

Jasim et al. (2013), used Kaolin and activated carbon as adsorbent for the adsorption of an anti-diabetic drug, glimepiride. Batch adsorptions as a function of initial drug adsorption, contact time, adsorbent dose, pH were performed. Lamgmuir and Freundlich adsorption isotherm models were used to analyze the data. It was found that the quantity of medicine adsorbed increased with increase in pH but with the increase in temperature the adsorption decreased [40].

P. K. Chayande et al. (2013) studied the adsorption of phenolic pollutants by almond shell activated carbon impregnated with phosphoric acid. The impregnation was done in the ratio of 1:2 for 48 hours and carbonized at 850 °C in the furnace reactor for 2 hours. It was found that the use of phosphoric acid greatly enhanced the surface property of the activated carbon. SEM revealed the highly developed micro and mesopores whereas FT-IT revealed the presence of –OH (hydroxyl group) for the phenolic binding sites [41].

Carlos A Rey-Mafull et al. (2014) investigated the adsorption of acetaminophen on activated carbons in simulated gastric fluid at pH 1.2 and residual adsorbate was monitored by UV visible. The model that best fit the experimental data was Langmuir isotherm and the adsorption process was determined to be spontaneous and exothermic [42].

2.2 OBJECTIVES

Broad objective

A number of fruit seeds, stones, husks, shells etc. are used as precursor for the preparation of activated carbon. Not much works are available about the use of activated carbon derived from *A. catechu* nuts. It contains high percentage of carbon and could be the potential precursor for the production of activated carbon that can be used as the antidote for acute poisoning in medicinal fields. Therefore, the basic purpose of the study is to prepare the activated carbon from *A. catechu* nuts as an adsorbent and study the adsorptive characteristics for the removal of optilan red dye and anti-diabetic medicine, glimepiride.

Specific objectives

The specific objectives of this research works are:

- To prepare activated carbon from the powdered *A. catechu* nuts by chemical activation with ortho-phosphoric acid, KOH and $ZnCl_2$ in different impregnation ratio at inert atmosphere.
- To characterize the prepared activated carbon from *A. catechu* nuts by iodine number, methylene blue number, XRD (X-ray diffraction), SEM (Scanning electron microscopy), FT-IR (Fourier transform Infrared) spectroscopy.
- To compare the adsorption capacity of the prepared activated carbon as an adsorbent with commercially activated carbon.
- To determine the surface functional groups (carboxyl, lactone, phenolic) present in the prepared activated carbon using Boehm titration method.
- To investigate the effect of pH, contact time and initial concentration of optilan red and glimepiride for their removal.
- To study the adsorption isotherm and the kinetics of adsorption.

CHAPTER 3

EXPERIMENTAL

3.1 Preparation and Activation of Precursor

3.1.1 Preparation of Powdered Precursor from *Areca catechu* Nuts

The precursor i.e. *Areca catechu* nuts was bought from the local market. It was then washed with distilled water and at last rinsed with deionised water. It was put in the hot air oven at the temperature of 110°C for 6- 12 hours. After the nut was completely dried it was grounded to fine powder. Then it was sieved to 425 µm particle size using sieving mesh.

3.1.2 Activation of Precursor

In general, activation of raw precursor can be done either by chemical or physical activation method.

Here, the activation method employed was the chemical activation in which fixed amount of precursor was treated with different chemicals such as H_3PO_4, $ZnCl_2$ and KOH in different ratios.

The amount of 15 grams of powdered precursor was taken and treated with 29.8 ml of H_3PO_4 (45.10 N) in 1:1 ratio and then it was left for 24 hours. Drying process of the chemically activated precursor was done using hot oven for about 24 hours at 110°C. The ACs in different ratios (0.4:1, 0.7:1, 1:1, 1.5:1 and 2:1) of chemical and precursor were prepared calculating the amount of ortho-phosphoric acid to be used.

For the activation of the precursor with KOH in the ratio 1:1, 43.0 gm of KOH pellet was taken and added to 30 gm of powdered precursor with small amount of water. It was left for 24 hours and then dried in oven for 24 hours.

For the activation of the precursor with $ZnCl_2$ in the ratio 1:1, 62.63 gm of $ZnCl_2$ was taken and added to 30 gm of powdered precursor with the small amount of water. It was left for 24 hours and then dried in oven for 24 hours.

The chemically activated precursor was carbonized using tubular furnace at the temperature of 400°C for 3 hours in an inert atmosphere of nitrogen at the flow rate of 100 ml per minute. After carbonization, it was cooled at the room temperature and washed with deionised water until the pH was neutral. The activated carbon impregnated with $ZnCl_2$ was washed with 5% HCl until the pH was neutral. It was then completely dried in oven and sieved to size 212 µm and kept in air tight container for the further research works.

Table 1. Preparation conditions of activated carbons

Sample	Carbonization temperature (°C)	Particle size (µm)	Activating agent	Ratio of activating agent (gm) and precursor (gm)
AC-1A	400	425	H_3PO_4	0.4:1
AC-1B	400	425	H_3PO_4	0.7:1
AC-1C	400	425	H_3PO_4	1:1
AC-1D	400	425	H_3PO_4	1.5:1
AC-1E	400	425	H_3PO_4	2:1
AC-2	400	425	KOH	1:1
AC-3	400	425	$ZnCl_2$	1:1
R-1	400	425	-	-

3.2 Characterization of Precursor

3.2.1 Moisture and Ash Content of Precursor:

Ash content of the sample was determined by heating 1gm of the sample in properly weighed crucible for 3 to 4 hours at a constant temperature of 110°C in a muffle furnace till the ash was obtained. The weight was taken after cooling it at room temperature.

For determining the moisture content of the powdered sample, 1gm of sample was weighed in a crucible and heated for 2 to 3 hours in an electric oven until the constant weight was obtained.

3.3 Characterization of Activated Carbon

3.3.1 Methylene Blue Number

Batch adsorption experiments were performed for the determination of methylene blue number of the activated, non-activated and commercial activated carbon. The amount of 0.1gm of AC was agitated with 50 ml of different concentration of methylene blue solution for 24 hours in the shaker. At the end of the experiment, the AC was allowed to settle down by centrifuging it. The upper part of the solution was analyzed for the residual concentration using spectrophotometer. The value of the absorbance for the solution after the adsorption was applied to the equation obtained from calibration curve for obtaining the final concentration [17].

3.3.2 Iodine Number

The amount of 0.1 gm of AC was added to 5 ml of 5 % HCl in a conical flask and swirled until all the AC was wetted by the acid. Then the solution was boiled for 30 seconds and cooled down to room temperature. To this 10 ml of 0.1 N iodine solution was added and was shaken thoroughly for 5 to 10 minutes. Then the solution was allowed to settle and was filtered using filter paper. The filtrate was titrated against 0.05 N sodium thiosulphate solution using starch as the indicator. Then the iodine number was determined [17, 18].

3.3.3 Surface Area

Determination of the surface area by chemical adsorption technique was done by taking 0.1 gm of AC and agitating with 50 ml of methylene blue solution of varying concentration. The final concentration of the solution was determined using spectrophotometer. From the result obtained, isotherm was plotted from which the value of q_e was determined using the formula given in equation 3, [19].

3.3.4 Surface Functional Group

The amount of 100 mg of the activated, non-activated carbon were taken separately in 125 ml reagent bottles containing 50 ml of 0.05 N solutions of NaOH, Na_2CO_3, $NaHCO_3$ and HCl. The reagents bottles were tightly closed and agitated for 48 hours. After that the solutions were left to decant and then filtered. The filtrates of each of the basic solutions were titrated with 0.05 N

HCl, while the acidic solution is titrated with 0.05 N NaOH solution using methyl orange as the indicator [29].

3.3.5 Fourier Transform-Infrared Spectroscopy

FT-IR analysis was carried out to find out the functional group present on the surface of the adsorbent. The carbon-oxygen functional groups present on the surface of the samples were identified using FT-IR measurements (FTIR model-IR Prestige-21, SHIMADZU) at DPR, Thapathali, Kaathmandu.

3.3.6 Scanning Electron Microscopy

SEM images were used to characterize the surface morphology of the adsorbent. The surface morphology of the activated carbon were investigated using SEM instrument.

3.3.7 X-Ray Diffraction

The XRD of the samples was taken using X-Ray Diffractometer [Bruker D27 Phaser; CuK_{α} radiation with λ=0, 15418 nm].

3.4 Adsorption Study

3.4.1 Determination of λ_{max} and Construction of Calibration Curve

To determine the λ_{max} and for the construction of calibration curves of different solutions of dyes and drugs following procedures were followed.

For the determination of λ_{max} of methylene blue, a 5 ppm solution of methylene blue was taken in glass cuvette of 1cm path length and the absorbance of the solution was measured for the varying wavelength ranging from 640 nm to 685 nm against the distilled water as the blank using spectrophotometer (SSI, UV 2101 Spectrophotometer). A plot of absorbance versus wavelength was plotted and the wavelength corresponding to maximum absorbance was noted.

Similarly, for determining the λ_{max} of optilan red and glimepiride, a 25 ppm solution of optilan red and glimepiride were taken separately in a glass cuvette of 1 cm path length and the

absorbances were measured against distilled water with the varying wavelength range of 460 nm to 550 nm and 190 nm to 214 nm respectively for optilan red and glimepiride.

For the preparation of calibration curve, the methylene blue solutions of different concentrations from 1 ppm to 10 ppm were prepared and the absorbances were taken against distilled water as blank at the λ_{max} value i.e. 665 nm obtained from the plot of absorbance versus wavelength.

Similarly, for the calibration curves of optilan red and glimepiride, each of the solutions of concentration ranging from 5 ppm to 40 ppm were prepared and the absorbances were noted against distilled water as the blank at the λ_{max} value i.e. 505 nm and 200 nm respectively obtained from the plot of absorbance versus wavelength.

3.4.2 Adsorption Isotherm

To determine the adsorption isotherm of methylene blue, the solutions of different concentration from 100 ppm to 300 ppm were taken in reagent bottles. To each of these, 0.1 gm of the adsorbents (AC-1C, AC-1D, CAC and R-1) were added and were agitated till the equilibrium time. After the equilibrium time the solutions were left to decant and were filtered. The residual dye and the medicine concentration were determined from the filtrate spectrophotometrically by measuring the absorbance at λ_{max} i.e. at 665 nm.

Similarly, for the determination of adsorption isotherms of optilan red and glimepiride, the 50 ml solution of varying concentration ranging from 50 ppm to 250 ppm and 20 ppm to 120 ppm respectively were taken in reagent bottles. To each of these, 0.1 gm of the adsorbents (AC-1C, AC-1D and CAC) were added and were agitated till the equilibrium time. After the equilibrium time the solutions were left to decant and were filtered. The residual dye and the medicine concentration were determined from the filtrate spectrophotometrically by measuring the absorbance at λ_{max} i.e. at 505 nm and 200 nm for optilan red and glimepiride.

3.4.3 Effect of pH

For the study of effect of pH on the adsorption of anti-diabetic medicine glimepiride, batch adsorption studies similar to that of isotherm studies were conducted maintaining different pH ranging from 2 to 6 for different solutions. The pH of the solutions were adjusted using 1N

NaOH and 1N HCl. The pH was measured using digital pH meter (CHEMI LINE, DIGITAL pH METER,CL110) and the optimum pH was selected for the further studies.

3.4.4 Effect of Initial Concentration

For the study of effect of pH on the adsorption of anti-diabetic medicine glimepiride, batch adsorption studies similar to that of isotherm studies were conducted with the initial concentration of the solutions different. The solutions were agitated till the equilibrium time and the final concentration of the solutions were determined spectrophotometrically.

3.4.5 Effect of Contact Time

The data for the effect of contact time were obtained from the kinetics studies itself. The solutions were withdrawn at desired contact time and were analyzed spectrophotometrically.

3.4.6 Kinetics of Adsorption

For the study of kinetics of optilan red, 0.1 gm of adsorbents (i.e. AC-1C, AC-1D and CAC) were added to 50 ml of 100 ppm solution in reagent bottles and were shaken in the shaker. The samples were withdrawn and filtered after desired contact time. The concentration of the dye was determined by measuring the absorbance spectrophotometrically. The solutions were withdrawn after each 10 minutes.

And for the kinetic studies of glimepiride, 0.1 gm of adsorbents (i.e. AC-1C, AC-1D and CAC) were added to 50 ml of 50 ppm solution in reagent bottles and were shaken in the shaker. The samples were withdrawn and filtered after desired contact time and the concentration of the medicine was determined same as that of optilan red.

CHAPTER 4

4. RESULTS AND DISCUSSION

4.1 Characterization of Precursor

4.1.1 Moisture and Ash Content of Precursor

The moisture and ash content of powder of *A. Catechu* nuts having the size of < 425 µm were found to be 2.04% and 1.66%, respectively, as given in Table 2.

Table 2. Moisture and ash contents of *A. catechu* nuts powder

Sample size	Moisture content %	Ash content %
<425 µm	2.04	1.66

4.1.2 FT-IR Spectra of Precursor

FT-IR spectroscopic technique was employed to analyze the surface functional group of the precursor, i.e, powdered *A. catechu* nuts and obtained FT-IR spectrum is shown in Figure 10. A peak at 1519.91 cm^{-1} is due to the skeletal vibration, involving C-C stretching within the ring of mononuclear aromatic hydrocarbon. A peak at 1620.21 cm^{-1} can be attributed to the unsymmetrical stretching of C=C in conjugated system. The presence of –C=O group can be concluded by the presence of a band at 1735.93 cm^{-1}. A band at 2916.37 cm^{-1} can be attributed to the unsymmetrical stretching of C-H bonds of methyl groups. The band at 3502.73 cm^{-1} clearly shows the presence of –OH group which could be of the alcohol or phenol [43].

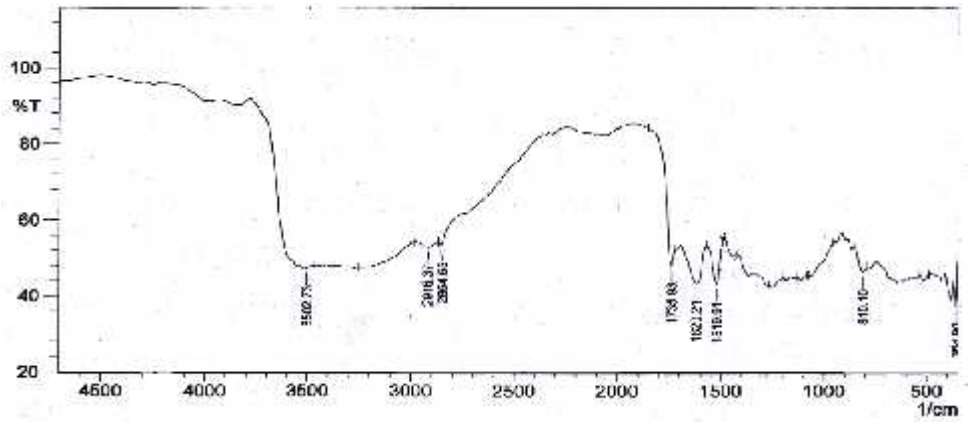


Figure 10: FT-IR spectra of R-1

4.2 Characterization of Activated Carbon

4.2.1 Methylene Blue Number

Table 3 shows the methylene blue number of the activated carbon.

Table 3. Methylene blue number of activated carbon

Samples	Methylene blue number (mg/gm)
AC-1A	331.222
AC-1B	344.162
AC-1C	**405.243**
AC-1D	384.176
AC-1E	247.032
AC-2	108.672
AC-3	242.79
CAC	272.60
R-1	129.825
H_2SO_4 char	156.266

From the results shown in Table 3 for the methylene blue adsorption we can see that AC-1C has the maximum adsorption with the value of 405.243 mg/gm which is very large value in comparision with CAC which has the value of only 272.60 mg/gm. With the increase in the ratio of phosphoric acid used for activation the methylene blue number also has increased but as the ratio reaches beyond 1:1, the value again starts to decrease. The values for R-1, H_2SO_4 char and AC-2 are very less in comparision to the ones activated with ortho-phosphoric acid. The ortho-phosphoric acid induces pyrolytic decomposition of the lignocellulosic material since it promotes depolymerization, dehydration and redistribution of constituent biopolymers, favoring the conversion of aliphatic compounds to aromatic compounds.

4.2.2 Iodine Number

The iodine number gives us the idea about the extent of presence of micro pores in the activated carbon. Table 4 shows the Iodine number of the activated carbon.

Table 4. Iodine number of activated carbon

Samples	Iodine number (mg/gm)
AC-1A	873.399
AC-1B	1012.207
AC-1C	**1080.122**
AC-1D	1035.001
AC-1E	980.772
AC-2	698.088
AC-3	855.032
CAC	887.723
R-1	609.839
H_2SO_4 char	817.31

The iodine number value is maximum for the AC-1C which is 1080.122 mg/gm, whereas the lowest is observed for the R-1, which is not activated with any of the activating agents. The carbons activated with ortho-phosphoric acid have more iodine number value than that of the ones activated with KOH, $ZnCl_2$ and that of the H_2SO_4 char.

4.2.3 Comparison of Methylene Blue Number and Iodine Number

Figure 11: Bar Diagram for methylene blue and iodine number

4.2.4 Surface Area Determination

Determination of surface area of *A. catechu* nuts powder (raw as well as activated carbon) was obtained from the adsorption process of methylene blue adsorption using Langmuir adsorption isotherm. The surface areas of activated carbon, non-activated carbon and commercially activated carbons are listed in Table 5. The surface area of the non-activated carbon was found to be very low, that is, about 412 m^2/gm but after treatment with phosphoric acid the surface areas of the chemically treated activated carbons were greatly increased. The highest surface area was found for the AC-1C with the value of 1380.801 m^2/gm.

Table 5. Surface area of different activated and non-activated carbon

Sample	Surface area (m^2/gm)
AC-1C	1380.801
AC-1D	851.861
CAC	865.736
R-1	412.304

4.2.5 Surface Functional Group Determination: Boehm's Titration

The functional groups (acidic and basic) present in the surface of the adsorbent were quantified by Boehm's titrimetric method. The oxygen containing functional group (acidic) was determined by allowing the carbon to react with different bases according to the following Boehm's assumptions:

(i) $NaHCO_3$ neutralizes carboxyl group only

(ii) Na_2CO_3 neutralizes carboxyl and lactone group

(iii) NaOH neutralizes carboxyl, lactone as well as phenol group.

If A, B and C referred to the miliequivalents (meq) of $NaHCO_3$, Na_2CO_3 and NaOH neutralized by charcoal then,

meq of carboxyl group =A

meq of lactone group =B-A

meq of phenol group =C-B

The calculation is illustrated in Figure 12.

(weak acid fraction)

Phenol

(moderate acid fraction)

Lactones

(Strong acid fraction)

Carboxylic acid

NaOH Na_2CO_3 $NaHCO_3$

Figure 12: Illustration of the calculations used in Boehm titration

The basic functionalities are measured as a single value from the meq of HCl neutralizes.

Table 6. Results of Boehm titration

Adsorbents	Volume consumed in ml			
	$NaHCO_3$	Na_2CO_3	NaOH	HCl
AC-1C	5	8.7	13.9	3.2
AC-1D	5.1	8.9	14.7	3.3
R-1	3.2	5.7	8	4.6

The amount of oxygen containing functional group per gram of AC is calculated by following the Boehm's titration on the basis of the volume of the acid or the bases consumed by the definite weight of the AC. The calculation of the carboxylic group from the results given in table is portrayed below.

Volume of 0.05N $NaHCO_3$ consumed by 2.1 gm AC-1C = 5 ml

Since $NaHCO_3$ is neutralized by carboxylic group, the meq of carboxylic present = 0.05×5 = 0.25 meq

That is, 0.1 gm of AC-1C contains 0.25 meq of carboxylic group.

Therefore, 1 gm of AC-1C contains 0.25/ 0.1 = 2.5 meq of carboxylic group

Hence, the amount of –COOH group in AC-1C is 2.5 meq per gram.

The meq per gram of other functional groups present are calculated similarly following the Boehm's procedure.

The results obtained from the Boehm's titration regarding the amount of acidic/basic functional group is presented in Table 7.

Table 7. Results of Boehm titration

Adsorbents	Functional groups milliequivelents per gram (meq/gm)			
	Carboxyl	Lactone	Phenol	Basic
AC-1C	2.5	1.85	2.6	1.6
AC-1D	2.55	1.9	2.9	1.65

R-1	1.6	1.25	1.15	2.3

4.2.6 FT-IR Spectra of Activated Carbons

The above Figure 13 shows the FT-IR spectra of AC-1C in which a peak at 1087.85 cm^{-1} is due to the in plane bending of C-H bonds of mononuclear aromatic hydrocarbon. A peak at 1234.44 cm^{-1} shows the asymmetrical C-O-C stretching in vinyl ethers and peak at 1604.77cm^{-1} can be attributed to C=C stretching of vinyl ethers. A broad band at 3425.58 cm^{-1} is due to –OH group of phenol or alcohol due to hydrogen bonding [43].

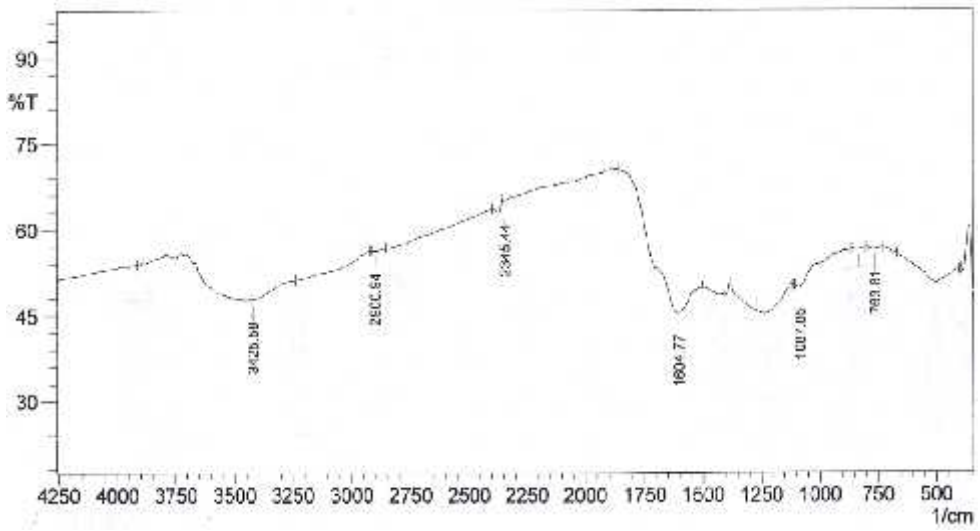


Figure 13: FT-IR spectra of AC-1C

The FT-IR spectra of the AC-2 is given in the Figure 14. A peak at 1087.85 cm^{-1} is due to the in plane bending of C-H bonds of mononuclear aromatic hydrocarbon. Peak at 1604.77cm^{-1} can be attributed to C=C stretching of vinyl ethers. A small peak at 1705.07cm^{-1} shows the presence of C=O group. Due to the asymmetric stretching of C-H bond of methyl group a peak can be seen at 2924.09cm^{-1}. The broad band in the range of 3400 to 3500 cm^{-1} can be attributed to the hydrogen bonding of –OH of the alcoholic or the phenolic group [43].

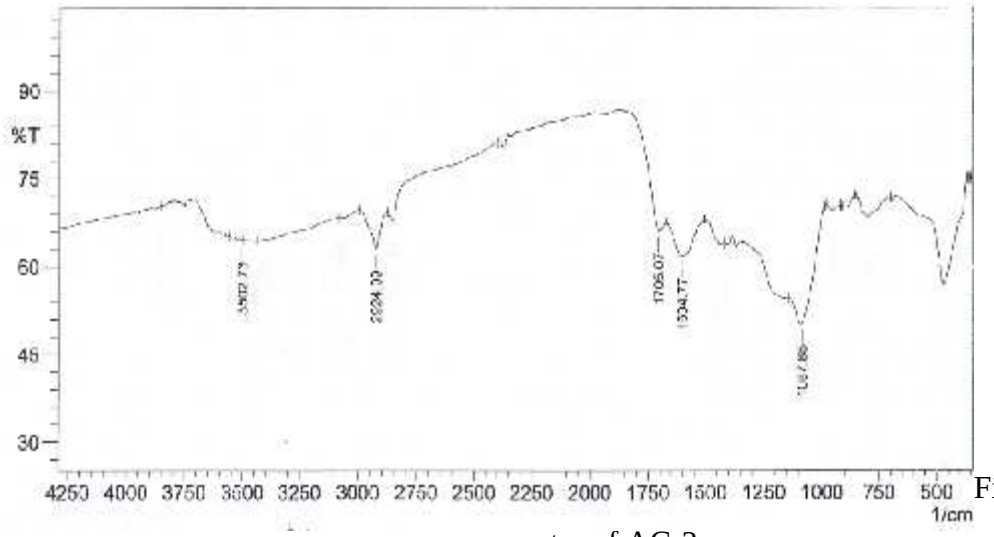


Figure 14: FT-IR spectra of AC-2

A peak in the range of 1230 to 1275 cm^{-1} usually shows the presence of asymmetrical stretching of C-O-C bond in vinyl ethers so the peak at 1273.02cm^{-1} may be due to the same as shown in Figure 15. A peak at 1604.77cm^{-1} is due to the C=C stretching of vinyl ethers and a band at 3525.88 cm^{-1} can be attributed to the -OH group of alcohol or phenol [43].

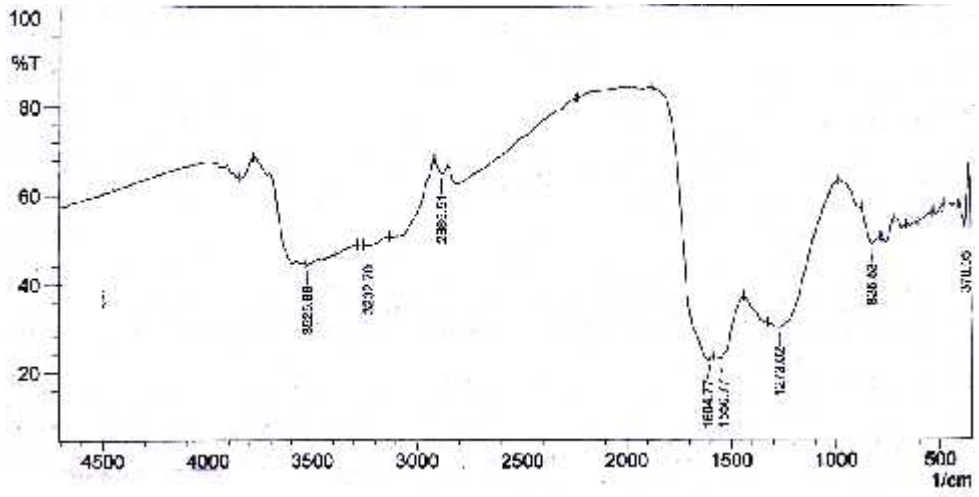
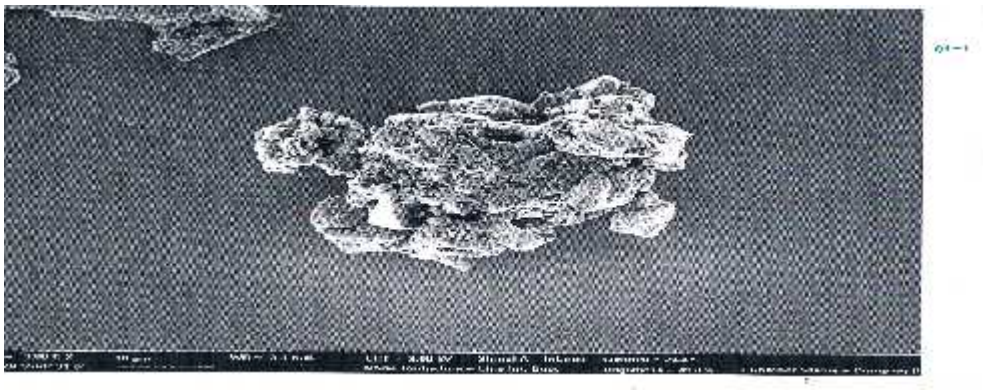


Fig 15: FT-IR spectra of AC-3

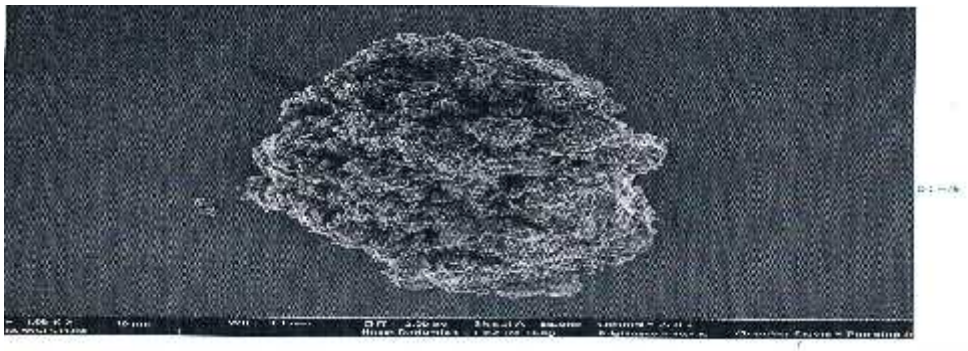
From the above FTIR spectra data, we can conclude that though there are certain and slight shifts in the bands of the spectra of the activated carbons in comparision to that of the spectra of the precursor, all the activated carbon samples used in this study show the presence of similar types of the functional groups.

4.2.7 Scanning Electron Microscopic Study

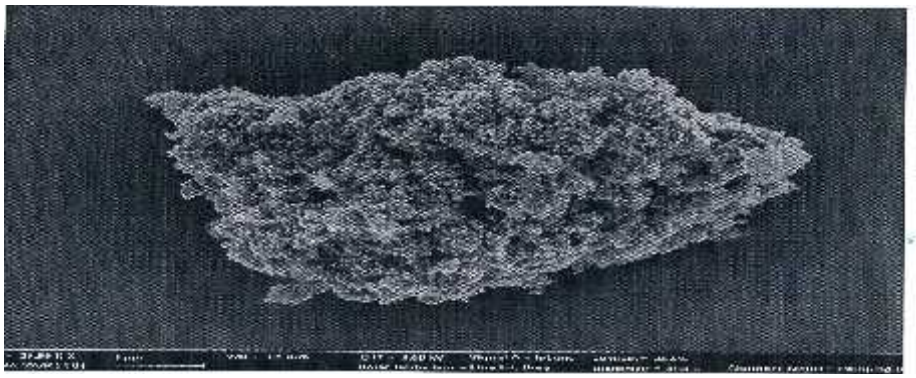
SEM images were used to observe the surface morphology of the activated carbon. Figure 16 shows that the activated carbon has lots of grooves with homogenously distributed macroporous surface area. We know that Phosphoric acid is one of the strong dehydrating agents and hence it accelerates the bond cleavage reaction leading to the generation of void spaces. These results can be ascertained that the precursor materials and the method for the preparation of activated carbon is adequate for the purpose of adsorbing large organic molecules [41].



(a) R-1

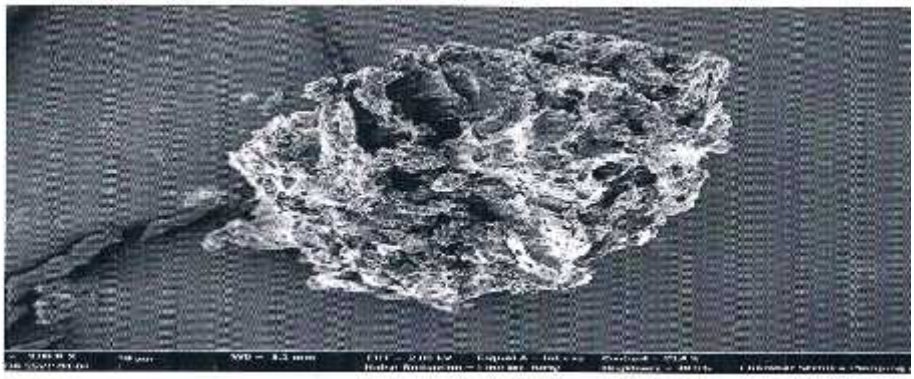


(b) AC-1C



(c) AC-1D

(d) AC-2



(e) AC-3

Figure 16: SEM images of different ACs (a) R-1, (b) AC-1C, (c) AC-1D, (d) AC-2, (e) AC-3

4.2.8 X-ray Diffraction

Figures 17 and 18 show the XRD patterns of the samples AC-1c and AC-1d, respectively. The XRD patterns of both the samples have a broad diffraction peaks at 2Θ value of 26 and 44. The

XRD pattern of the sample AC-1C has two broad peaks around 30 and 45 as shown in Figure 17. However the boardening of XRD peaks for sampe AC-1D is not clearly seen as compared with the AC-1C sample. These results showed that the sample AC-1C has more amounts of amorphous structure as compared with the sample AC-1D. Furthermore, sample AC-1D has the mixtures of amorphous and nano-crystaline phases, whereas only amorphous phase of sample AC-1C is confirmed.

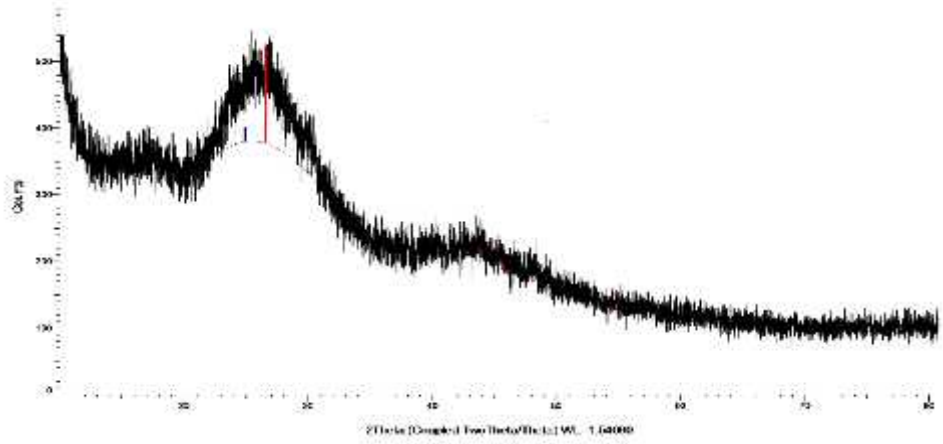


Figure 17: XRD- pattern of AC-1C

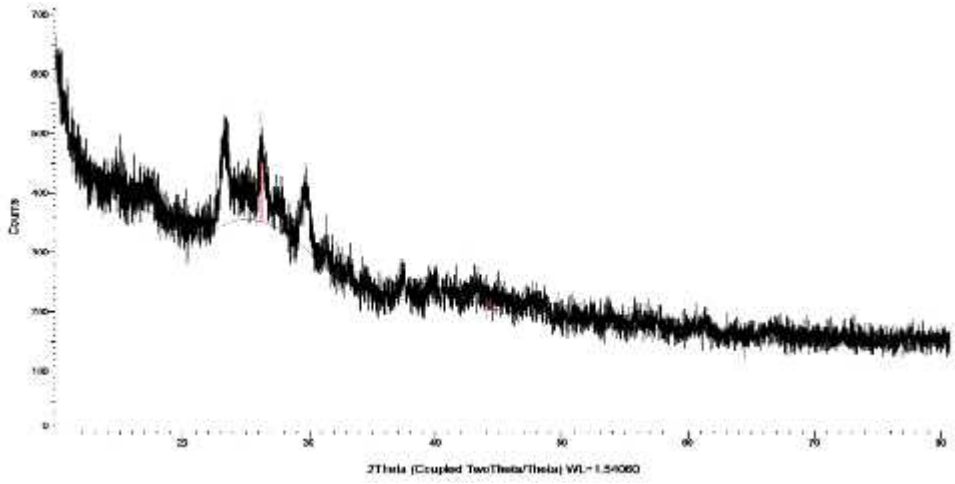


Figure 18: XRD patterns of AC-1D

4.3 Adsorption Isotherm for Methylene Blue, Optilan Red and Glimepiride

The adsorption of methylene blue, optilan red and glimepiride was carried out using batch experiments following Lambert-Beer's Law. The calibration curves were used to estimate the

concentration of each adsorbent and each calibration curves are shown in the appendix of this thesis. To obtain the calibration curves, first of all the λ_{max} values were found. The λ_{max} values for methylene blue, optilan red and glimepiride were found to be 665 nm, 505nm and 200nm, respectively. The data obtained from different batch experiments were analyzed from Langmuir and Freundlich adsorption isotherms.

Langmuir Isotherm

The linearized Langmuir plot for the adsorption of methylene blue, optilan red and glimepiride are shown in Figures 19 to 22. The points are the experimental data and the straight lines are the lines of best fit with correlation coefficient as given in tables8 to 10. The values of q_m and b were determined from the slope and intercept of the Langmuir plots of $1/q_e$ vs 1/ Ce which are also tabulated in Table 8 to 10. The q_m is the maximum adsorption capacity of ACs to adsorb dye and the glimepiride (used as the medicine) from aqueous solution which helps to evaluate the quality of adsorbent.

Figure 19: Linearized Langmuir isotherm for methylene blue adsorption

The q_m is the maximum adsorption capacity to adsorb methylene blue from aqueous solution and is found to be 434.782 mg/g for AC-1C.

Table 8: Langmuir adsorption isotherm constants for methylene blue

Adsorbent	Langmuir constants		
	q_m(mg/gm)	b(L/mg)	R^2
AC-1C	434.782	0.165	0.9797

Figure 20: Linearized Langmuir isotherm for optilan red adsorption

Figure 21: Linearized Langmuir isotherm for optilan red adsorption

The q_m for AC-1C was found to be 909.090 mg/g. Similarly, the adsorption capacities for AC-1D and CAC is found to be 357.142 mg/gm and 250 mg/gm, respectively. The sample impregnated with acid shows better adsorption than the non-impregnated sample. This may be due to the fact that the impregnation with acid helps in increasing the oxygen containing functional group and nanoporosity in the activated carbon. Here, the sample impregnated with acid in the ratio 1:1 shows the best result than the sample impregnated with acid in the ratio 1.5:1, because the use of acid in larger amount could breakdown the porous structure formed during the activation process.

Table 9. Langmuir adsorption isotherm constants for optilan red

Adsorbents	Langmuir constants		
	q_m (mg/gm)	b (L/mg)	R^2
AC-1C	909.090	0.010	0.9803
AC-1D	357.142	0.140	0.9816
CAC	250	0.113	0.8556

Figure 22: Linearized Langmuir isotherm for glimepiride adsorption

The maximum value of q_m is for the sample AC-1C and is equal to 140 mg/gm. The values for maximum adsorption capacities and Langmuir constants are given in Table 10.

Table 10. Langmuir adsorption isotherm constants for glimepiride

Adsorbents	Langmuir constants		
	q_m (mg/gm)	b (L/mg)	R^2
AC-1C	140.845	0.266	0.9856
AC-1D	128.205	0.052	0.9815
CAC	79.365	0.033	0.9888

Freundlich isotherm

The plots of log q_e against log Ce for different adsorbents are shown below. The value of K_F and n were calculated from the slope and intercept obtained from the linearized plots of logq_e vs

$\log C_e$ as shown in Figures 23 and 24. The values of these constants are tabulated in Tables 11 and 12.

Figure 23: Linearized Freundlich isotherm for optilan red adsorption

Table 11. Freundlich adsorption isotherm constants for optilan red

Adsorbents	Freundlich constants		
	K_F (mg/gm)	n	R^2
AC-1C	12.682	1.26	0.9656
AC-1D	75.822	2.894	0.9332
CAC	39.518	2.176	0.8612

The constant K_F is an appropriate indicator of adsorption capacity, while n is the adsorption intensity. If the value of 1/n is less than one, then it indicates the normal adsorption. The smaller the value of 1/n indicates the heterogeneity of the sample surfaces. If the value of n lies between one to ten, this indicates a favorable adsorption process. From the Table 11 we can see that the values of n are from one to ten and also the value of 1/n lies below one which indicates that these adsorption isotherms of optilan red on these ACs are favorable.

Figure 24: Linearized Freundlich isotherm for glimepiride adsorption

Table 12. Freundlich adsorption isotherm constants for glimepiride

Adsorbents	Freundlich constants		
	K_F (mg/gm)	n	R^2
AC-1C	41.409	3.233	0.8492
AC-1D	15.747	2.265	0.8489
CAC	7.333	2.106	0.9328

As discussed in the case of adsorption of optilan red, in the case of adsorption of glimepiride also, we see that the values of n for all the ACs lie between one to ten and also the values of 1/n lie below one. Therefore, it can be said that these isotherms are favorable for the adsorption of glimepiride on these prepared ACs.

4.4 Effect of pH

The effect of pH on the adsorption of the solute from the solution is very significant. The degree of ionization of adsorbate molecules and the degree of dissociation of functional group on the active site of the adsorbent is greatly influenced by the pH of the solution. Because of the change in the degree of dissociation of the active functional groups with difference in pH causes the changes in the interactions between solute-surface, solvent-solute and solvent-surface species. And this leads to the difference in the extent of adsorption. In highly acidic medium (below pH 2), oxygen containing surface functional groups are not dissociated and consequently there is decrease in the active site for adsorption. And again, the solubility of glimepiride may increase with decreasing pH due to the increase in the positive charges on the nitrogen atoms of the drug molecule which makes them more soluble and hence, decrease the adsorption affinity towards the activated carbon surface. The effect of pH from 2 to 6 on the adsorption of glimepiride by three types of ACs (AC-1C, AC-1D and CAC) is given in Figure 25. The adsorption capacity of CAC at pH 2 was found to be 37.144% which increased to 71.43% when pH rose to 6. Similarly, the adsorption capacities of AC-1C and AC-1D was found to increase from initial capacities of 51.43% and 71.43 %to 77.144 %and 91.43% when pH rose from 2 to 6. It was observed that the adsorption capacities of all the adsorbent increased linearly with the increase in pH.

Figure 25: Effect of pH on the adsorption of glimepiride

4.5 Effect of Initial Concentration

The effect of initial concentration of glimepiride on its adsorption was studied with adsorbent dose 25 mg in 50 ml of glimepiride solution keeping the contact time fixed at 1 hour and pH 6. The concentration of the solution was varied from 20 ppm to 120 ppm. From the Figure 26, it is obvious that the extent of adsorption is greatly influenced by the initial concentration of the solute. The extent of adsorption increased from 10 mg/gm to 27.142 mg/gm for CAC, from14.286 mg/gm to44.286 mg/gm for AC-1D and from 18.572 mg/gm to 62.858 mg/gm for AC-1C. But as the concentration increases more and more, the adsorption reaches the limiting value and no further adsorption is seen. This is due to the fact that at lower concentration the ratio of number of solute molecules to the number of active site in adsorbent is low but as the concentration rises, the available number of functional sites of the adsorbent become fewer compared to the number of solute molecules and hence, the uptake of solute becomes independent of the initial metal ion concentration.

Figure 26: Effect of initial concentration on the adsorption of glimepiride

4.6 Effect of Contact Time

The amount of adsorption on the adsorbent is increased with time upto about 60 minutes and after this time the amount of adsorption remained almost constant. But the further increase in the contact time does not decrease the concentration of the glimepiride significantly because of the decomposition of the solute on the available sites of the adsorbent. From the Figure 27, we can see that the equilibrium was reached after 1 hour. Therefore, the shaking time for each experiment was set for 1 hour.

Figure 27: Effect of contact time on the adsorption of glimepiride

4.7 Kinetics of Adsorption for Optilan Red and Glimepiride

4.7.1 Kinetic Study of Optilan Red

For the kinetic study of the adsorption of optilan red, the kinetic parameters involved in the process of adsorption were obtained for contact time between 10 to 100 minutes. The initial concentration of the optilan red solution was taken as 100 ppm and the pH was maintained at 6.

Linear plots of log ($q_e - q_t$) vs. t and t/q_t vs t are shown in Figure 28 and 29 respectively. The values of kinetic parameters k_1 and k_2 as well as the equilibrium adsorption capacity q_e were determined from the slopes and intercepts of these plots. The first and the second order kinetics constants are presented in the Table 13.

Figure 28: Pseudo first order kinetics for optilan red adsorption

Figure 29: Pseudo second –order kinetics for optilan red adsorption

Table 13. Kinetics parameters for optilan red adsorption

Adsorbents	pH	Pseudo first order		Pseudo second order		
		K_1(L/mol)	R^2	K_2 (g/mg.min)	h (g/mg.min)	R^2
CAC	6	214×10^{-4}	0.971	2.16×10^{-3}	5.681	0.9986
AC-1C	6	230×10^{-4}	0.9784	2.245×10^{-3}	3.508	0.9989
AC-1D	6	290×10^{-4}	0.8521	2.550×10^{-3}	4.830	0.9988

It is clearly observed that R^2 values for pseudo first order kinetics of the adsorption of optilan red onto activated carbons were found to be lower than that for the pseudo second order adsorption kinetics.

4.7.2 Kinetic Study of Glimepiride

For the kinetic study of the adsorption of glimepiride, the kinetic parameters involved in the process of adsorption were obtained for contact time between 10 to 100 minutes. The initial concentration of the glimepiride solution was taken as 50 ppm and the pH was maintained at 6.

Linear plots of log ($q_e - q_t$) vs. t and t/q_t vs t are shown in Figure 30 and 31 respectively. The values of kinetic parameters k_1 and k_2 as well as the equilibrium adsorption capacity q_e were determined from the slopes and intercepts of these plots. The first and the second order kinetics constants are presented in the Table 14.

Figure 30: Pseudo first order kinetics of glimepiride adsorption

Figure 31: Pseudo second order kinetics for glimepiride adsorption

Table 14. Kinetics parameter for glimepiride adsorption

Adsorbents	pH	Pseudo first order		Pseudo second order		
		K_1(L/min)	R^2	K_2 (G/mg.min)	h (g/mg.min)	R^2
CAC	6	163×10^{-4}	0.9665	7.144×10^{-4}	4.572	0.9918
AC-1C	6	138×10^{-4}	0.9069	3.21×10^{-4}	4.058	0.9941
AC-1D	6	131×10^{-4}	0.9609	3.43×10^{-4}	3.431	0.9904

It is clearly observed that R^2 values for pseudo first order kinetics of the adsorption of glimepiride onto activated carbons were found to be lower than that for the pseudo second order adsorption kinetics.

CONCLUSIONS

From the present study it can be concluded that *A. catechu* nuts which are very rich in lignocellulosic materials can be used to produce nanoporous activated carbons as adsorbent by chemical activation method using ortho-phosphoric acid, potassium hydroxide and zinc chloride as activating agents.

The *A. catechu* nuts powder of size < 425 µm was impregnated with ortho-phosphoric acid, potassium hydroxide and zinc chloride. The precursor was impregnated in the ratio of 0.4:1, 0.7:1, 1:1. 1.5:1 and 2:1 with ortho-phosphoric acid and in the ratio of 1:1 with potassium hydroxide and zinc chloride.

The moisture and ash content of the *A. catechu* powder of size <425 µm are found to be 2.08% and 1.66% respectively.

The methylene blue number for AC-1C is found to be the highest i.e. 405.243 mg/gm which is greater than that of CAC with the methylene blue value of 272.60 mg/gm.

Iodine number value for AC-1C is the highest i.e. 1080.122 mg/gm which is high in comparision to CAC with iodine value of 887.723 mg/gm. It is also seen that iodine number values of activated carbons are much higher than for R-1. The iodine value goes on decreasing as the activation ratio goes on increasing as in case of the methylene blue value. It can be attributed to

the fact that the use of acid in larger amount causes the breakdown of the porous structure formed during the activation.

Surface area of different activated carbons was found out by chemical adsorption technique. The surface area of AC-1C is found to be 1380.801 m^2/gm whereas for that of R-1 it is only 412.304 m^2/gm. The surface area value of AC-1C is much higher than that of CAC i.e 865.736 m^2/gm.

The result of Boehm titration shows that the carbonyl, lactone and phenol content of AC-1D is the highest with the values of 2.55 meq/gm, 1.9 meq/gm and 2.9 meq/gm respectively in comparision to that of AC-1C and R-1.

From the adsorption study it is seen that in case of methylene blue, optilan red and glimepiride adsorption, AC-1C has the highest capacity of adsorption in comparision with other prepared activated carbon. The maximum adsorption capacity (q_m) for methylene blue is 434.782 mg/gm, for optilan red is 909.090 mg/gm and for glimepiride is 140.845 mg/gm. The kinetic analysis of the data shows that the adsorption of optilan red and glimepiride on AC-1C can be well described by pseudo-second order kinetic model and the rate constant of the process are 2.245×10^{-3} gm/mg.min and 3.21×10^{-4} gm/mg.min.

For the glimepiride adsorption on AC-1C, the initial concentration has the significant effect but as the concentration increases, the adsorption reaches the limiting value since the available number of functional site of the adsorbent becomes fewer compared to the number of solute molecules. Effect of contact time on the adsorption of glimepiride on AC-1C had the similar effect as that of the initial concentration. In the study of effect of pH (from 2 to 6) for glimepiride adsorption on AC-1C, the effect was seen to be linear i.e. as the pH rose from 2 to 6 the amount of adsorption also rose linearly.

Thus, this study shows that not only *Areca catechu* nuts are suitable for preparing activated carbons but also ortho-phosphoric acid, potassium hydroxide and zinc chloride are good activating agents. The activated carbons prepared from *Areca catechu* impregnated with ortho-phosphoric acid show better adsorption capacity for optilan red and glimepiride. Hence, it can be employed to treat waste water from the carpet industries before letting them into water resources and also for treating toxicity in human body by the overdose of anti-diabetic medicine, glimepiride.

REFERENCES

- www.nano.gov/nanotech-101/what/definition., 26th March 2016, 3:30pm.
- www.aep.cornell.edu/research/nanoscience.cfm., 26th March 2016, 3:45pm.
- Rajbhandari R., Shrestha L.K., Pokhrel B. P. and Pradhananga R.R., *J. Nanosci. Nanaotech.,* **2013,** *13,* 1-13.
- Rajbhandari R., Pokhrel B. P. and Pradhananga R.R., *J. Nanosci. Nanaotech.,* **2012,** *12,* 7002-7009.
- Ekpete O.A. and Horsfall M. JNR., *Res. J. Chem. Sci.,* **2011,** *1(3).*
- Dougall G.J., *J. S. Afr. Inst. Min. Metall.,* **1991,** *91,* 109-120.
- Kaufman R. C., *J. Mega/earth. Soc.,* **1989.**
- Azpiroz. F. and Serra. J., "Treatment of Excessive Intestinal Gas." *Current Treatment Option in Gastroenterology 7*.,**2004,** 299-305.
- draxe.com/activated-charcoal-uses/. 28th March 2016, 1:00 pm
- Karimi H., *Ind. J. Sci. Tech.,* **2012,** *5,* 2346-2353.
- Alicia Pelaez-Cid A and Margarita Teutli-Leon M.M., *Benemerita Universidad Autonoma de Puebla.*
- Entheology.com.by keith cleversky/Jan1/2002/plants/ 5th April 2016, 9:45 pm.
- Rimal S., Poudel R., Shrestha B.S., *Agribusiness Promotion Program.,* **2012.**
- Begum M., Begum T., *Amer. J. Bio.Sci.,* **2015,** *3(2-1),* 19-22.
- Caturla F., Sabio M.M., Rodriguez-Reinoso F., *Carbon.,* **2012,** *29(7),* 1-8.
- Laine J., Calafat A., Labady M., *Carbon.,* **1989,** *27(2),* 191-195.
- Cleiton A., Nunes e Mario C. Guerreiro., *Quim. Nova.,* **2011,** *34,* 472-476.
- ASTM., "Standard test method for determination of iodine number of activated carbon," *ASTM Annual Book 4,* D4607-D4694.
- Itodo A.U., Itodo H.U., Gafar M.K., *J. Appl. Sci. Environ. Manage.,***2010,** *14(4),* 141-145.

- Kwon J.H., Sorption Studies of the Surface Modified Activated Carbon with β-Cyclodextrin. A dissertation submitted to the college of Graduate Studies and Research, University of Saskatchewan, **2007,** pp 1-2.
- Fidel R.B., Evaluation and Implementation of Methods for Quantifying Organic and Inorganic Components of Biochar Alkalinity. A dissertation submitted to Iowa State University, **2012,** pp 10-24.
- Djomgoue P., Njopwouo D., *J. Surface. Eng. Mat. Adv. Technol.,* **2013,** *3,* 275-282.
- Luyapaert J., Zhang M.H., Massent D.L., *Analytica Chimica Acta.,***2003,** *478,* 303-312.
- Pradhan S., Production and characterization of Activated Carbon Produced from a Suitable Industrial Sludge. A report submitted to Department of Chemical Engineering, National Institute of Technology, Rourkela, pp 25-27.
- Gandhimath R., Vijayaraj S., Jyotirmaie M.P., *Intl. J. Pharm. Res. Ana.,* **2012,***2,* 72-78.
- Vogel., "Vogels' Text Book of Quantitative Chemical Analysis," sixth edition, Pearsons Education Ltd, New Delhi., 2003.
- Atkins P., Paula J.D.," Atkins' Physical Chemistry," eight edition, Oxford UniversityPress.,2002,pp 909-921.
- Ademiluyi F.T., Vjile A.A., *Intl. J. Eng. Technol.,***2013,** *3(6).*
- Vijayaraghavan K., Jegan J.R., Palanivelu K., Velan M., *Elec. J. Biotech.,* **2004,**7.
- Erol A., Hoda N., *Chemosphere.,* **2005,** *60,* 1600-1607.
- Asadullah M et al., *J. Surface. Sci. Technol.,* **2007,** *23,*73-80.
- Shawabkeh R.A., Abu-Nameh E.S.M., *Colloid Journal.,* **2007,** *69(3),* 355-359.
- Hamdaoui O and Naffrechoux E., *J. Haz. Mat.,* **2007,** *147,* 381-394.
- Ip A.W.N., Barford J.P., McKay G., *Bioresource Technology.,***2008,** *99,* 8901-8916.
- Patnukao P., Pavasant P., *Bioresource Technology.,* **2008,** *99,* 8540-8543.
- Amin N.K., *Desalination.,* **2008,** *223,* 152-161.
- Tahvildari K., Bigdeli T., Esfahani S.N., Farshchi M., *J. App. Chem. Res.,* **2009,** *11,* 47-55.
- Wang X., Li D., Li W., Peng J., Xia H., Zhang L., Guo S., *Bioresource.,* **2013,** *8(4),*6184-6195.

- Stoyokova M., Koumanova B., Morl L., *J. Chem. Technol. Metal.,* **2013,** *48(5),* 469-474.
- Jasim S.M., Baban R.S., Jasim H.S., *Iraqi. J. Med. Sci.,* **2013,** *11(1).*
- Chayande P.K., Singh S.P., Yenkie M.K.N., *Chem Sci Trans.,* **2013,** *2(3),* 835-840.
- Ray-Mafull et al., *SpringPlus.,* **2014,** *3(48).*
- Silverstein R.M., Webster F.X., "Spectrometric Identification of Organic Compounds," Sixth edition, Wiley India Pvt. Ltd, New Delhi,2011.

ANNEX

1. Preparation of Reagents

1.1Stock Methylene Blue Solution, 1000 mg/L

Stock solution of methylene blue was prepared by dissolving 1 gm of methylene blue(S.D. Fine Chemicals Ltd., Biosar, C.I. 52015) in a 1000 ml volumetric flask and volume of the solution was made up to the mark with deionised water.

1 ml stock solution of methylene blue = 1000 µm of methylene blue

1.2 Stock Optilan Red Solution, 1000 mg/L

Stock solution of optilan red was prepared by dissolving 1 gm of optilan red in a 1000 ml volumetric flask and volume of the solution was made up to mark with deionised water.

1 ml stock solution solution of optilan red= 1000 µg of optilan red

1.3 Stock Glimepiride Solution, 1000 mg/L

Stock solution of glimepiride was prepared by dissolving 1 gm of glimepiride (Mfd. By USV Limited) in a 1000 ml volumetric flask and the volume of the solution was made up to the mark with deionised water.

1 ml stock solution of glimepiride = 1000 µg of glimepiride

1.4 Working Dyes and Medicine Solution

Working solution of optilan red dye and anti-diabetic medicine were prepared by necessary dilutions of stock solution in the same solvent.

1.5 Buffer Solutions

Buffer solution of pH 4, pH 7 and pH 9.2 were prepared by dissolving buffer tablets of pH 4, pH 7 and pH 9.2 (BDH) respectively into 100 ml distilled water.

1.6 Sodium Hydroxide Solution, 1.0 M

10 gm of sodium hydroxide pellet were transferred into 250 ml volumetric flask and distilled water was added up to the mark to make 1.0 M sodium hydroxide solution.

1.7 Sodium Hydroxide Solution, 0.05 M

25 ml of 1.0 M sodium hydroxide solution was transferred to 500 ml volumetric flask and distilled water was added up to the mark.

1.8 Hydrochloric Acid Solution, 1.0 M

8.5 ml of conc. hydrochloric acid was transferred into 100 ml volumetric flask and distilled water was added up to the mark to prepare 1 M hydrochloric acid solution.

1.9 Hydrochloric Acid Solution, 0.05 M

25 ml of 1.0 M hydrochloric acid solution was transferred to 500 ml volumetric flask and distilled water was added up to the mark.

1.10 Sodium Bicarbonate Solution, 0.05 M

1.05 gm of sodium bicarbonate powder was transferred into a 250 ml volumetric flask and distilled water was added up to the mark.

1.11 Sodium Carbonate Solution, 0.05 M

1.325 gm of sodium carbonate powder was transferred into a 250 ml volumetric flask and distilled water was added up to the mark.

1.12 Iodine Solution, 0.1 N

12.7 gm of iodine and 19.1 gm of KI were transferred into 1 L volumetric flask and distilled water was added up to the mark.

1.13 Sodium thiosulfate solution, 0.05 N

12.41 gm of sodium thiosulfate was transferred into a 1 L volumetric flask and distilled water was added up to the mark.

1.14 Hydrochloric acid solution, 5% by weight

275 ml of distilled water was added to 35 ml of conc. HCl acid to prepare 5% by weight of hydrochloric solution.

1.15 Determination of λ_{max} and Calibration Curve for Dyes Methylene blue, Optilan Red and an Anti-diabetic Medicine, Glimepiride

Figure 1: A plot of absorbance vs wavelength for the determination of λ_{max} methylene blue

Figure 2: Calibration curve for methylene blue at λ_{max}=665 nm

Figure 3: A plot of absorbance vs wavelength for the determination of λ_{max} of optilan red

Figure 4: Calibration curve of optilan red at λ_{max}= 505 nm

Figure 5: Plot of absorbance vs. wavelength for the determination of λ_{max} of glimepiride

Figure 6: Calibration curve of glimepiride at λ_{max}= 200 nm