STUDY ON THE REMOVAL OF IMPURITIES FROM GROUND WATER OBTAINED FROM SHAHBAJPUR AREA

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree

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MASTER OF TECHNOLOGY

in

CHEMICAL ENGINEERING

(With Specialization in Industrial Pollution Abatement)

By

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DECLARATION

I hereby declare that the work being presented in the seminar report entitled **"Study on the removal of impurities from ground water obtained from Shahbajpur area"** in partial fulfillment of the requirements for the award of the degree of M. Tech. (with Specialization in Industrial Pollution Abatement) and submitted in the department of Chemical Engineering of the Indian Institute of Technology Roorkee. This is an authentic record of my own work carried out during the period from June, 2012 to June, 2013 under the supervision of Dr. Shishir Sinha, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, India. The matter presented in this report has not been submitted by me for the award of any other degree of this or any other institute.

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

Removal of pyridine is very important from the contaminated area because it can easily evaporate and mix with air, it is very harmful compound. In this study various parameters were studied during the adsorptive removal of Pyridine by BFA. Following major conclusions can be drawn from the present study: The kinetic study showed that removal by BFA exhibited 1^{st} order kinetics. It was also found that BFA exhibited significantly higher adsorption capacity for the adsorption of Pyridine due to higher surface area. Various isotherms fitting were tested which showed that for BFA, comparing R^2 values, it was clear that R-P isotherm best fits the experimental data at higher temperature as well as at lower temperatures, for BFA.

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NOMENCLATURE

FTIR	Fourier Transform Infrared spectroscopy
XRD	X-ray diffraction
TGA	Thermogravimetric analysis
BET	Brunauer–Emmett–Teller
q_e	Extent of adsorption, mg/g
C_o	Initial concentration, mg/l
C_f	Final concentration, mg/l
BFA	Bagasse fly ash
DTA	Differential thermal analysis
BJH	Barrett, Joyner and Halenda.
SEM	Scanning electron microscope

1 INTRODUCTION

Gajraula is a prominent industrial area of district Jyotiba Phuley Nagar (J P Nagar) in western Uttar Pradesh. It is situated on the National Highway no. 24 and is 120 km from Delhi on Delhi-Moradabad highway and Moradabad is 53 km from Gajraula. The geographical extent of Gajraula is 28° 49 to 28° 51 N latitude and 78° 14 to 78° 16 E longitudes. Various types of industries are located in Gajraula which includes large distilleries along with other ancillary industries i.e. chemical and pharmaceutical units, paper mills, phosphatic fertilizer plant etc. Jubilant Organosys Limited (JOL), formerly known as Vam Organics Chemicals Limited, is a company unit engaged in manufacturing organic chemicals, drug intermediates, bulk drugs and formulations situated in Shahbajpur area in Gajraula.[Goel et al., 2010] The company had set up its distillery unit in 1982 for manufacturing ethyl alcohol and subsequently set up other units of chemicals and drug intermediaries based on alcohol. In addition, the company had also set up a 100% export oriented unit for manufacturing drug intermediates. They also manufacture the pesticides and other chemical compounds and due to this the waste water stream containing the different harmful compounds like cyanides, pyridine etc. and expose to the environment. In this study we point out these harmful chemicals and performed the suitable and economical method to remove the more harmful pyridine by making the synthetic aqueous solution.

We collected the samples from twenty wells form different locations near the industrial area and examined the samples with FTIR spectroscopy for the identification of various compounds presents in the ground water samples (figure 1.1 shows the locations of that wells) and found the aromatic ketones group, aliphatic amide group, aliphatic nitro, nitrite, and nitrate compounds, aliphatic and aromatic halides, olefin functional groups, aromatic carboxylic acid groups, aliphatic ether compounds and cyanide group in traces. Presence of C-N bond indicates the presence of pyridine compound because they manufacture the pyridine in large scale. Firstly we decided to remove the cyanide groups from the original ground water samples but these samples became useless over some time period so we decided to remove pyridine compound from the synthetic aqueous solution which is very harmful for living organism.

1.1 Pyridine

Pyridine is an organic compound having colorless appearance. It is also known as azabenzene and azine **[Mohan et. al., 2004]**. It is a liquid of strong unpleasant odor (with odor index of 2390) with toxicity and mixes very easily with water and is soluble in alcohol, ether, and benzene. Pyridine can be produced largely from coal tar (which is nothing but the condensate obtained from coking ovens in the steel industry). It is also widely produced from the chemical synthesis process for commercial purpose. The most widely used method for the production of pyridine is the reaction between acetaldehyde and formaldehyde the in the presence of ammonia. This method is also useful to make other pyridine derivatives **[Peng et al., 2012].**

Fig.1.1 Sampling locations of ground water

1.1.1 Uses of Pyridine

Pyridine is widely used as a solvent and also act as intermediate in the production for many chemical compounds like

1. Different pyridine derivatives like pipridine
2. As a catalyst for isoniazid, cetylpyridinium bromide, analgestic dermol and cephalexin etc.
3. In pharmaceuticals, dyestuffs and paints, rubber products, vitamins, food flavorings.
4. Polycarbonate resins and textile water-repellents
5. In laboratory
6. Agricultural chemicals like herbicides, insecticides, fungicides etc. **[Mohan et al, 2004]**.

1.1.2 Physical properties of Pyridine

Pyridine is also known as Azabenzene, Azine, Pridina etc. these are the synonyms of pyridine. As we all know that pyridine is basically a water-soluble and colorless liquid, which is highly flammable and weakly alkaline in nature, with a very unpleasant and penetrating odor. The other physical properties of pyridine are given below in table- 1.1.

Table 1.1 Chemical and physical properties of pure substance

S. NO.	Characteristics	Values
1.	Molecular formula	C_5H_5N
2.	Molar mass	79.10 g/mol^1
3.	Density	0.9819 g/cm^3
4.	Boiling-point	115.2°C
5.	Melting-point	-41.6°C
6.	Solubility	Soluble in water, alcohol, ether
7.	Vapour pressure	18 mmHg
8.	Flash-point	21^o C
9.	Threshld limit value	5 mg/l
10.	Critical parameters	Pressure 6.70 MPa Temperature 620 K
11.	Refractive index	1.5093 (at λ=589 nm, 20 °C)

12.	Standard enthalpy of formation	1. 100.2 kJ/mol (in the liquid phase) 2. 140.4 kJ/mol (in the gas phase)
13.	Viscosity	0.88 mPa/s at 25^o C
14.	Enthalpy of fusion	8.28 kJ/mol at the melting point
15.	Enthalpy of vaporization	35.09 kJ/mol at the boiling point and normal pressure

Source: [http://en.wikipedia.org/wiki/Pyridine/ date 30/5/2013]

1.1.3 Maximum permissible limit

MOEF has set a maximum concentration level of 5.0 mg/l of Pyridine in the industrial effluents for safe discharge into surface waters. The IDLH value which represents the immediately dangerous to life and health concentrations is 1000 mg/dm^3 and it falls on sub category 3 on UN hazard class. [U.S. Environmental Protection Agency, 2009]

Due to several application of pyridines in chemical field the production of pyridine is increasing day by day, so the exposure to the environment is also increasing because these industries discharge huge amount of wastewater containing pyridine and these pyridine and pyridine derivatives are hazard in nature and due to poor substrates to indigenous microorganism they persist in the environment for long time and create many health problems for living organisms.

It easily evaporates into the air and if exposed to air, water or soil it takes several months to breakdown into other possible compounds due to very high half-life. On exposing pyridine to flame or spark in vapor form, it is fire and explosive hazardous compound [Lataye et al., 2006].

Degree of hazardousness of such chemical, exposed to the environment, depends on several factors like whether harmful health effects will occur or not if yes than type and extent of hazardousness and its effect on health besides these things dose (quantity), duration (time period), route of contact (drinking, eating, skin contact or breathing). Degree of hazardousness also depends on the individual characteristics of person like sex, age, life style, nutritional status, family traits and state of health.

Exposure of pyridine may cause several dangerous possible effect of on human health. It is mildly toxic by inhalation. The most important effect is damage of liver and kidney which is very common in affected humans; other possible health concerns for humans may be headache, neurological effects like nervousness, insomnia, frequent urination, renal effects, and irritation of the skin and eye. We do not know whether pyridine can cause cancer, birth defects, or problems with reproduction [Lataye et al., 2006].

1.2 Methods of removal of pyridine

There are many methods for the removal of pyridine from waste water. Some important methods included adsorption, bio-degradation, solvent extraction, ozonation, electrochemical oxidation, ion exchange etc.

Among these methods adsorption is found to be best method for removal of pyridine from aqueous solution in point of pyridine carried out capacity and overall cost estimation.

1.2.1 Adsorption

Adsorption is a process to accumulate the adsorbate on the surface of adsorbent. In adsorption process adsorbate are generally gas or liquid solute particles, while adsorbent are solid or liquid substances and in this process adsorbate form a molecular or atomic film on adsorbent. This is one of the most natural process occurs in physical, biological and chemical systems, and due to the effectiveness and ease of operation it is widely used in industrial applications. Absorption is different process than adsorption, in absorption a substance diffuses into a liquid or solid to form a solution. The one more term sorption, which have wider applications area in removal process, included both processes, while desorption is the reverse process. Similar to surface tension, adsorption is a consequence of surface energy**.** [http://en.wikipedia.org/wiki/Adsorption]

1.2.1.1 Mechanism of adsorption

The main reason behind the adsorption is because of difference in the environment of surface particle to the particle inside the bulk of adsorbent. In a bulk material, all the bonding requirements (ionic, covalent or metallic) of the constituent atoms of the material are filled. So that atoms present in the bulk of a material is in balance stage due to facing the force from all sides. But it is not same for the surface atoms because they experience a bond deficiency due to lack of surrounding atoms so that they have unbalanced or residual attractive forces. Thus these particles having the tendency to attract the particles of adsorbate and to make bond with the adsorbate at the surface. The main key factor in the adsorption process is surface area, at a given temperature and pressure, if surface area per unit mass of adsorbent is high than the adsorption process will high.

Although the nature of bond is depends on the behavior of involved species, but we can classify the adsorption in two category, physisorption and chemisorptions. In physisorption, there is only Vander Waals (weak intermolecular) force is involve, which adhere the adsorbate to the surface of adsorbent. This force is also responsible for the non-ideal behavior of real gases. In chemisorptions, adsorption takes place with the help of chemical bond formation between surface and adhere molecule.

1.2.1.2 Factors controlling adsorption

There are number of factors which are responsible for the adsorption process from bulk of the fluid phase to adsorbent phase. These factors are-

1. Nature and surface area per unit mass of adsorbent used
2. Adsorbent dosage
3. Temperature
4. pH of solution
5. Contact time
6. Initial concentration of adsorbent

1.2.2 Adsorbent uses in adsorption process

There are many adsorbents that can be used in adsorption process like GAC, Saw dust, Bagasse fly ash, Rundle oil shale, montmorillonite and kaolinites etc. among these adsorbents bagasse fly ash is found to be best due to its high availability, very low cost and high removal efficiency **[**Lataye et al., 2008**]**

1.2.2.1 Bagasse Fly Ash

Bagasse is nothing but the fibrous residue, which is obtained from sugarcane juice extraction process. It is very useful by product obtained from the sugar mill. It contains 4-5% ash contains with approximately 50% moisture contents and also having calorific value of around 8000 kJ/kg so that very useful in boiler for steam and electricity generation in sugar mills with efficiency of 60- 70%. Thus, the fly ash coming from the stacks of bagasse-fired boilers contains high amount of unburned carbon and such a big amount of BFA suffer with disposal problem. [Batra et al., 2008]

To overcome this disposal problem bagasse fly ash can be utilize as an adsorbent, as an additive in cement and concrete industry but due to containing high carbon contents it not suitable for use in concrete. BFA has been converted into an inexpensive and effective adsorbent for waste water treatment processes and currently it is being used as filler in building materials.[Mall et al., (2005)]

India has been the world's largest producer of sugar since last few years with more than 575 sugar factories, which generate about 1500 tones of BFA as by product per season. BFA was used as obtained from a nearby sugar mill (Uttam Sugar mill, U.K., India), without any pretreatment for the removal of pyridine from synthetic aqueous solutions in a batch treatment process.

1.2.2.1.1 Uses of BFA

1. Most of the ash is utilized in low level land filling. However, Inappropriate dumping method of BFA creates soil pollution and also causes air pollution with an allergic problem to human being.

2. A few parts are being utilized by ceramic, fertilizer and cementing industries.

3. The conversion of low cost waste by product (BFA) into higher level product zeolitic bagasse fly ash (ZBFA) would make the environmentally friendly disposal.[Shah et al., (2010)]

4.

1.2.2.1.2 Advantages of using BFA

The fly ash adsorption is a low cost method with high pyridine carrying capacity over other adsorbent options, which is economically affordable and easily available for the application in small and medium scale industries.

2 LITERATURE REVIEW

2.1 General

Different methods for the treatment of pyridine containing water was developed so far and different new techniques are also introducing day by day because of the seriousness of the harmful effects of pyridine although different physico-chemical treatments methods are present in this time but researcher are focusing on the methods which also utilized the agro based substances during the treatment process like adsorption and to replace the conventional adsorbents because these adsorbents are eco friendly, as well as easily available at low cost.

2.2 Various methods for the removal of pyridine

There are many methods for the removal of pyridine from waste water. Some important methods included adsorption, bio-degradation, solvent extraction, ozonation, electrochemical oxidation, ion exchange etc.

The physico-chemical methods use for the removal of pyridine have these own advantages like this is a less time taking method other than biological method along with this the physico-chemical method also have the flexibility in temperature change in operation and ease of operation also these treatments requires low space plant and also the installation cost is also less than the cost of biological methods but the operational cost is higher than the biological method.

2.3 Adsorption by using different adsorbents

Mohan et al. [2005] examined the ability of activated carbon, which was developed from coconut shell for the adsorption of different pyridine derivatives like α- picoline, β- picoline, γ- picolin from aqueous solution. Basically the aim of this study was to utilized the agricultural waste for the production of different quality of activated carbon for adsorption purpose . in his experiment he developed two different type of activated carbons. Class I carbon was prepared by treating coconut shell with concentrated sulfuric acid and designated as ATSAC (activated carbon derived from acid treated coconut shells) and the Class II carbon was prepared without using any chemical but treated at different temperatures and this was designated as SAC (activated carbon derived from coconut shells without any treatment). Both were utilized in batch method of adsorption to determine kinetic and various equilibrium parameters and after experiment it was found that Langmuir model was best fitted for equilibrium isotherm data and the adsorption followed the pseudo-second order rate kinetics. They also studied the thermodynamic parameters (which included effective diffusion coefficients, activation energy and activation entropy) and these results indicate that the adsorption was governed by particle diffusion at temperature 10 and 25 and at concentrations 25 and 50 mg/l while adsorption was controlled by film diffusion mechanism at temperature 40 C and at concentrations >50 mg/l. They concluded the result the capacity of ATSAC was found to be higher than SAC they added also that sorption capacity was found to be in γ- picolin > β- picoline > α- picoline this order.

Lataye et al. [2007] examined the adsorption ability of commercial grade granular activated carbon (GAC) and rice husk ash (RHA) for adsorption of pyridine from synthetic aqueous solutions. Under this study Batch experiment was performed for the estimation of various parameters like initial pH, adsorbent dose (m), contact time (t), initial concentration (C_0) temperature (T) on the removal of Pyridine. It was found that the maximum removal by RHA was about 96% at lower concentrations (<50 mg dm^{-3}) and about 79.5% at higher concentrations (600 mg dm^{-3}) by using 50 kgm^{-3} dose and the maximum removal by GAC was about 97% at lower concentrations (<50 mg dm^{-3}) and about 84% at higher concentrations (600 mg/dm^3) by using 30 kgm^{-3} at 30±1 °C. They found that adsorption rate is very fast in initial 2 min of contact and about 80% removal was achieved in it by RHA while about 86% removal was achieved in the initial 2 h of contact between GAC for (C_0 = 300 mg/dm^3) pyridine solution and at 303 K.
They also studied the kinetic, equilibrium and thermodynamic aspects of Pyridine sorption and found that the adsorption of pyridine was endothermic in nature so that the pyridine removal was increases with increasing temperature. They also added that Toth and Redlich–Peterson isotherm equations were found to be best for equilibrium data for GAC and RHA respectively, for pyridine. They also carried out the leaching study for recovery of pyridine and suggested that acidic water and 0.1N H_2SO_4 can be used together to recover pyridine from the spent adsorbents. They concluded the result that the overall adsorption of pyridine on GAC was more than RHA.

Cooke and Gaikwad [1983] interested to remove pyridine and quinoline from coal and coal extracts and their experiment was focused on the removal of solvent from coal after extraction step. Here they were taken the sample of pyridine and quinoline as solvent. In his experiment had taken the bituminous coal which was obtained from Fording Coal Mines in Fording, British

Columbia. They thoroughly mixed the coal sample with pyridine and after that it was irradiated ultrasonically for 0.5 h at 60 kHz. Then mixture was evaporated for drying at 20°C with 3m/s air velocity for 16 to 18 h and then dried in a vacuum oven at 1.3 kPa and 90°C for 3-5 h. it was found that pyridine was completely removed by experiment but in case of quinoline it was completely removed after Soxhlet extraction by repeated washing with methanol and after that mixer was dried at 110°C and 1.3 kPa for 2 h. It was found that for complete removal of quinoline three such cycles were sufficient.

Srivastava et al. [2005] examined the adsorption capacity of BFA and activated carbon in process of phenol removal and found the optimum conditions like pH was about 6.5, doze of adsorbent was 10g/l, time was 5hr for each adsorbent and found that the removal percentage was higher in case of laboratory grade activated carbon than BFA and the lowest removal was found in case of commercial grade active carbon and this process of adsorption was governed by pseudo-second order reaction kinetics for each adsorbent and also the data obtained from isotherm experiment was best fitted by R-P isotherm.

Lataye et al. [2007] performed the adsorption process by bagasse fly ash for the removal of 2-picoline, which is also known as α- picoline, a derivative of pyridine. Its characteristics are very similar like pyridine like colorless appearance, strong unpleasant odour and having number of agrochemical and pharmaceutical applications. In this experiment author studied the various parameters like initial pH, dose of adsorbent, time of contact, initial concentration and temperature for optimum removal of 2-picoline during batch adsorption experiment. They also carried out the kinetic studied for the sample. It was found that this adsorption follows the kinetics of second order and on increasing the initial concentration the adsorption was also increases and with help of equilibrium data the adsorption was best fitted by Redlich–Peterson isotherm equations and by Langmuir equation. They also found that at the concentration lower than the 50 mg/dm^3, removal was up to 98% and at higher concentration (600 mg/dm^3) the removal was 49%. The dose of BFA was 5 kgm^{-3} for the adsorption experiment. They added that thermodynamic studies indicated that the adsorption of aqueous sample on taken adsorbent was endothermic in nature. They also performed the desorption operation for removing 2-picoline from bagasse fly ash by using simple water at various pH and also by other solvents. They found that recovery of 2-picoline was done successfully by using acidic water and H_2SO_4 at 0.1N normality. They also compared BFA with activated charcoal (for uptake capacity, adsorption rate and operation cost) and found that BFA is superior to activated charcoal.

Rameshraja et al. [2011] performed the adsorption experiment for the removal of quinoline by two well known adsorbents i.e. activated carbon and bagasse fly ash in a batch system. In this they studied the behavior of different parameters like various parameters such as pH, adsorbent dose (m), temperature (T), initial quinoline concentration (C_o) and contact time (t), and optimized these parameters. From results he found that the optimum pH for this study was 5.5 and Equilibrium contact time was found to be 8 hr for both GAC and BFA. They also found the optimum doze of adsorption, for GAC it was 5 g/l and for BFA it was 10 g/l, and with the help of kinetic data and equilibrium data, he found the adsorption followed the Pseudo-second-order reaction, and best fitted by Redlich and Peterson (R–P) isotherm and endothermic in nature. They added further that entropy change for GAC and BFA were found to be 112.96 kJ/mol K and 77.78 kJ/mol K respectively, and heat of adsorption were 12.64 kJ/mol and 6.86 kJ/mol, respectively.

Bouyarmane et al. [2010] examined the three apatite adsorbents to remove pyridine and phenol from aqueous solution. In these adsorbents one was natural phosphate rock and other two were synthetic mesoporous hydroxyapatites. They found that the results indicated that the sorption process of removal was first order reaction for both samples and with the help of kinetics and equilibrium data, removal of phenol was best fitted by Freundlich model equation. They also found that sorption capacity for all three apatites were same. They concluded that natural phosphate rock found to be more efficient for removal of pyridine, he added further that although it had low specific surface area, but it had better efficiency and lower processing cost than popular activated carbons.

Mohan et al. [2004] illustrated the cost effective process for the removal of pyridine and for this porpose he developed the activated carbon from agricultural waste materials. In this experiment they studied the different parametertes which affect the adsorption process i.e. optimum temperatures, particle size, pH and adsorbent doses etc., form the results they concluded that Langmuir adsorption isotherm model best fitted the obtained data, and from the kinetic and equilibrium data he concluded that adsorption of pyridine by agricultural based activated carbon was showed the kinetics of first order. They added further that the temperatures at 10°C and 25°C adsorption occurred due to the particle diffusion mechanism, but at 40°C it was due to film diffusion mechanism**.**

Perez et al. [2010] examine the overall adsorption rate with diffusional modal for the removal of pyridine by GAC. They also examined the various factor like impeller speed, adsorption doze, initial concentration of pyridine in detailed. He performed the experiment in rotating basket adsorber and found the data by using the diffusion model for this they observed the effect of mass transfer, intraparticle diffusion etc. and from the result he came to know that in intraparticle diffusion more than 93.5% was done by surface diffusion so that this was the rate controlling mechanism for adsorption process. They also observed that the dominating mechanism coefficient was increases with increases in temperature and found to be not dependent on particle diameter. They also added that removal of pyridine from aqueous solution by adsorption with the help of GAC was independent from the effect of external mass transport.

2.4 Advantages of bagasse fly ash

Batra et al. [2008] performed the detailed study on the characteristics of Bagasse has been given in this paper. They added that Bagasse is one of the important biomass sources and it is used in the sugar industry as a fuel in India. This gives large quantities of fly ash generated by this process and creates a serious disposal problem. Under this study, the unburned carbon in bagasse fly ash is characterized by thermal analysis, electron microscopy and adsorption. BET surface areas found to be 200m^2/g for the separated carbons based upon N_2 adsorption measurement. .After the analysis of the isotherms it is found that the large fraction of pores in the size falls in the range of 10–12 Å. They added further that the unburned carbon is amorphous in nature and it is also found in the study of Scanning and transmission electron microscopy that the morphology retained the cellular characteristics of the parent bagasse fibers.

Chandra et al. [2011] proposed a method for maximum utilization of bagasse fly ash for the removal of industrial waste by adsorption process. In this literature they proposed a method for chemical activation of bagasse fly ash by two methods, first on was the one step method in which they used the $ZnCl_2$ for the activation of BFA and the second method involved the use of chemical with CO_2 which provide the facility of physical activation and due to these methods, they observed the development of porosity. They also studied the relation of porosity generated with activation method, temperature and ratio of $ZnCl_2$ to BFA used. From the result he found that at the temperature 600◦C and the used mass ratio were 2, provide the micropore and mesopore volume were 0.528 cc/g and 0.106 cc/g respectively and he also found the surface area was 1200 m^2/g. They also examined the adsorption capacity of prepare adsorbent by using the different samples like phenol and methylene blue and performed the batch study for adsorption process and on comparison with the original bagasse fly ash to the chemically activated bagasse fly ash, they found that chemically active BFA provided the better removal efficiency with lower operational cost.

2.5 Other physico-chemical methods

Niu and Conway [2001] examined the adsorption and electrosorption techniques for the removal of pyridine for the treatment of industrial waste water. In this experiment he used the electrode of carbon cloth of high area and coupled this to spectrophotometer and scanned the kinetics obtained from the experimental results and also obtained the other parameters simultaneously. They also found that is pH of the solution was changing than the removal efficiency would be decreasing so he maintained the pH at 6.8 of the solution. After polarizing the anode he found the complete removal of pyridine and he also added that by using galvanostatic polarization he increases the removal rate of pyridine due to the fact that the changing was in double layer in galvanostatic polarization.

Rehakova et al. [2011] compared the result obtained from the applications of different zeoadsorbents i.e. natural zeolite and copper form synthetic zeolite and he also studied the results obtained from the different characterization techniques like CHN, X- ray diffraction, FTIR analysis and different thermal analysis and also performed the process for the analysis of surface area and pore volumes. They also found that there was a strong bond between the pyridine and zeolite because when he applied the thermal application on the zeolite containing sample, the removal of pyridine was found at higher temperature rather than the boiling point of the pyridine which neglect the possibility of escape of pyridine at normal temperature. They also added that different characterization showed the efficiency and viability of this process.

Stapleton et al. [2009] performed the photolytic method for removal of pyridines and they had taken 2-halogenated pyridines for the experiment purpose. They also suggested that pesticides, surfactants, dye etc. such type of organic pollutants can be gone to degradation process by heterogeneous photocatalysis based on TiO_2. They were basically using ultraviolet irradiation for destruction and mineralization of taken sample at 254 nm. They were found that degradation process satisfied the kinetics of pseudo-first order reaction. In this experiment he found the decomposition products and also proposed a primary reaction pathway for this reaction. They also found that sample taken for the experiment was dehalogenated rapidly on decreasing pH sharply. They added further that rate of removal by photolytic process was not affected significantly by aeration, pH or agitation. After experiment it was found that removal of TOC was fastest in 2-fluoropyridine and they added further that after destruction of different halogenated pyridines, 2-Hydroxypyridine was produced as a primary intermediate during process which was further gone to destruction process to form Dewar pyridine. They added that 2-iodopyridine was found to be most photo stable product which is also aliphatic in nature and effect on the production was also demonstrated, it was found to be high at high concentration and at low pH.

Bokhove et al. [2007] proposed a hybrid technology which included the advantages of both conventional technologies i.e. adsorption and liquid-liquid extraction. According to the author on applying the adsorption process alone for removal of pyridine, the regeneration of used adsorbent was difficult in case of aromatics compounds so it requires thermal treatment which was costly process and in case of liquid-liquid extraction process, it was more effective process for removal of pyridine because of selective removal tendency of solvent but for such case there were possibilities of irreversible emulsification and entrainment. So that they proposed solvent impregnated resins used in fixed bed operation to hold the advantages of both technologies. They prepared a solvent for removal of 4-cyanopyridine from aqueous solution and he found that the optimized solvent was a 1:1 mixture of (E)-3-bromo-4-(3-ethylhept-1-en-1-yl)phenol and (Z)-3-bromo-4-(3-ethylhept-1-en-yl)phenol which was design by using COSMO-RS as a tool and this solvent also meet the prerequisite of suitable solvent i.e. high tendency for pyridine and insolubility with water. From experiment they were found that the distribution coefficient was 254 and capacity of 44 g/kg with the solubility of 9.3 mg/l.

Warzinski and Holder [1991] mixed the coal with pyridine and separated the pyridine soluble and pyridine insoluble fraction from the solution after that they examined the pyridine insoluble fraction with morphological and liquefaction analysis and found that the behavior of that fraction depended on the manner of pyridine removed. There was a loss in surface area and pore structure of coal because of vacuum drying at 110^o C but when supercritical CO_2 was used to remove pyridine then macro pore and micro pore surface area and porosity were found to be increases. They also added to prevent that retrogressive reactions in the fraction of pyridine-soluble material it was necessary to use a hydrogen-donor solvent or catalyst. They also performed the catalytic liquefaction process and found that the conversion was lower than evaluated for original coal but that was higher than separated both fractions estimated conversions values.

Peng et al. [2012] proposed a new method for pyridine removal from aqueous solution with the help of emulsion liquid membrane with the advantage of easily demulsification by application of heating. This membrane consists of different chemicals like HCl used as stripping phase and for organic solvent and surfactant he used kerosene and OP-4 respectively. In this experiment he studied the different important parameters like concentration of surfactant, salt and internal phase and its type speed of emulsification volume ratio of MP to IP and MP to EP, pH values and stirring speed. After optimizing the various parameters he found that the removal of pyridine was 96.5% within 20 min of contact time. They also performed the experiment for the demulsification of emulsified membrane by thermal application at 70 °C so the efficiency of process was very high because of recycling of surfactant and solvent. They concluded that this technology was found to be very effective and alternative to the conventional method for the treatment of pyridine containing waste water.

2.6 Biological methods

Pandey et al. [2006] performed the biological method for treatment of pyridine containing gas. In this experiment he used the biofilter unit (laboratory scale) and packed this unit with compost material and wooden chip and after this fill the unit with Pseudomonas pseudoalcaligenes-KPN which was the pyridine degrading microorganism and continuously feed them for more than 2 years. From result he found the different parameters like optimum moisture contents 68%, and bed retention time was 28.50 sec. for degradation of pyridine more than 99% on 434 g pyridine

m^{-3} h^{-1} loading. At the end they concluded that the downstream of gas was found to be free from pyridine odor.

Mudliar et al. [2007] proposed a new type of rotating rope bioreactor which had overcome the disadvantages of conventional bioreactor for treatment of volatile compound such as pyridine. In general the conventional type of biological reactors like biofilter, suspended growth bioreactor, packed bed bioreactor and rotating rope bioreactor systems struggled with poor oxygen rate due to intense mixing and forced aeration for volatile compound treatment so that there were limitations related to loading and high concentration. Theirs designed immobilized bioreactor was found to be efficient enough to treat the pollutants containing high volatility compounds of high solubility to water and low microbial yields. The designed reactor had higher interfacial area per unit reactor volume and also provide higher oxygen transfer rate with higher stability for microorganisms and due these facilities the reactor was provided higher removal rate than the other conventional reactors. The results showed that the reactor successfully degrade the pyridine molecules and the removal efficiency was found to be more than 85% at high concentration of pyridine (up to 1000 mg/l) and high loading rate (66.86 $g/m^3/h$), nevertheless the hydraulic retention time was also decreases (9–18 h). They concluded with the fact that the reactor run continuously 15 month with same efficiency.

Sunil et al.[2007] used the aerobic bio degradation method for the removal of pyridine in this experiment they firstly cultivated the aerobic granules in phenol medium with the concentration of 500 mg/L. he studied the degradation process over wide range (250–2500 mg/L) of pyridine concentration and with the help of result they found that the maximum degradation was occur at the pyridine concentration of 250 mg/L he also found the rate of maximum degradation 73.0mg pyridine g/VSS/h and he also illustrate the Michaelis–Menten kinetics parameters that are Vmax, Km and K_I and he found 63.7 mg/Lh^{-1}, 827.8 and 1388.9 mg/L, respectively. They added further that microbial strain was existing in both aerobic granules.

Li et al. [2008] investigated the characteristics and biodegradation efficiency of Streptomyces sp. HJ02 for removal of pyridine. The novelty in this microorganism was to have the ability of growth on the pyridine only and in this study he examined the effect of pH, temperature and concentration of sample. They also examined the effect on the addition of sucrose on the removal process. They found that 2000 mg/l of pyridine was degraded successfully in 8 day by the proposed microorganism. He also find that in comparison between SSD and amidase, SSD was found to be more stable over 25^0C to 40^0C range and over pH range between 7.0 to 10.0. They also added that the due to metabolism of pyridine the pyridine was found to be hydrolyzed, and form succinate semialdehyde and formamide.

Zhang et al. [2009] used the pyridine for the degradation purpose and to generate electricity from this by using microbial fuel cell because there were no research on that field was held before that area. In this experiment they also examined the metabolic pathway of pyridine degradation process and electricity generation root. Firstly they used the graphite-packed microbial fuel cell with constant pyridine concentration of 500 mg/L and adding different concentration of pyridine and from the result (after total pyridine degradation) they obtained the voltage of 116mV and power density of 1.7W/m^3 these were the maximum values of the obtained results and within 12 h. In experiment he varied the glucose concentration to 500, 250, and 100 mg/L which provided the voltages of 623, 538, and 349 mV and power densities were 48.5, 36.2, and 15.2W/m^3 these are the maximum values of the obtained result. They also added that the degradation of pyridine was found to be 95% within 24 h. They also performed the experiment by using graphite fiber brush and on comparison he found that in case of graphite fiber brush the charges of electricity was found to be higher than in case of graphite for and this was checked for various glucose-to-pyridine ratios. They also added that the metabolism started with the braking of pyridine ring they also suggested that this method was found to be very good for waste water containing pyridine.

Lin and Wanga [2009] worked on the alternative method of adsorption for pyridine removal from waste water stream and studied over microbiological degradation of pyridine by converting to the other harmless compounds like carbon dioxide, water, ammonium ions etc. the main aim of his study was to degradation of pyridine by biological method using Paracoccus sp. KT-5 and also examined the effect of various substances like glucose, NH_4Cl and other elements present in trace amount. They found from the result that after adding 100 mgL^{-1} glucose and 950 mgL^{-1} of pyridine that removal of pyridine and growth of microorganism were increases but had no effect on the generated ammonia and added further that 100 mgL^{-1} of addition of NH_4Cl reduced the removal rate of pyridine. They concluded with the fact that due to lack of traces element the growth rate of microorganism as well as the rate of removal of pyridine was also decreases and it also not affect the ammonia generation step.

Bai et al. [2010] suggested the biological treatment method for removal of pyridine and quinoline from waste water stream because of its cost effective advantages over other techniques. They found that ammonia was generated in the biodegradation process of pyridine and quinoline due to their N transfer. They added that zeolite was an effective sorbent for the removal of ammonia and they modified the zeolite to performed like a macroporous carrier for biological treatment of the sample. In his experiment they used a special type of bio-zeolite which comprises the mixed bacteria of both pyridine and quinoline and modified zeolite for adsorption and biodegradation treatment. They performed the experiment for sterile synthetic and coking wastewater. They found that both pyridine and quioline degraded simultaneously by the mixed bacteria and NH_4^+ generated was successfully removed by modified zeolite and with the help of different experiment they concluded that the microorganism easily and rapidly attached to the modified zeolite and bio zeolite was found to be cost effective and efficient for removal of pyridine and quioline simultaneously.

Table 2.1 Important remarks and conclusion obtained from different literatures

Adsorbate	**Adsorbent**	**Remark/conclusion**	**Reference**
Pyridine	Platinum and Nickel	1. Chemisorptions process was carried out for pyridine removal on platinum which was supported by silica. 2. Pyridine was adsorb on nickel strongly and adsorption was improved it was treated with $O_2/C_{o.}$	MORROW et al., (1976)
Pyridine and Quinoline	Rundle spent shale	1. They found that the isotherm in this study was Langmuir type and also found that the used spent shale was given the same type of results as clay-like material.	Zhu et al., (1988)
Pyridine	Mo and C/N–Mo	1. Performed the adsorption experiment of Mo and C/N modified Mo. 2. Using DFT theory and temperature operated study the pyridine adsorb on the adsorbents in <530K temperature.	Abdallah et al., (2004)
Quinoline Yellow	de-oiled soya and Bottom ash	1. Fixed bed column study was done for the removal process. 2. Both adsorbents have kinetics of 1st order. 3. Recovery can be done by using dil. NaOH.	Gupta et al., (2005)
2-picoline	sawdust	1 This process follows the kinetic of pseudo- 2nd order and also the nature of process was endothermic in nature. 2 SD can be reused after desorption by combustion only.	Hashemian and Mirshamsi (2012)

Adsorbate	Adsorbent	Remark/conclusion	Reference
α-picoline	granular activated carbon and rice husk ash	1. Isotherm data obtained from the result was best fitted by R-P isotherm model equation. 2. Both adsorbents had the adsorption of endothermic nature. 3. GAC showed the better removal efficiency than RAC (90% and 85%)	Lataye et al., (2009)
γ-picoline	activated bentonite	1. Adsorbent used in the study was acid activated. 2. Adsorption process was found to be pseudo 2nd order. 3. Langmuir isotherm was found to be best fitted with obtained data and the process was found to be endothermic in nature.	Rawajfih and Nsour, (2010)
α-picoline, β-picoline, and γ-picoline	phillipsite and faujasite	1. Equilibrium data was best fitted by BET model. 2. γ-picoline was adsorbed higher extent on phillipsite than other adsorbate on adsorbent. 3. The nature of process was found to be exothermic in nature.	Zahir et al., (2010)
phenol	activated carbon	1. Rattan sawdust was used as the carbon source for the study. 2. Langmuir isotherm was found to be best fitted with obtained data with the kinetics of pseudo 2nd order.	Hameed and Rahman (2008)

3 OBJECTIVE

1. To collect the ground water samples from different wells from Shahbajpur area.
2. Characterization of the obtained ground water samples with Fourier Transform Infrared (FTIR) spectroscopy for the detection the functional group and also finds out the possible compounds present in the samples.
3. To select the suitable adsorbent, this was easily available and can be used in large scale without serious environmental limitations.
4. The characterization (FTIR), X-ray diffraction (XRD), Thermogravimetric analysis (TGA), Brunauer–Emmett–Teller (BET) surface area of adsorbents before and after the adsorption process.
5. Removal of Pyridine from synthetic wastewater by adsorption, using BFA as adsorbent and to optimize some parameters during the experiment like pH, Contact time, Adsorbent dose (mg/l), Temperature for adsorption process.
6. Following study will be carried out to determine the nature of adsorption mechanism. The kinetic study for determination the nature of reaction i.e. the pseudo 1st order or 2nd order reaction. Best isotherm representing the equilibrium data at various temperatures. Define the values of thermodynamic parameters by using the adsorption data.

4 EXPERIMENTAL PROCEDURE

Pyridine removal from the synthetic aqueous solution has been performed in the present work, by adsorption process in batch system, on the surface of bagasse fly ash (adsorbate) with the required objectives given in the previous chapter. This study involved the preparation and characterization of used adsorbate i.e. bagasse fly ash, preparation of sample, experimental procedure are discussed here.

4.1 Adsorbate and Adsorbents

Pyridine was purchased from Local market of Roorkee, India and BFA was obtained from Uttam sugar mill dist. Haridwar, Uttarakhand, India which was collected from the particulate collection device and used without any pre-treatment other than sieving and washing. Stock solution of 1 ml/l was prepared by mixing 1 ml of accurately measured pyridine in 1l of distilled water. The test solutions were further diluted to desired concentration by adding distilled water in the stock solution.

4.2 Characterization of the adsorbent

4.2.1 Pretreatment of adsorbent- In this study adsorption was screened through the standard sieves and this was the only pretreatment step involved in this experiment. In this process sieves of different mesh sizes were kept one over the above and then started shaking and at the end of the process, adsorbent of particle size 750 µm to 1000 µm were obtained.

4.2.2 FTIR analysis (Fourier Transform Infrared spectroscopy)– The main objective of this instrument is to identify the functional group present in the samples and this instrument is applicable for both organic and inorganic compounds. The principle behind this technique is to utilize the molecular bonds vibration at various frequencies which is highly specific and depends on the elements and the type of bonds. In this method IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through that is transmitted after that the adsorbed infrared spectrum is compared to the library of system to identify the chemical bond and these data are display after decoding by Fourier transformation method for user friendly output. Here, FTIR (FTIR, NICOLET AVTAR 370, USA, software-

OMNIC) spectrometer was used employed to determine the type of functional groups present on the adsorbents surface before and after adsorption.

For this experiment sample is mix with KBr in very less proportion and then mixed it thoroughly to form uniform mixture after that this mixture is kept in dye to press by hydraulic press for pallet preparation than pallet is placed in sampling port to analyze functional group. The spectral range chosen was from 4000 to 400 cm^{-1}.

4.2.3 BET surface area

Brunauer–Emmett–Teller (BET) theory is basically an extension of Langmuir theory of monolayer molecular adsorption while this consider the multilayer adsorption of gas and done by using Surface Area and Porosity analyzer ((Micromeritics Chemisorb 2720). Here analyzer was mainly used to find the BET surface area of bagasse fly ash along with BJH adsorption/desorption cumulative volume of pores and surface area of pore and also the single point total pore volume where BJH stand for Barrett, Joyner and Halenda.

4.2.4 XRD analysis- X-ray diffraction utilizes the X- ray scattering techniques to find out the information about the crystalline structure (which is nothing but the set of atoms arranged in a particular way, and lattice exhibiting long-range order and symmetry) of an unknown material, which includes the gap between the layers of atoms and the single crystal orientation. This technique is also used to find out the size, shape and internal stress of small crystalline region.

For the characterization of BFA X-Ray Diffraction analysis was done by X-Ray Diffractometer (Bruker AXS, Diffractometer D8, Germany). In the diffractometer copper is used as the target while nickel is used as the filter media and for the experiment some important parameters was maintained as constant

K radiation was 1.542 Å, Goniometer speed was 1^{o}/ min, chart speed was 1 cm/min along with these parameters scanning angle (2θ) was set to be in the range of 10-90^{o}. In the result the peak of high intensity was obtained which indicate the value of (2θ), shows the applicability of Bragg's law [http://en.wikipedia.org/wiki/X-ray_scattering_techniques/30/5/2013].

4.2.5 SEM- Morphology of the BFA before and after the adsorption was studied by the scanning electron microscope (SEM). For the morphological study firstly the samples were coated with gold to enhance the conductivity of the sample and then energy dispersive X-ray and SEMs spetra were obtained.

4.2.6 TGA analysis- Thermal gravimetric analysis or can say thermogravimetric analysis is basically a technique to study the physical (like vaporization, absorption, adsorption, desorption and sublimation basically the processes involve the transformation of thermodynamic system from one phase or state of matter to another of second order) as well as chemical properties (like chemisorptions, dehydration, decomposition, oxidation and reduction etc.) changes with increasing temperature at constant rate of heating. TGA analysis usually applies for the study of mass loss or gain due to decomposition and from the pattern of decomposition it defines the characteristics of sample and also for the determination of organic and inorganic contents present in the samples. [http://en.wikipedia.org/wiki/Thermogravimetric_analysis/30/05/2013].

Thermogravimetric analysis (TGA) of BFA was carried out using Perkin Elemer (Pyris Diamond) thermogravimetric analyzer. From the output of the analyzer thermo gravimetric (TG) and differential (DTG) curves obtained and to find out the desirable characteristics of the samples five temperature ranges of mass losses were considered (table 4.1).

Table 4.1 The possible losses in mass in increasing Temperature range

S. No.	Temperature Range (in °C)	Losses
1.	25-250°C	Moisture, crystallisation and zeolitic water
2.	250°C-400°C	Organic compounds, hydroxides or hydrated iron oxides.
3.	400ºC-500º C	Combined water (ex dehydroxylation of hydroxyl groups from clay minerals)
4.	590ºC-720 ºC	Carbonates from dolomite
5.	500ºC – 900 ºC	Carbonates from aragonite and calcite

4.3 Batch study

Batch study was carried out to evaluate the different process parameters like adsorbent doze, pH, initial concentration of pyridine, time of contact, temperature and to optimize them and with the help of these results define the design parameters like rate constants and isotherm constants. For each experiment the 100 ml aqueous sample of pyridine of 100 mg/l concentration was taken. Adsorption was carried by absorbent name Bagasse fly ash of known amount (g/l) in 100 ml of pyridine solution. The mixture was agitated in a temperature controlled orbital shaker with a constant speed of 150 rpm at a specific temperature (like 15^oC, 30^oC and 45^oC).

The percentage removal of pyridine was calculated using the following relation:

$$\text{Percent Removal} \quad \frac{´C_o - C_e)100}{C_o} \qquad (4.1)$$

Similarly for the equilibrium adsorption uptake, qe (mg/g) were calculated as:

$$q_e = \frac{(C_o - C_e)}{w} V \qquad (4.2)$$

Where,

- C_e is the equilibrium adsorbate concentration,
- V is the volume of the adsorbate (l),
- w is the mass of adsorbent (g).

4.3.1 Adsorption

Adsorption is the process which involves the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface which may be of liquid or solid but mainly in most cases it is a solid surface, so that in adsorption process a film adhered molecules forms on that surface. The substances which adhere to the surface are known as adsorbate and the surfaces which get the adhesion of molecules, are known as adsorbent. This process is different from the absorption process because in absorption process one fluid either permeate or dissolve by the liq. or solid so that whole volume of the substance involves in the process while in case of adsorption process is surface phenomena while the term sorption involves the both processes.[http://en.wikipedia.org/wiki/Adsorption]. Here adsorption can be occur in liquid-solid interface, which involve the adsorption of the pyridine on the surface of the bagasse fly ash and gas-solid interface, which involve the adsorption of the volatile compounds present in the sample on the surface of bagasse fly ash.

The mechanism of adsorption involves is very simple because the required driving force for the process is due to the reduction in interfacial (surface) tension between the fluid and the solid adsorbent because due to the environment around the surface atoms, they experience a bond deficiency due to lack of surrounding atoms so that they have unbalanced or residual attractive forces. Thus these particles have the tendency to attract the particles of adsorbate and to make bond with the adsorbate at the surface.

4.3.1.1 Factors consider for the study of adsorption process

4.3.1.1.1 Nature of adsorbent-

Surface area per unit mass it the most important factor of adsorption process and directly proportional to it. Adsorption capacity is also depends on physicochemical characteristic, and its affinity for adsorbate. Adsorbent capacity is also depends on porosity, if it is porous then adsorption capacity is not depend on particle size while if it is non porous then adsorption capacity is inversely proportional to particle size diameter. According to international union of pure and applied chemistry IUPAC [IUPAC, 1982], particle is said to be micro-pores if its diameter is less than 20 Å, for meso-pores the diameter should be between 20 Å to 500 Å, and for macro pores diameter should be greater than 500 Å. In case of micro-pores compounds if diameter is less than 7 Å than the particle is said to be ultra micro-pores and if diameter is between 7 Å to 20 Å in size than it said to be super micro-pores. For liquid, it is found that meso-pores particle of adsorbent having high intra particle migration tendency.

4.3.1.1.2 pH of solution

pH of the solution is strongly effect the adsorption process because it effect the surface charge and degree of ionization in adsorption process due to the fact that hydroxyl and hydrogen ions absorbs rapidly on the adsorbent surface. It is found that the adsorbent surface favors to adsorb anions at low pH and to absorb cations at high pH.

For the batch study aqueous solution of pyridine of 100 mg/l concentration was prepared for the study by using distilled water and 100 mL of the prepared solution was taken in 6 different conical flasks (batch) of 250 ml capacity. Then the pH was adjusted by using 1 N NaOH and .1N H_2SO_4 solution and checked by pH meter. Different pH (2, 4, 6, 8, 10) was adjusted for different batch for the experiment while one sample was kept at its natural pH of the solution after that 0.7 g of BFA was added in each conical flask and kept in to the incubator cum shaker at 30 ± 1^{o} C temperature and agitation speed 150 rpm for 6 hr. after completion the time of contact these samples were filtered and analyzed by UV spectrophotometer for the determination of percentage removal of pyridine.

4.3.1.1.3. Adsorbent dosage

On increasing the adsorbent doze the removal of pyridine is also increases rapidly because on increasing the dosage the more surface area is available for sorption so the rate of sorption is also increases and after saturation the rate is decreases.

The optimum doze of adsorbent for the removal of pyridine form the aqueous solution in adsorption experiment was carried out by taken the samples of different BFA dozes at same operating condition, so for this study firstly aqueous solution of pyridine of 100 mg/l concentration was prepared by using distilled water after that 7 samples of that concentration were taken in 7 different conical flasks (batch) of 250 ml capacity then BFA as a adsorbent was added in different amounts (0.01g, 0.05g, 0.1g, 0.2g, 0.5g, 1.0g, 2.0g in 100 ml of pyridine sample) in each batch and kept in to the incubator cum shaker at 30 ± 1^{o} C temperature and agitation speed 150 rpm for 8 hr after that the samples were filtered and analyzed by UV spectrophotometer for the determination of percentage removal of pyridine.

4.3.1.1.4. Contact time

Adsorption due to physisorption is more rapidly than chemisorptions and occurs within very short time period but bonded by weak Vander Waals forces while chemisorption is slow process but bonded by strong chemical bond at the attainment of equilibrium. Initially the rate of adsorption is high because adsorption process is the function of available vacant sites which are higher at initial stage and when the major active sites filled with adsorbate than repulsion of adsorbate molecules from adsorbent surfaces are increasing rapidly so that the uptake capacity is slower at equilibrium stage and between these two stages the rate of adsorption is found to be constant.

Same procedure was repeated for the preparation of the sample but for the study of optimum contact time, 10 sample of 100 mg/l concentration of pyridine was prepared and kept into different conical flask (batch system) of 250 ml capacity and feed by optimum doze of adsorbent i.e. BFA and kept in the shaker at 30 ± 1^{o} C temperature and agitation speed 150 rpm for different time periods (15 min, 30 min., 1 hr, 2 hr., 3 hr., 4 hr., 5.5 hr., 7 hr., 8.5 hr., 10 hr.,). After each time period the samples was taken out from the shaker and filtered through filter paper and after that each sample was analyzed by UVS for the determination of percentage removal.

4.3.1.1.5. Initial concentration of adsorbate

It is very important factor because given mass of adsorbent can absorb only fixed amount of adsorbate i.e. pyridine. On increasing the concentration of adsorbate for fixed adsorbent the rate of adsorption are also increases because the resistance of solute uptake in the solution is decrease due to high availability of solute molecules so the driving force for adsorption is increase and thus rate of adsorption is also increase.

For this study 7 samples of different concentration of pyridine (50mg/l, 100mg/l, 150mg/l, 200mg/l, 250mg/l, 300mg/l, and 350mg/l) were prepared with distilled water and optimum doze of BFA and kept for optimum time in shaker and filtered followed by UVS for the removal analysis was conducted.

4.3.1.1.6 Kinetic study

Same experiment, as performed for the study of the optimum contact time, was performed for the 100mg/l and 200mg/l sample of pyridine and other condition were remained same for the study of kinetic of the adsorption process. The initial rapid uptake indicates surface bound sorption and the slow second phase due to long range diffusion of adsorbate onto the interior pores of the adsorbent. The increase in C_o adds to the interaction between Pyridine and the adsorbent. The rate of intake also increases with the increase in Co due to increase in the driving force. Also, the rate of uptake is limited by solution components affinity to the adsorbent, diffusion coefficient of the adsorbate in the bulk and solid phases, the pore size distribution of the adsorbent, and the degree of mixing.

Pyridine adsorption on BFA could be represented by-

1. Pseudo-first-order model-

$$q_t = q_e[1 - \exp(-k_f t)] \quad (4.3)$$

Where -

q_t is amount of Pyridine adsorbed (mg/g) at time (t) (min) and k_f is the rate constant of pseudo first-order adsorption (min^{-1}).

2. pseudo-second-order model

$$q_t = \frac{t k_s q_e^2}{1 + t k_s q_e} \quad (4.4)$$

The initial adsorption rate, h (mg/g min), at t→ 0 is defined as;

$$h = k_s q_e^2 \quad (4.5)$$

Where, ks is the rate constant of pseudo second-order adsorption (g/mg min).

4.3.1.1.7 Adsorption isotherm models

Adsorption process are generally exothermic in nature so that on increasing the temperature the adsorption process are decreasing in most of the cases while in some cases on increasing the temperature, the bonds near the edge of active surface sites are breaking which generates more active sites for adsorption so that rate is increase in some cases. It may also possible if the adsorption process is occur due to diffusion process because diffusion is endothermic in nature because the mobility of ions are increases and simultaneously retardation forces are decreases on increasing the temperature so that sorption capacity is also increases.

Adsorption is usually described through isotherms. Isotherm is nothing but the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. [http://en.wikipedia.org/wiki/Adsorption].

Adsorption equilibrium (the ratio between the adsorbed amount with the remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration [Foo and Hameed, (2010)]. There are different types of isotherms out of which two are well known isotherms namely Langmuir and Freundlich isotherms-

(a) Freundlich isotherm – It is two parameter isotherm provide the information about the non ideal and reversible adsorption and also not limited by monolayer adsorption assumption so that the empirical equation of the isotherm is applicable for the multilayer adsorption also have the non uniformly affinities over the surface so that highly applicable in the area of heterogeneous system. The heterogeneity of the surface is represented by the slope of range 0 to 1 and if it is close to the 0 then it is the indication of more heterogeneousness of the surface, this also represent the adsorption intensity. The value of slope less than 1 is also represent the occurring of chemisorptions process while if the value of 1/n is higher than 1, represent the cooperative adsorption process. Disadvantage of the isotherm are lack of thermodynamic basis and not use of Henry's law at very dilute concentration.

In Freundlich isotherm the heat of adsorption decreases in magnitude with increase in adsorption

$$Q_e = K_F \, C_e^{(1/n)} \qquad (4.7)$$

$$\ln Q_e = \ln K_F + (1/n)\ln C_e \qquad (4.8)$$

It is clear from the equation that for high K_F and low n values the rate of adsorption will high throughout the concentration range.

(b) Langmuir isotherm- This isotherm belongs to the homogeneous adsorption and also a two parameter isotherm.

It is a semi-empirical isotherm derived from a proposed kinetic mechanism. It is based on four assumptions:

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.

2. Adsorbed molecules do not interact.
3. All adsorption occurs through the same mechanism because the active sites are finite and fixed in number and no hindrance is exists even between the adjacent sites molecules
4. At the maximum adsorption, only a monolayer is formed means the adsorbed layer is have the thickness of only one molecule so that molecules of adsorbate do not deposit on other and the adsorbed molecules only on the free surface of the adsorbent.

$$Q_e = \frac{Q_m K_A C_e}{1 + K_A C_e} \tag{4.9}$$

$$\frac{C_e}{Q_e} = \frac{1}{K_A Q_m} + \frac{C_e}{Q_m} \tag{4.10}$$

where,

Q_e=Amount of adsorbate adsorbed per unit of adsorbent at equilibrium

Q_m= Amount of adsorbate adsorbed per unit of adsorbent required for monolayer adsorption (limiting adsorbing capacity)

K_A = Constant related to enthalpy of adsorption

C_e = Concentration of adsorbate solution at equilibrium

Redlich–Peterson isotherm model

It is a three parameter isotherms which include the featuring of both Langmuir and Freundlich isotherms and can represent adsorption equilibria for wide range of concentration for both homogeneous and heterogeneous system.

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \tag{4.11}$$

Where K, a, g are constants. The other isotherms includes Dubinin–Radushkevich, Temkin, Flory–Huggins, Hill, Flory– Huggins, Sips, Toth, Koble–Corrigan, Khan, etc. [Foo and Hameed (2010)].

5 RESULTS AND DISCUSSION

This Chapter covers the discussion and interpretation of results of the present study and divided into three sections-

1. Characterization of groundwater obtained from the Shahbajpur area.
2. Characterization of the adsorbent used in study.
3. Study of adsorptive removal of pyridine from prepared aqueous solution.

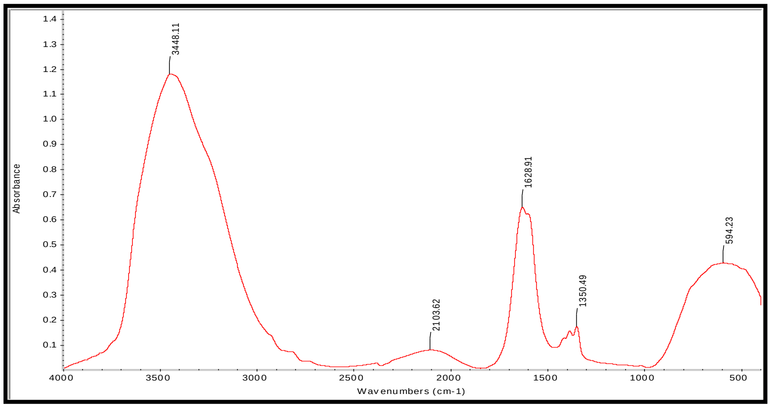
5.1 Characterization of groundwater

FTIR spectra of each sample, obtained from the shahbajpur area, was analyzed fro the determination of functional groups present in the samples. The resigon of FTIR study was limited in the range of 4000-400 cm^{-1} and in this region several peaks were observed. From the FTIR study the possibility of various groups were observed these included amide, aromatic nitrile, hydroxyl, methyl, carboxyl groups, cyanide group etc. Strong vibration peak in between 1650-1550 cm^{-1} was find out in major samples which indicate the presence of pyridine along with small peak between 2200-2100 cm^{-1} indicate the presence of cyanide group.

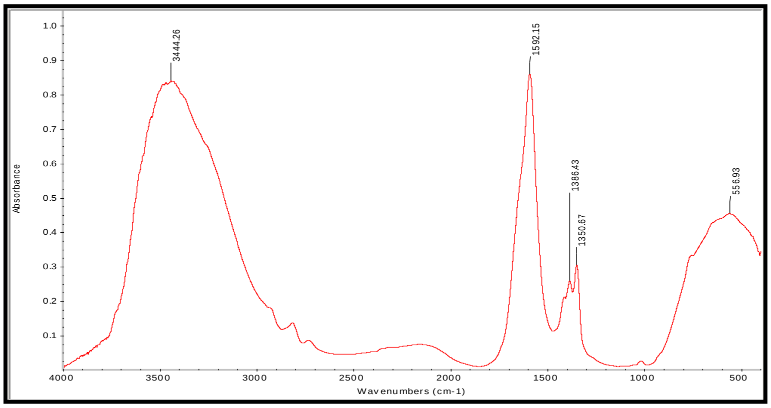
Table 5.1 Fuctional groups present in ground water sample of L-1 to L-21 (Figure-5.1)

WELL NO.	**Functional group present in the sample**
L-1	Aliphatic Amide Group
L-2	Aliphatic Amide Group
L-3	--------------------------
L-4	Aliphatic Amide Groups
L-5	Aliphatic Ether group
L-6	Aliphatic Nitro, Nitrite, and Nitrate Compounds
L-7	Aliphatic Amide Groups
L-8	Aliphatic Amide Groups, Alcohol Functional Groups, Inorganic Nitrate group.
L-9	Aliphatic Amide Groups
L-10	Aliphatic Amide Groups
L-11	Aliphatic Amide Groups, Alcohol Functional Groups
L-12	--------------------------
L-13	Aliphatic Nitro, Nitrite, and Nitrate Compounds
L-14	Aliphatic Amide Groups, Inorganic Carbonate Compounds.
L-15	Aliphatic Amide Groups, Aromatic hydrocarbon group, Aromatic Nitrile group, Isocynate group
L-16	--------------------------
L-17	Alcohol Functional Groups
L-18	Aliphatic Amide Groups, Alcohol Functional Groups
L-19	Aliphatic Amide Groups, Aliphatic Ether group
L-20	Aromatic Nitrile group, Isocynate group, Inorganic Carbonate Compounds
L-21	Aliphatic Amide Groups, Aromatic hydrocarbon group, Aromatic Nitrile group, Isocynate group

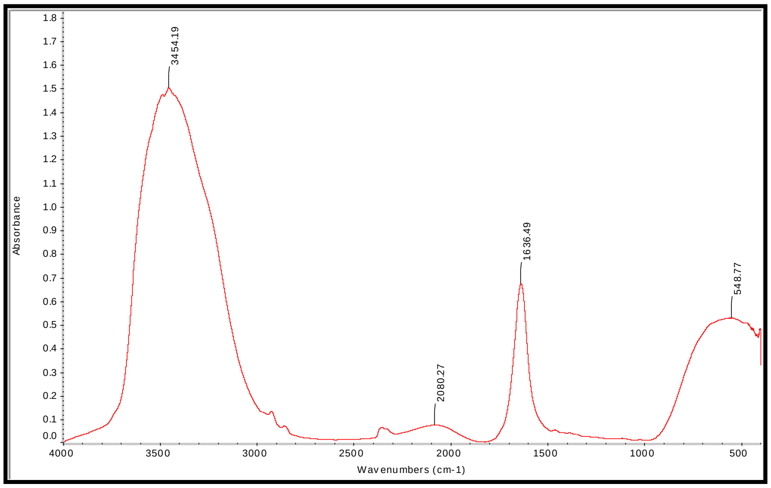
FTIR Spectra of different wells



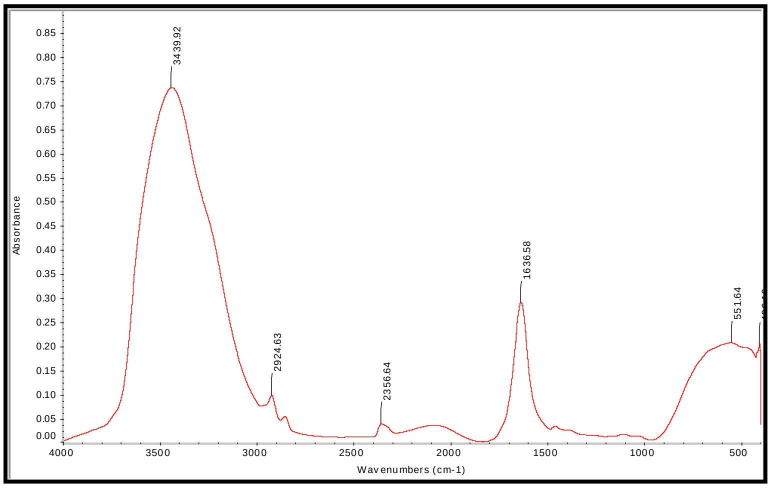
(L-1)



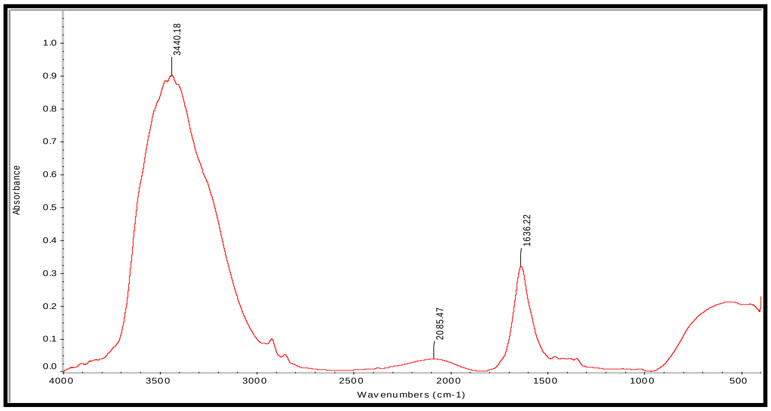
(L-2)



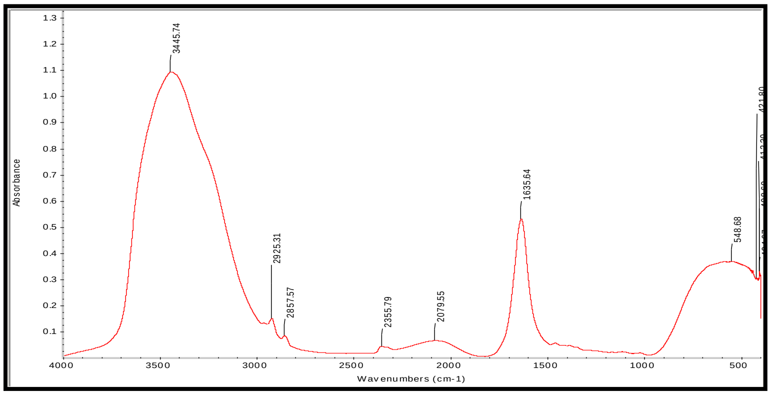
(L-4)


3439.92
2924.63
2356.64
1636.58
551.64
Absorbance
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

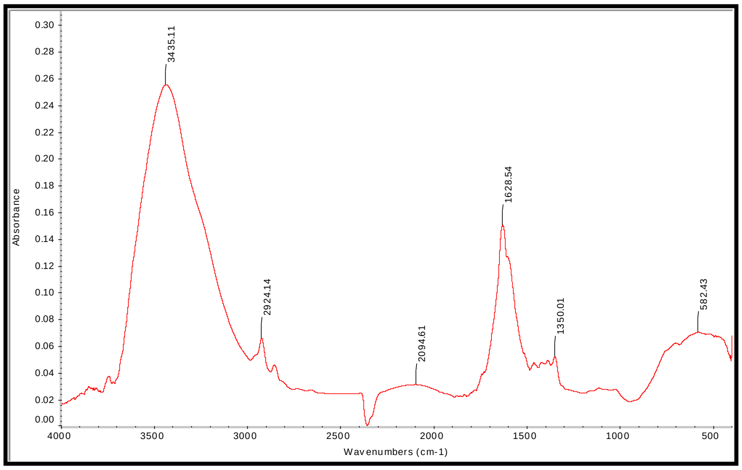
(L-5)


3440.18
2085.47
1636.22
Absorbance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

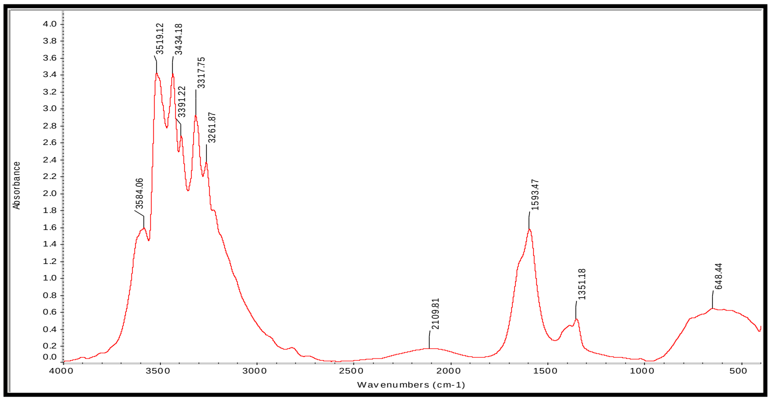
(L-6)


3445.74
2925.31
2857.57
2355.79
2079.55
1635.64
548.68
421.80
412.20
Absorbance
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

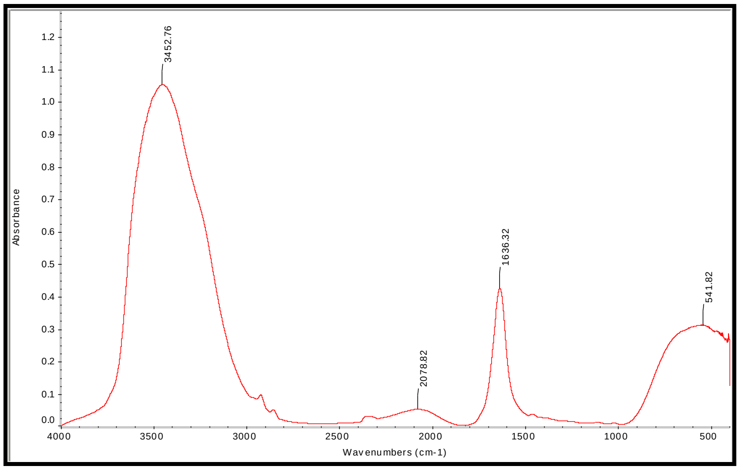
(L-7)


Absorbance
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
3435.11
2924.14
2094.61
1628.54
1350.01
582.43
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

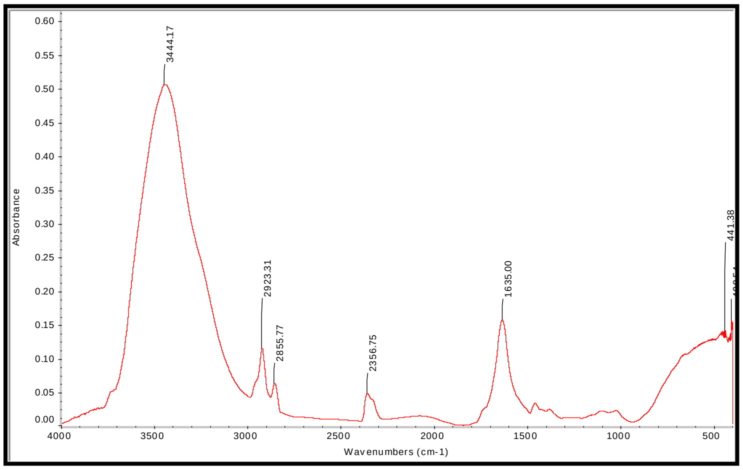
(L-8)


Absorbance
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
3584.06
3519.12
3434.18
3391.22
3317.75
3261.87
2109.81
1593.47
1351.18
648.44
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

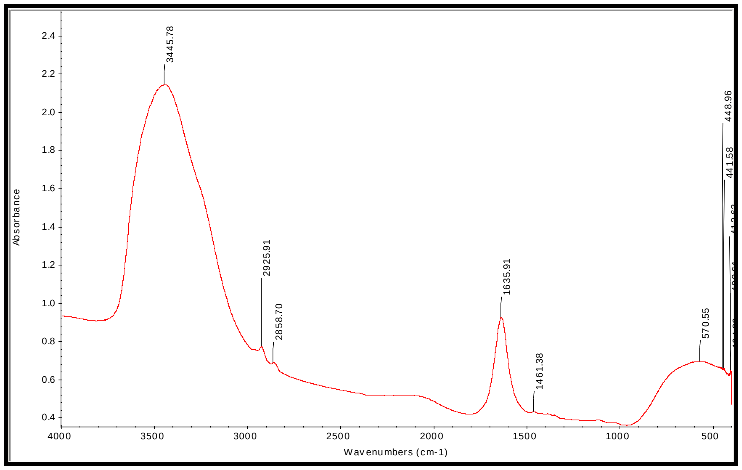
(L-9)


Absorbance
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
3452.76
2078.82
1636.32
541.82
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

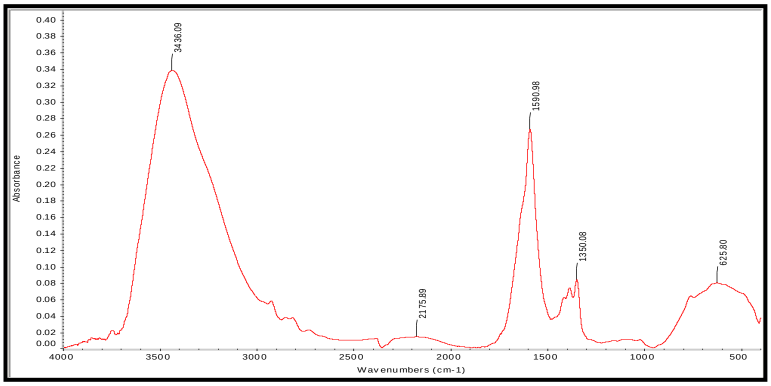
(L-10)


0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Absorbance
3444.17
2923.31
2855.77
2356.75
1635.00
441.38
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

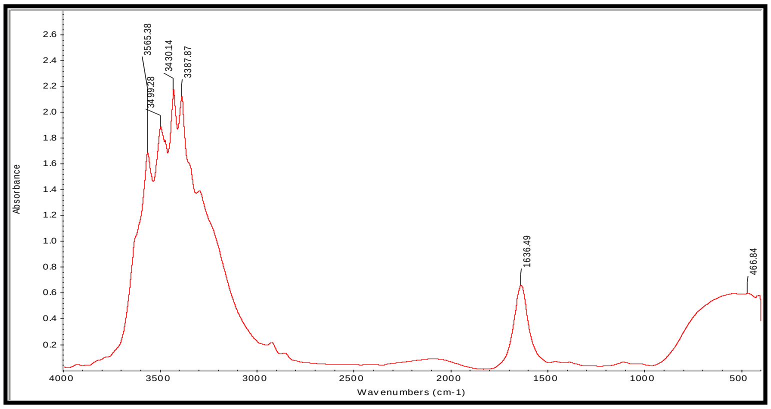
(L-11)


2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
Absorbance
3445.78
2925.91
2858.70
1635.91
1461.38
570.55
448.96
441.58
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

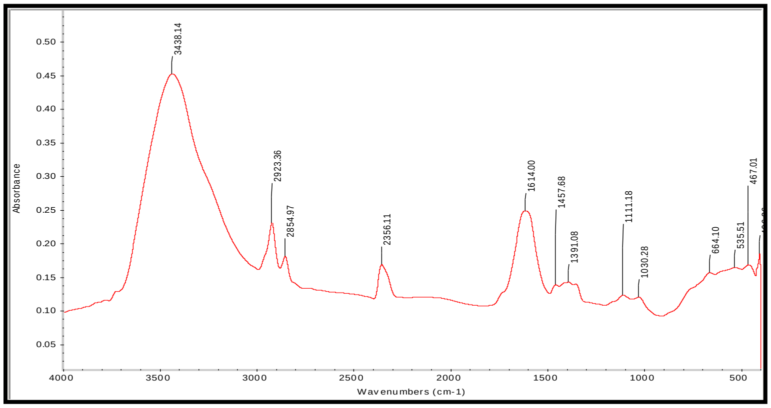
(L-13)


0.40
0.38
0.36
0.34
0.32
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Absorbance
3436.09
2175.89
1590.98
1350.08
625.80
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

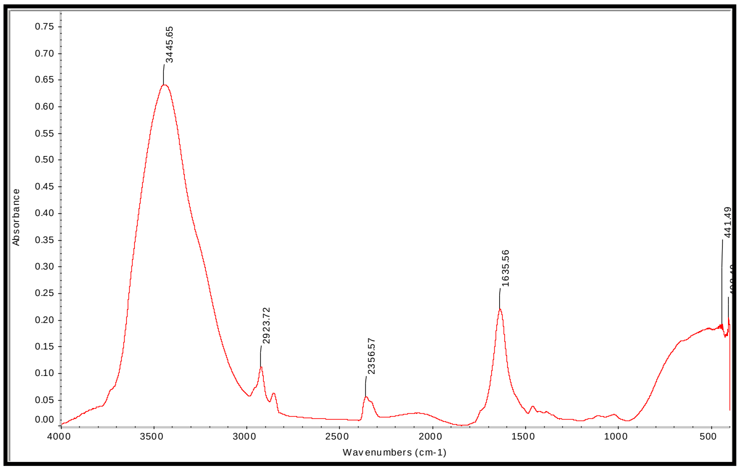
(L-14)


3565.38
3499.28
3430.14
3387.87
1636.49
466.84
Absorbance
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

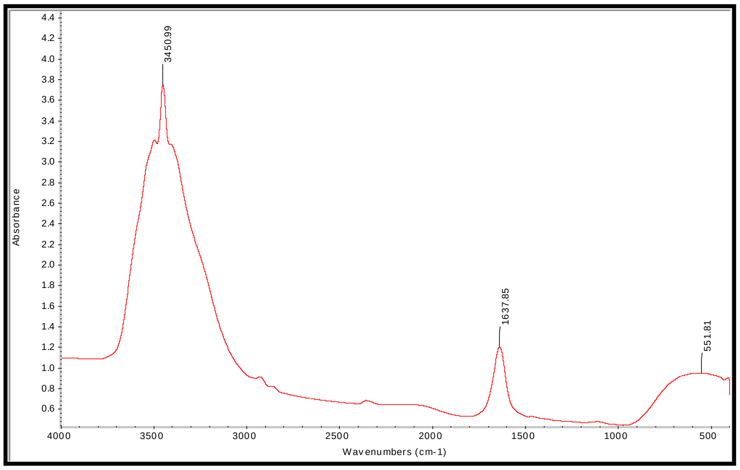
(L-15)


3438.14
2923.36
2854.97
2356.11
1614.00
1457.68
1391.08
1111.18
1030.28
664.10
535.51
467.01
Absorbance
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

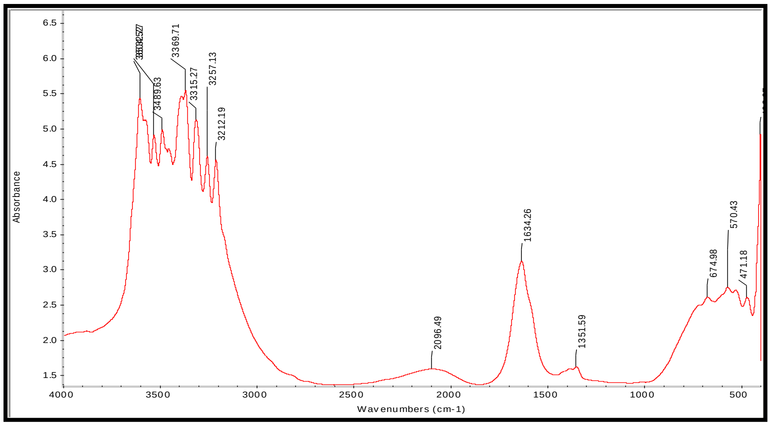
(L-17)


3445.65
2923.72
2356.57
1635.56
441.49
Absorbance
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

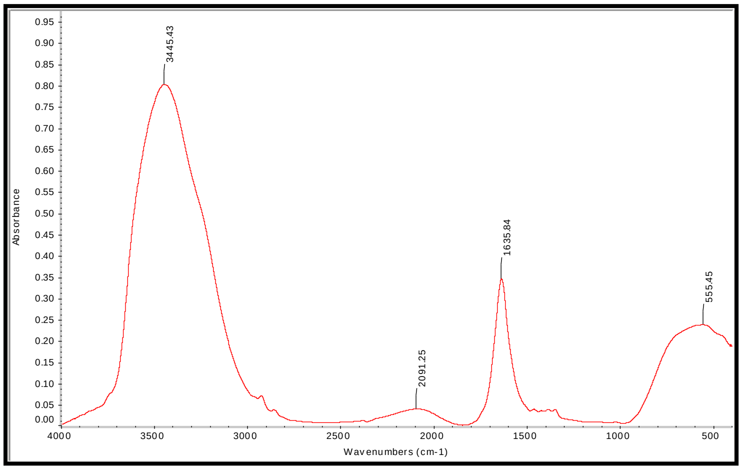
(L-18)



(L-19)



(L-20)



(L-21)

Figure 5.1

5.2 Characterization of the adsorbent

In this section the results of different tests of characterizations are discussed. These includes-

5.2.1 Proximate analysis-

Proximate analysis of adsorbent was performed for the estimation of different parameters like moisture contents, volatile matter, ash content and fixed carbon and from the analysis it was found that the moisture content was 3.63%, volatile matters present was 2.34% , parentage of ash 73.36% in the adsorbent was and fixed carbon was 20.67% present in the adsorbent sample.

5.2.2 Ultimate analysis

This analysis was performed for the estimation of major compounds present in the adsorbent sample. In this study the percentage of carbon, oxygen, hydrogen was found along with the percentage of sulfur (if present). The results on analysis of blank and loaded BFA were listed below-

Table 5.2 Percentage of major elements present in the sample (Ultimate analysis)

S.no.	Elements	Blank BFA (%)	Loaded BFA (%)
1.	C	74.66	76.68
2.	N	0.89	0.90
3.	H	0.64	0.95
4.	S	0.00	0.00
5.	Initial weight	5.0390mg	4.0970mg

5.2.3. BET surface area

BET surface of the adsorbent (BFA) was found to be 264.64 m^2/g and the other information like Monolayer Volume was found to be 60.79 cm^3/g, total pore volume was 0.14 m^2/g, after the analysis of blank adsorbent.

5.2.4. Bulk density

For the estimation of bulk density of bagasse fly ash, a measuring cylinder of bulk density meter was filled up to the 50 ml mark by BFA was taken and started tabbing for 15 min then noted down the reduction in volume in the measuring cylinder then applying the formula to find out the bulk density.

$$\text{Bulk density} = \frac{\text{Mass}}{\text{Reduced volume}} \tag{5.1}$$

It was found that the bulk density of the BFA was 0.078 g/ml and tapered density was found to be 0.085 g/ml.

5.2.5. X-Ray Diffraction Analysis

X-ray diffraction utilizes the X- ray scattering techniques to find out the information about the crystalline structure of BFA. It is basically a nondestructive technique and also useful for providing the information about the orientation of crystalline structure.

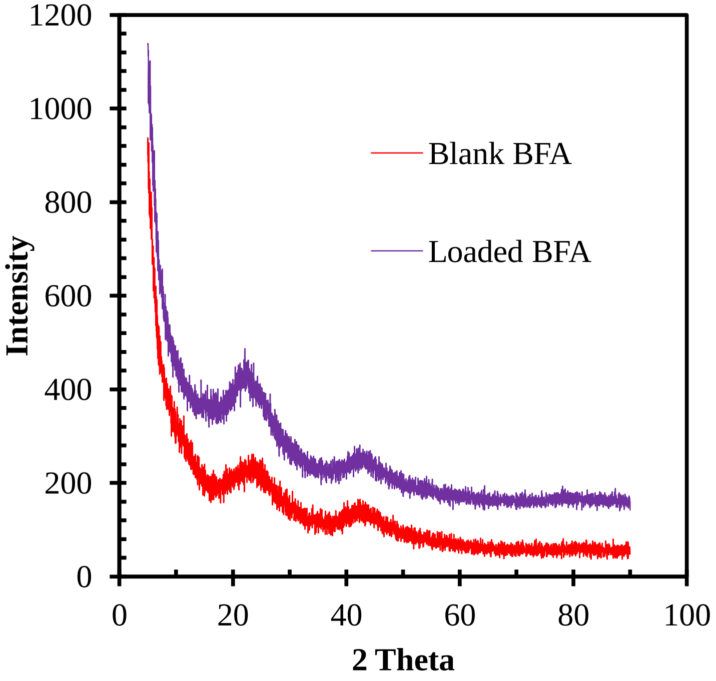


Figure 5.2 XRD analysis of the sample

Due to no sharp peak present in the 2 Theta versus intensity plot which indicates the lacking of crystalline structure present in the BFA sample.

5.2.6. Thermal analysis of adsorbent

Thermogravimetric analysis (TGA) of BFA was carried out by using thermogravimetric analyzer which is basically a method to analyze the loss in weight on increasing the temperature at constant rate and here the rate of increment in temperature was 10^{o}C/min. In the figure (5.3) (Represents the graph of blank BFA), the line at the bottom of the graph represents the decomposition of the compounds or can say the loss of mass on increasing the temperature. It is clear from the graph that 7.7% loss was occur on increasing the temperature from 27^{o}C to 86^{o}C and from temperature increment 86^{o}C to 363^{o}C loss was only 4.9% while from 363^{o}C to 427^{o}C, it was 10.2%. There was a sharp decreases in mass was observed from temperature 427^{o}C to 475^{o}C loss of 53.3% was observed and from 475 to 525^{o}C the loss in mass was only 13.2% and after this the loss in mass was found to be very less that is only 0.7% from 525^{o}C to 821^{o}C. Green line in the figure represents the DTA which stand for differential thermal analysis and the sharp peak present in this line shows that the process of decomposition was exothermic in nature and the energy of decomposition was found to be 6.24J/mg while the pink line is DTG which is also known as first derivative curve and shows the rate of weight loss. From the graph it is clear that the sudden decomposition was occur in the temperature 455^{o}C to 482^{o}C and the rate of decomposition was found to be 3.31mg/min to 1.19mg/min.

The Figure (5.4) represent the decomposition pattern of loaded BFA, this graph represent that after adsorption the increment in temperature from 22^{o}C to 98^{o}C the loss was 5.4% and from 98oc to 357^{o}C the loss in weight was 5.1% but there was a rapid change shown from 442^{o}C to 489^{o}C the graph was sharply decrease and loss was 38.6% and from 489^{o}C to 555^{o}C the loss was high that was 28.9% but from 555^{o}C to 821^{o}C the loss in weight was only 1.2%. As describe above the green line in the graph represents the DTA and from the graph it is clear that the process of decomposition was exothermic in nature and the energy of decomposition was found to be 5.06J/mg while the DTG line in the figure (5.4) was represented by pink line which shows that for loaded BFA, sudden decomposition was occur in the temperature 470^{o}C to 492^{o}C and the rate of decomposition was found to be 2.90 mg/min to 1.90mg/min.

It is clear from the graphs that the weight loss in decomposition process was found to be high in loaded BFA in comparison with blank BFA and this is happen because of the fact that the loaded BFA contains more compound after the adsorption process because of the presence of pyridine which also goes for the thermal decomposition in this thermal analysis.

5.2.7 SEM and EDX analysis

SEM stand for Scanning Electron Microscopy, in the figure (5.5) the scan electron micrograph of bagasse fly ash are shown which was used in the study of adsorption. It is clear from the figures that the adsorbent used in the study had irregular and porous surface and the pores on the surface of BFA is seem to be blocked by pyridine so that number of active sites were less than the blank BFA. With the help of EDX analysis the elements present in the sample was detected and the detail of present elements are given in the table. It is clear from the table that the percentage of carbon in blank and loaded was 81.50% and 88.59% the increment in the carbon percentage was due to the adsorption of pyridine. Oxygen was found to be the second major compound in the both samples while other compounds were present in very less amount in the samples and there percentage were also varied in blank and loaded BFA.

Table 5.3 Relative percentage of elements presents in the samples

Element	**Blank BFA**		**Loaded BFA**	
	Wt%	At%	Wt%	At%
C	81.50	86.47	88.59	91.43
O	15.46	12.31	10.60	8.21
Si	1.08	0.49	0.62	0.27
S	0.01	0.01	0.14	0.05
Mg	0.44	0.23	-	-
Al	-	-	0.06	0.03
K	1.05	0.34	-	-
Ca	0.45	0.14	-	-

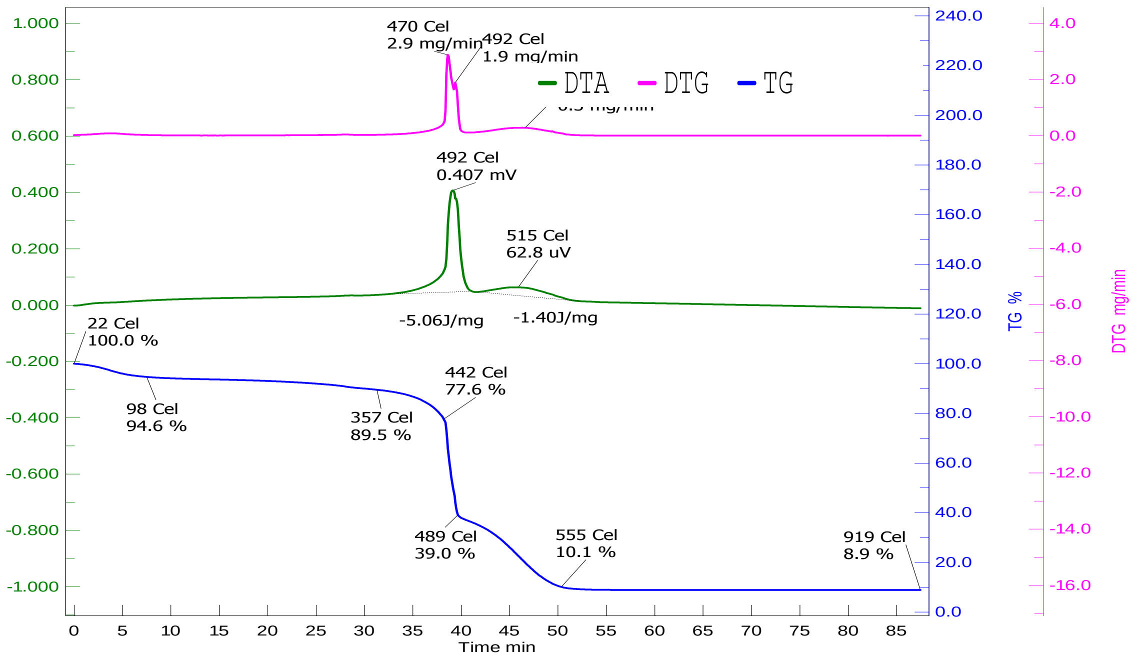


Figure 5.3 TGA/DTG/DTA of Blank BFA

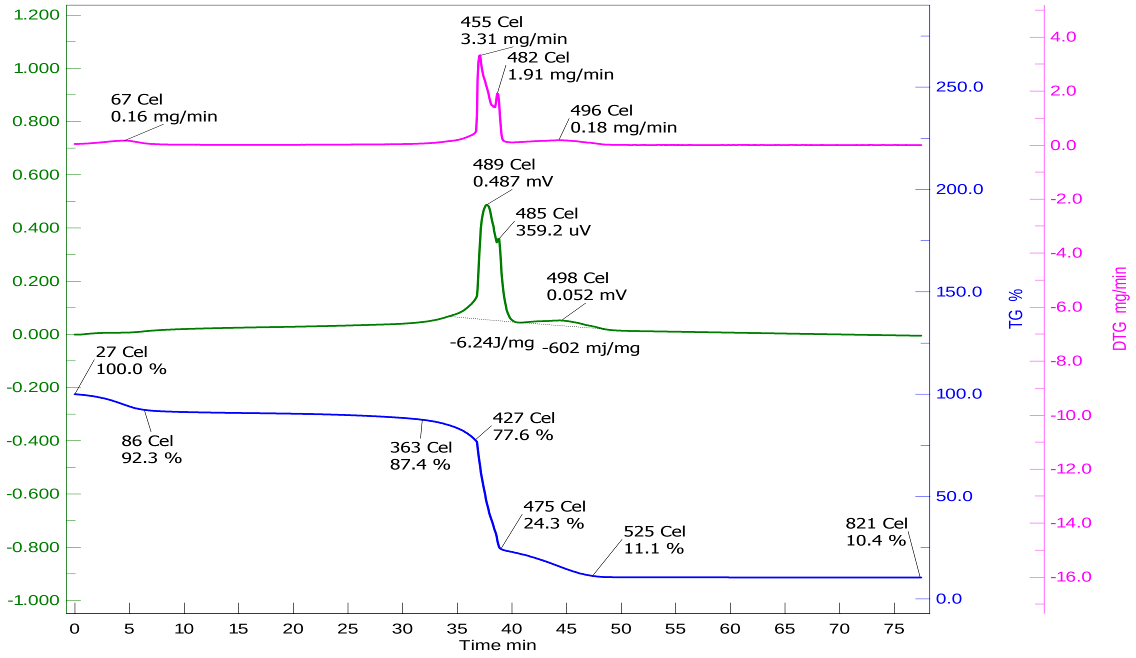
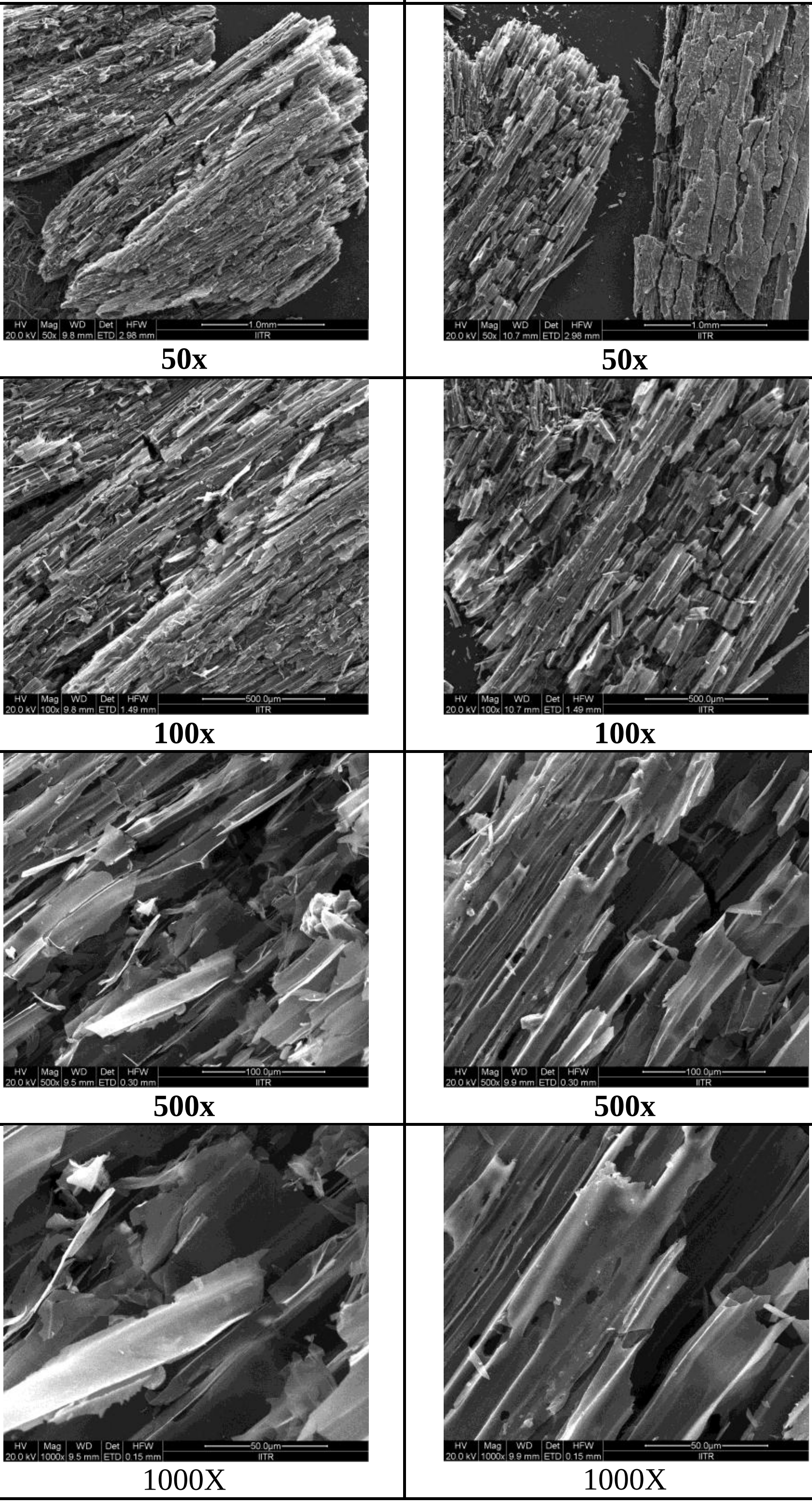


Figure 5.4 TGA/DTG/DTA loaded BFA



Blank adsorbent BFA	**loaded adsorbent BFA**
50x	**50x**
100x	**100x**
500x	**500x**
1000X	1000X

Figure 5.5 The SEM of Blank and loaded BFA

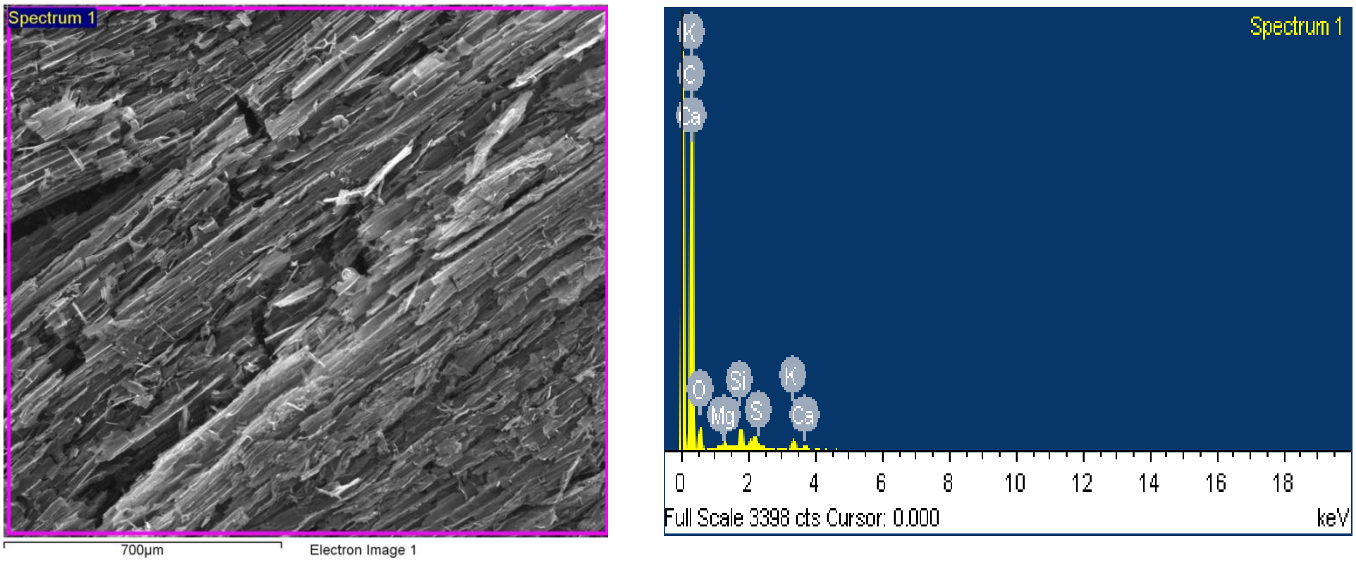


Figure 5.6 EDX of blank BFA

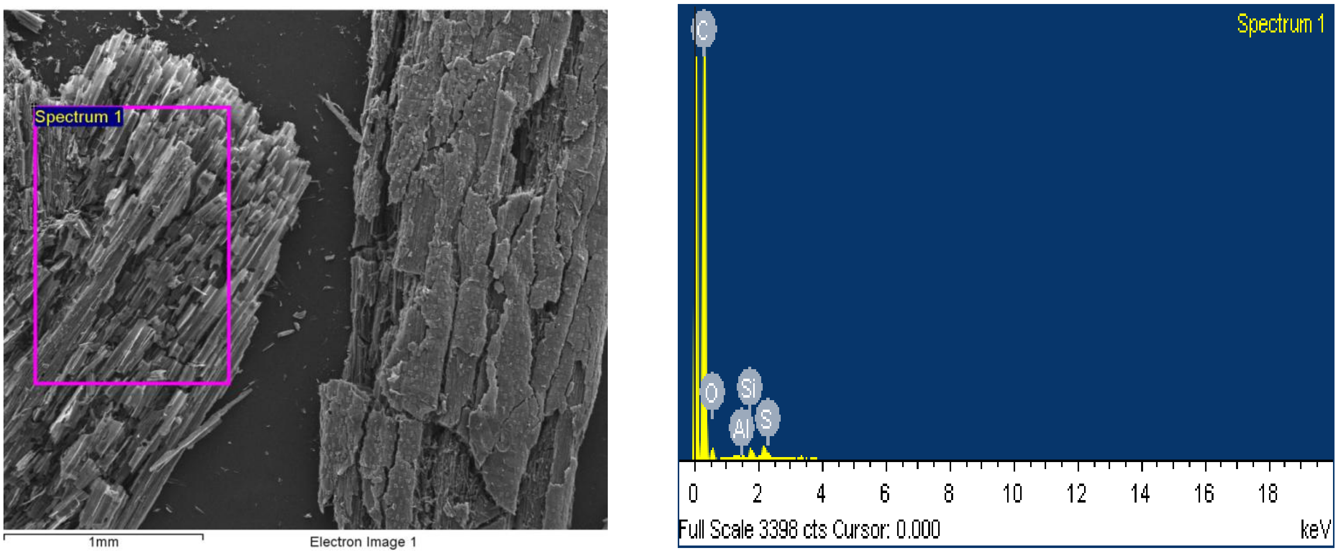


Figure 5.7 EDX of loaded BFA

5.2.8. FTIR study

In the study of FTIR spectroscopy of the adsorbent and adsorbate samples, the different functional groups were detected.

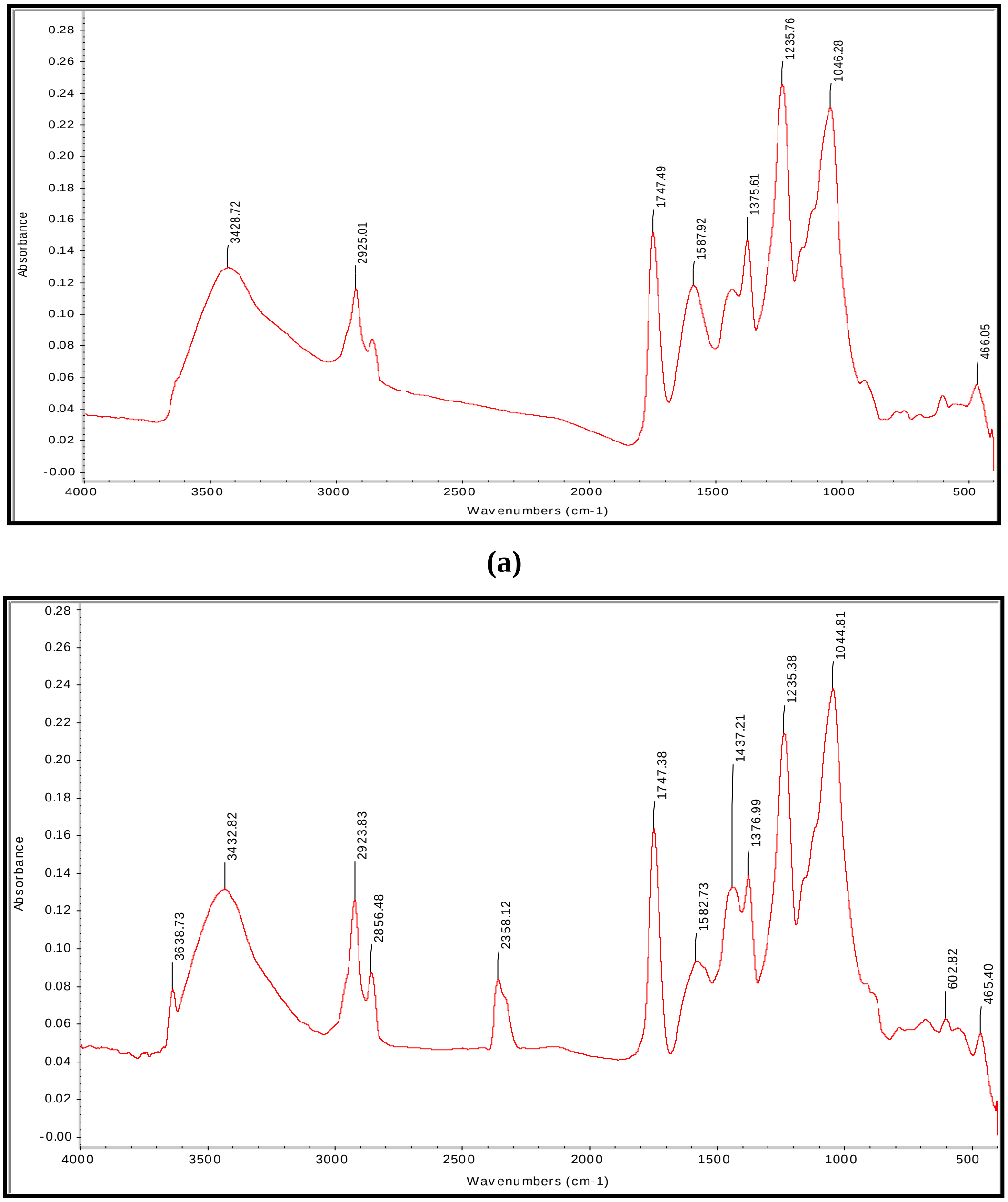
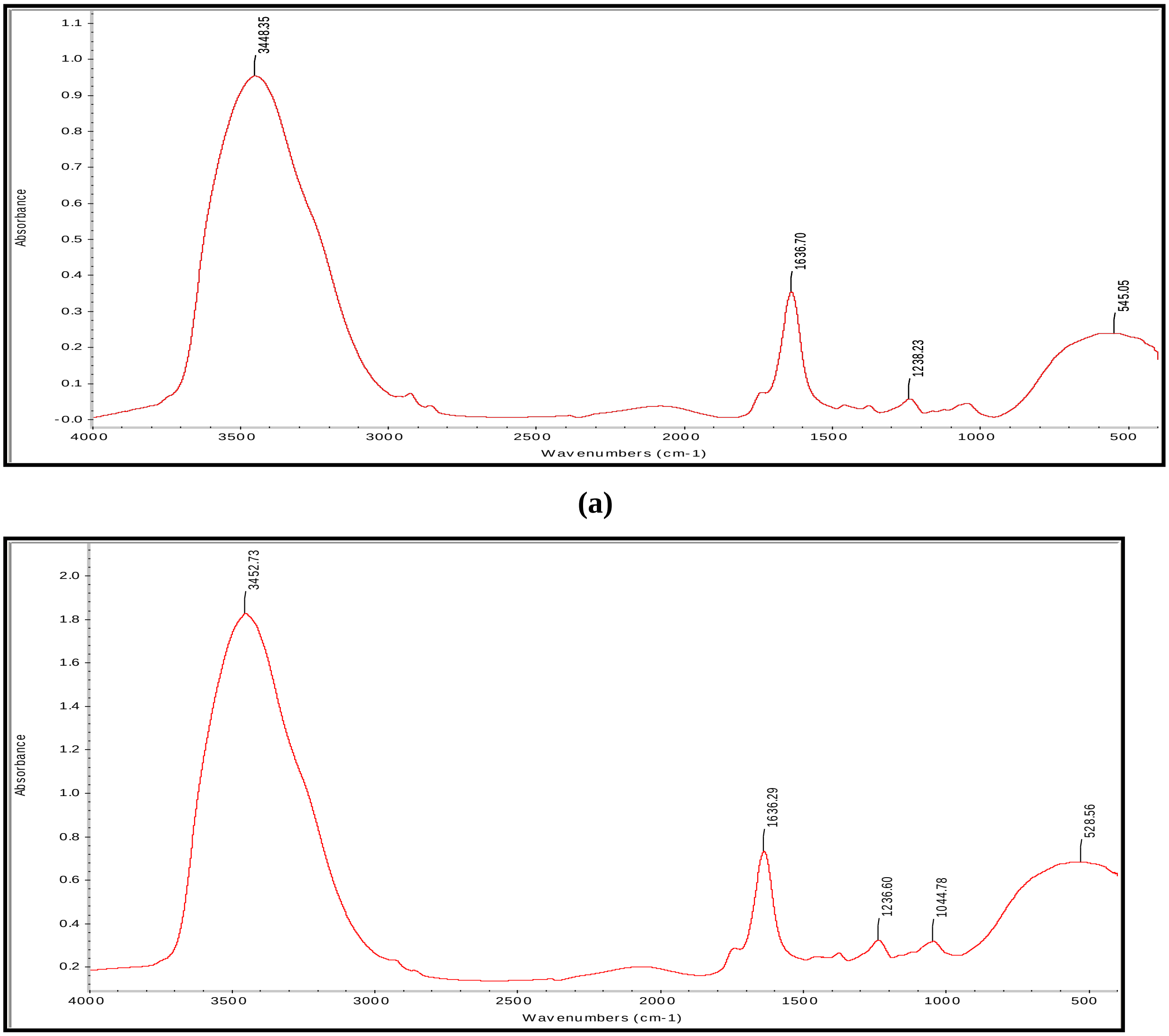


Figure 5.8 FTIR spectra of (a) before and (b) after adsorption of BFA (for the adsorptive study of pyridine removal)

The blank adsorbate sample had the peak at 3452.73 cm^{-1} which indicated the presence of O-H (range 3446-3450 cm^{-1}) another peak was shown at 2923 cm^{-1} which represent the C-H stretching (Range 2850-3000 cm^{-1}), at 1747 cm^{-1} the peak indicated the presence of C=O (cyclic kenotic compound) while peak at 1583 indicate the N-N bond bending (1550-1640 cm^{-1}) and peak at 1236 cm^{-1} indicate the possibility of C-O bond and the possibility of phenolic or acetate group while peak at 1044cm^{-1} indicate the presence of primary alcohol.[http://www2.ups.edu/faculty/hanson/Spectroscopy/IR/IRfrequencies.html/ 06/05/2013].



(a)

(b)

Figure 5.9 Shows the FTIR spectra of pyridine containing aqueous solution (a) before and (b) after adsorption.

After adsorption the number of peaks were found to be increases, a peak at 2856 cm^{-1} was generated in the graph which represent the =C-H group (2820-2850 cm^{-1}) while the vibration in the ring of pyridine was found to be in the range of (1400-1650cm^{-1}) it was also found that the pure pyridine have the peak in 1583cm-1[Rehakova et al., (2011)] which was shown in the figure (5.8) also the peak was shown at 602cm^{-1} which indicate the presence of alkyl halide stretch (range 600-800 cm-^{1}). It was clear from the figure that the peak which represented the presence of pyridine, after adsorption which was carried by BFA, was high enough to detect the compound. Same peak was observed in case of before and after samples of prepared aqueous solution of pyridine shown in the figure no (5.9)

5.3 Study of adsorptive removal of pyridine from prepared aqueous solution

5.3.1. Calibration curve

The function the calibration curve is to define the percentage of pyridine present in the samples. This is very simple method to evaluate the pyridine concentration in the sample with the help of UV Spectrophotometer, for this study firstly the valve of λ_{max} was find out for this study the value of λ_{max} was 256nm and after that at different known concentration find out the absorbance and plot the graph between absorbance versus concentration. Figure (5.10) shows the calibration curve of pyridine solution.

5.3.2. Effect of pH

The study of pH effect is very important in the adsorptive process of pyridine removal by BFA because the surface charge on the BFA is significantly changed by pH solution, and simultaneously there is also the possibility that it can change the stability of pyridine, so that to find out the concentration change of pyridine sample, samples of different pH were prepared and found the absorbance to detect the concentration of the pyridine solution. For this experiment different samples of pyridine of 100mg/l concentration were prepared at different pH to find out the effect of pH on removal efficiency.

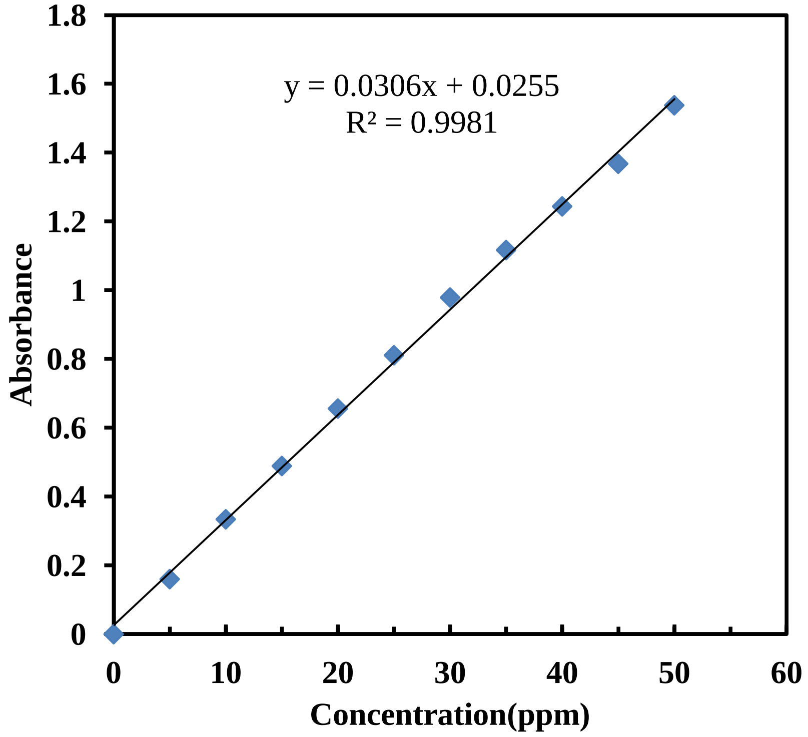


Figure 5.10 UV-spectrophotometer Calibration for pyridine, at wavelength = 256nm

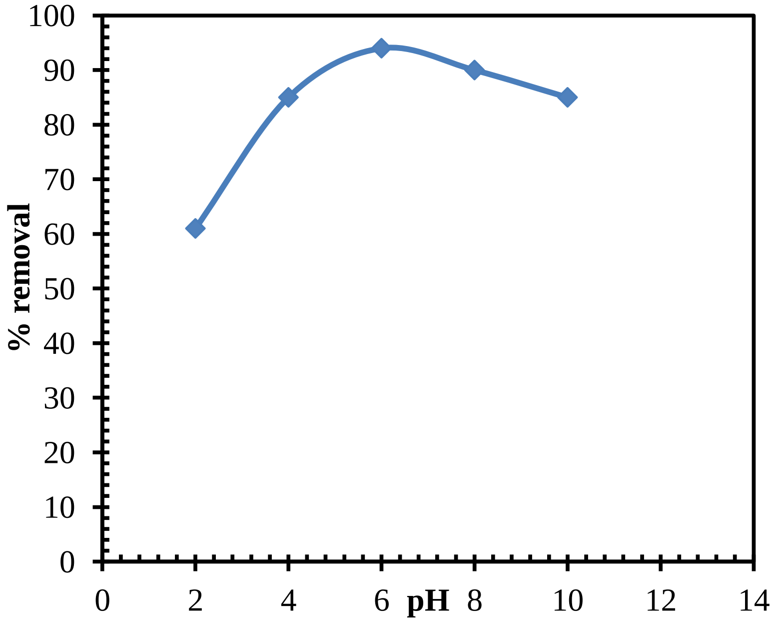


Figure 5.11 Effect of pH on % removal of pyridine in adsorptive study by BFA, doze=7g/l, time=6 hr, conc. 100mg/l

It is clear from the plot that the in the range of 5 to 7 the removal efficiency was not significantly changed it indicate that the pyridine molecules were stable over this range of pH and maximum removal was obtained in the neutral pH which followed the eq. (5.3) while at low pH the removal was very less (at pH 4 the removal was only 85%, while at 2, it was only 60%) which was due to the fact that pyridine is basic in nature and have the tendency to migrate on positively charged surface but at low pH the molecules of pyridine itself positively charged (eq.5.4) so that the tendency of migration get reduced and result of it the removal was also decreases.

Reactions which may be involved in the adsorptive removal of pyridine by BFA at acidic and neutral medium [**Lataye et al., (2006)].**

$$\mathrm{Py} + \mathrm{H}^{+} \Leftrightarrow \mathrm{PyH}^{+} \tag{5.2}$$

$$\mathrm{Py} + \mathrm{BFA} \Leftrightarrow \mathrm{Py\text{-}BFA} \tag{5.3}$$

$$\mathrm{PyH}^{+} + \mathrm{M}^{+} - \mathrm{BFA} \Leftrightarrow \mathrm{PyH}^{+} - \mathrm{BFA} + \mathrm{M}^{+} \tag{5.4}$$

$$\mathrm{H}^{+} + \mathrm{PyH}^{+} - \mathrm{BFA} \Leftrightarrow \mathrm{H}^{+} - \mathrm{BFA} + \mathrm{PyH}^{+} \tag{5.5}$$

$$\mathrm{H}^{+} + \mathrm{BFA} \Leftrightarrow \mathrm{H}^{+} - \mathrm{BFA} \tag{5.6}$$

$$\mathrm{Py} - \mathrm{H}^{+} - \mathrm{BFA} \Leftrightarrow \mathrm{PyH}^{+} - \mathrm{BFA} \tag{5.7}$$

5.3.3 Study of optimum doze

The effect of adsorbent doze was studied by using different concentration of BFA from 0.01 to 2.0 g in 100 ml batch of pyridine containing aqueous solution with the other parameter was kept same, that were temperature was 30 ± 1^{o} C, time of contact was 8 hr. in shaker the solution of pyridine of 100mg/l.

It clear from the plot (Figure 5.12) of percentage removal versus adsorbent doze that only 29% removal was achieved by 0.1g/l of adsorbent doze but on increasing the adsorption doze the removal was increasing due to presence of more active sites but a condition was achieved when on increasing the doze no significant effect was obtained on removal, with the help of results obtained it is clear that the optimum doze was found to be 7g/l.

5.3.4 Study of the effect of contact time and kinetic study

For the study of contact time 10 samples of 100mg/l concentration was prepared and feed by optimum doze which was 7g/l and kept of different time (15 min, 30 min., 1 hr, 2 hr., 3 hr., 4 hr., 5.5 hr., 7 hr., 8.5 hr., 10 hr.) period at 30 ± 1^{o} C temperature after experiment the sample was

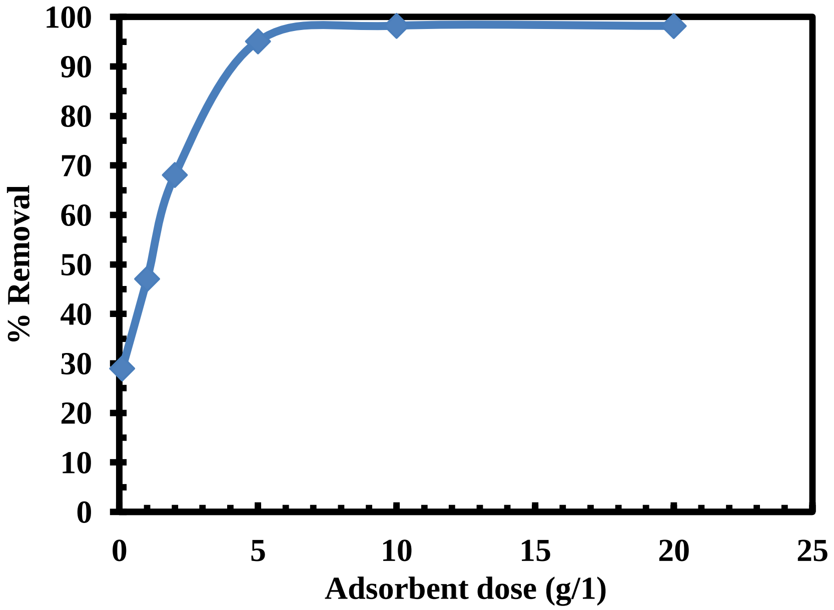


Figure 5.12 Effect of adsorbent dosage on the removal of Pyridine by BFA (Conc. 100 mg/l, T=303 K, t=8 h).

analyzed after the given time period. It is clear from the plot that initially the rate of adsorption was very high due to abundance of active sites at initial stage and shows that the pyridine intake increases with time and achieved the equilibrium at t = 1hr. for BFA after that only small increment in the removal was observed till 10 hr. so that optimum time of contact was taken as 1 hr.

At stage of initial the pyridine was rapidly adsorb on the BFA surface due to presence of active site in good amount on the adsorbent surface and it belong to the surface bond sorption while on increasing the time the active sites presents on the surface were blocked so that adsorption was occurred on the interior pores of the adsorbent so that the rate of adsorption was decreases and percentage removal was almost constant on increasing the time.

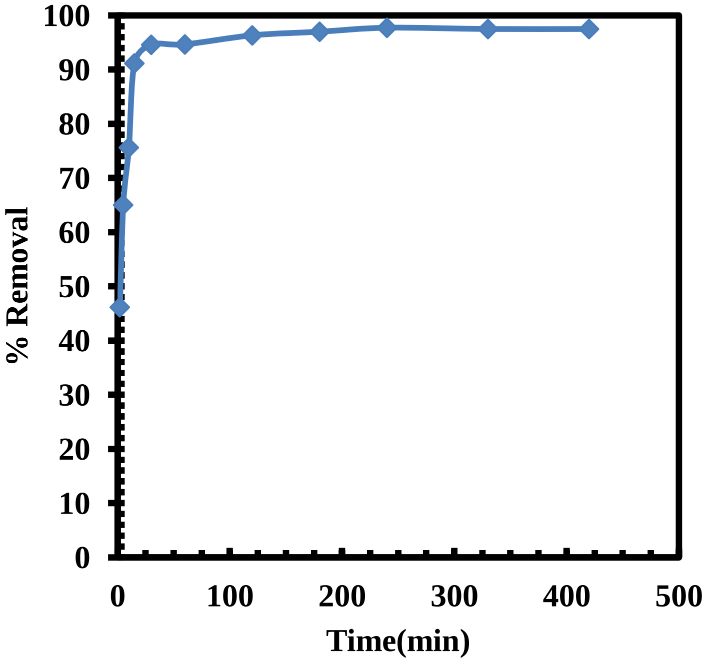


Fig 5.13 Effect of Contact time on the adsorption of Pyridine by BFA (Conc. 100 mg/l, m=7 g/l of BFA, T=303 K).

Pyridine adsorption on BFA could be represented by-

Pseudo-first-order model-

$$q_t = q_e[1 - \exp(-k_f t)] \qquad (5.2)$$

Where -

q_t is amount of Pyridine adsorbed (mg/g) at time (t) (min) and k_f is the rate constant of pseudo first-order adsorption (min^{-1}).

pseudo-second-order model

$$q_t = \frac{t k_s q_e^2}{1 + t k_s q_e} \qquad (5.3)$$

The initial adsorption rate, h (mg/g min), at t→ 0 is defined as;

$$h = k_s q_e^2 \qquad (5.4)$$

where,

ks is the rate constant of pseudo second-order adsorption (g/mg min).

Kinetics of the process was found by using the same experiment for different initial concentration as done on the study of contact time optimization and for this experiment initial concentration 100mg/l and 200mg/l were taken and other parameters like optimum doze, temperature and shaking speed were kept and experiment was run for the different time period as done for the evolution of time of contact. Figure (5.14) shows the best fit values of kinetic parameters such as k_f, h, q_e and k_s along with the correlation coefficients, SSE and RMSE values for both pseudo-first order and pseudo second order models. The R^2 values show that the pseudo-first-order model best fits adsorption kinetic data for BFA as adsorbent.

5.3.5 Adsorption Isotherm Modelling

After the study of adsorption isotherm it was found that the removal capacity of BFA was decreases with increases in temperature. The batch experiment was carried out for three different temperature i.e. 15^{o}C, 30^{o}C, and 45^{o}C and the removal was highest in lower temperature so that it is clear that the removal of pyridine with the help of BFA was an exothermic process. The nature of the process might be this because of rapture of some active sites due to increasing temperature.

Adsorption is usually described through isotherms. Isotherm is nothing but the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature.

The various R^2 values and various parameters for the Langmuir, Freundlich, R-P, etc. isotherms are shown in Table 5.5 For BFA, comparing R^2 values, it is clear comparing R^2 values, it is clear that R-P isotherm best fits the experimental data at lower as well as at higher temperature.

Table 5.4 Isotherm parameters for the removal of Pyridine by BFA (t=1 h, m=7 g/l)

Pyridine – BFA system							
Co=100mg/l							
Pseudo 1st order				**Pseudo 2ndorder**			
k_f (min^{-1})	q_e (mg/g)	SSE	R^2 (non-linear)	k_f (min^{-1})	q_e (mg/g)	SSE	R^2 (non-linear)
0.080799	19.47476	2.008029	0.9465	0.008682	20.10577	7.226624	0.8133
Co=200mg/l							
Pseudo 1st order				**Pseudo 2ndorder**			
k_f (min^{-1})	q_e (mg/g)	SSE	R^2 (non-linear)	k_f (min^{-1})	q_e (mg/g)	SSE	R^2 (non-linear)
0.031416	16.46515	2.039692	0.9828	0.009916	14.45082	265.7163	0.7387

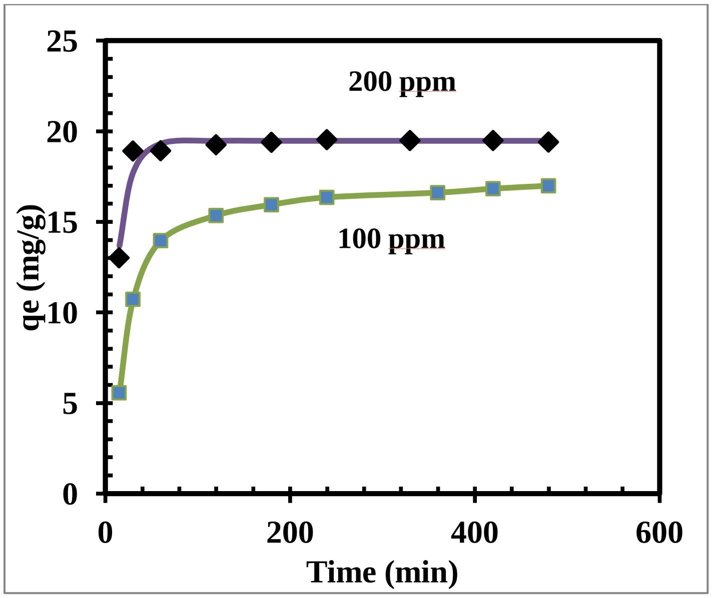


Figure 5.14 Effect of contact time on the adsorption of Pyridine by BFA Experimental data points given by the symbols and the lines predicted by pseudo-first-order model for BFA. m_{opt} =7 g/l of BFA, T=303 K

Table 5.5 Isotherm parameters for the removal of Pyridine by BFA at optimum conditions (t = 1 h, m=7 g/l for BFA)

Isotherms	**Parameters**	**Compound-BFA**		
		Temperature (K)		
		288	**303**	**318**
Langmuir $q_e = \frac{Q_o b C_e}{1 + b C_e}$	Q_o	54.21	45.22	45.24
	b (mg/g)	0.05464	0.08784	0.05235
	R^2	0.9643	0.9814	0.9688
Freundlich $q_e = K_F {C_e}^{1/n}$	K_F (L/mg)	6.031	7.687	6.255
	n	2.031	2.478	2.441
	R^2	0.9811	0.9756	0.9143
Redlich-Peterson $q_e = \frac{K_R C_e}{1 + a_R C_e^g}$	a_R (L/mg)	2.618015	0.328694	0.015916
	K_R (L/mg)	19.56873	6.349716	1.886788
	g	0.552805	0.801765	1.209456
	R^2	0.9815	0.9905	0.9741
Hill $q_e = \frac{Q_{sH} C_e^{nH}}{k_D + C_e^{nH}}$	Q_{sH}	304.8	57.87	40.28
	k_D(L/mg) D k	52.33	10.01	32.7
	n	0.5371	0.7374	1.287
	R^2	0.9813	0.9875	0.9739
Sips $q_e = \frac{K_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}}$	K_s	5.823	5.783	1.232
	a_s (mg/g)	0.01911	0.09992	0.03058
	β_S	0.5371	0.7373	1.287
	R^2	0.9813	0.9875	0.9739
Koble–Corrigan $q_e = \frac{A C_e^n}{1 + B C_e^n}$	A	5.823	5.783	1.232
	B	0.01911	0.09993	0.03058
	n	0.5371	0.7374	1.287
	R^2	0.9813	0.9875	0.9739

Isotherms	**Parameters**	**Compound-BFA**		
		Temperature (K)		
		288	**303**	**318**
Toth $q_e = \frac{K_T C_e}{(a_T + C_e)^{1/t}}$	K_T (L/mg)	9.349	8.079	0.7016
	t	5.464	5.593	64.48
	a_T	15.55	11.35	19.1
	R^2	0.962	0.9814	0.9688

In the study of thermodynamics parameters which were involve in the removal process of pyridine by BFA in adsorption process, these parameters are ΔG^o (Gibbs free energy change), ΔH^o (change in enthalpy), ΔS^o (entropy change). These thermodynamic parameters were determined at different temperatures mainly 288, 303 and 318 K respectively. For estimation of these parameters values, firstly the relation between adsorption equilibrium constant (K_{ads}) and ΔG^o was focused and these parameters are related with Van't Hoff equation that is -

$$\Delta G^O = -RT\ln K \qquad (5.5)$$

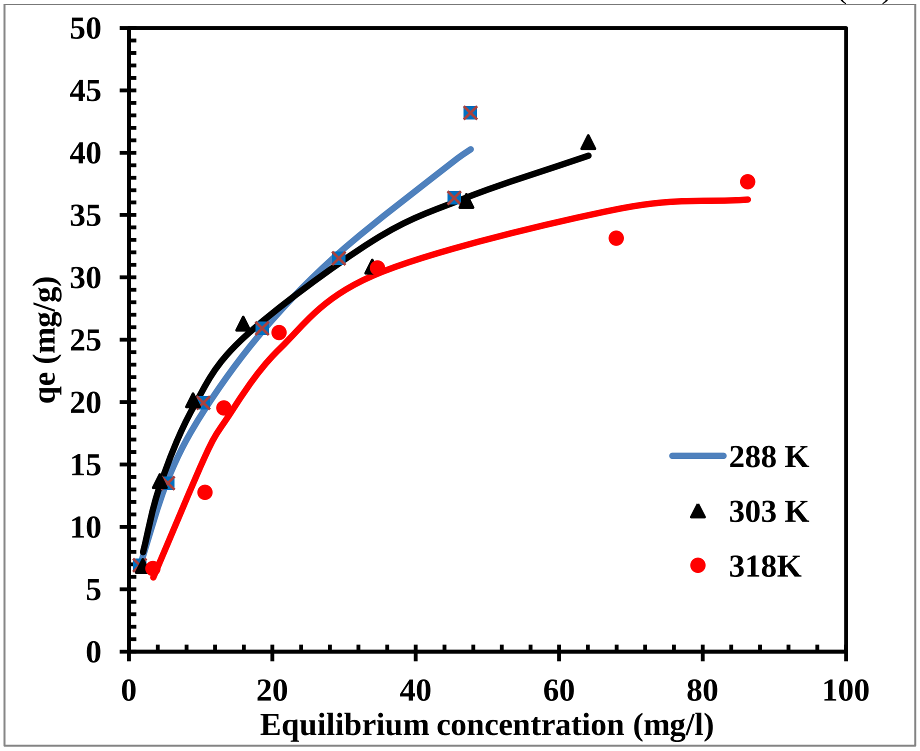


Figure 5.15 Equilibrium adsorptions isotherms at different temperatures for Pyridine loaded BFA system, t= 1h, Co= 50-350 mg/L; m=7g/L. Experimental data points given by symbols and the lines predicted by Redlich-Peterson.

5.3.5 Thermodynamic parameters

While at constant temperature the relation between ΔS^o, which is the change in entropy, ΔH^o which is the heat of adsorption, with ΔG^o is given by the equation.

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (5.6)$$

On combining the equation no. and the resultant equation was obtained as

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^o}{RT^2} \qquad (5.7)$$

Where ΔG^o in kJ/mol, ΔH^o in kJ/mol, ΔS^o in J/mol K, and T in Kelvin is which represent the absolute temperature. For the determination of ΔH^o, a plot between ln K and 1/T was drawn which is nothing but the Van't Hoff equation in linear form. The related equation are-

After integration and rearrangements of the equation no gives (van't Hoff equation);

$$\ln K = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad (5.8)$$

Table 5.6 Thermodynamic parameters for the removal of pyridine by BFA at optimum conditions (t = 1h, m = 7 g/l)

Thermodynamic Parameters	**Values**
Enthalpy (ΔH), KJ/mol	-1.62163
Entropy (ΔS), J/mol/K	0.012134
Gibbs Free Energy (ΔG), KJ/mol at different temperatures (K)	
ΔG_{288}	-5.11626
ΔG_{303}	-5.29827
ΔG_{318}	-5.48028

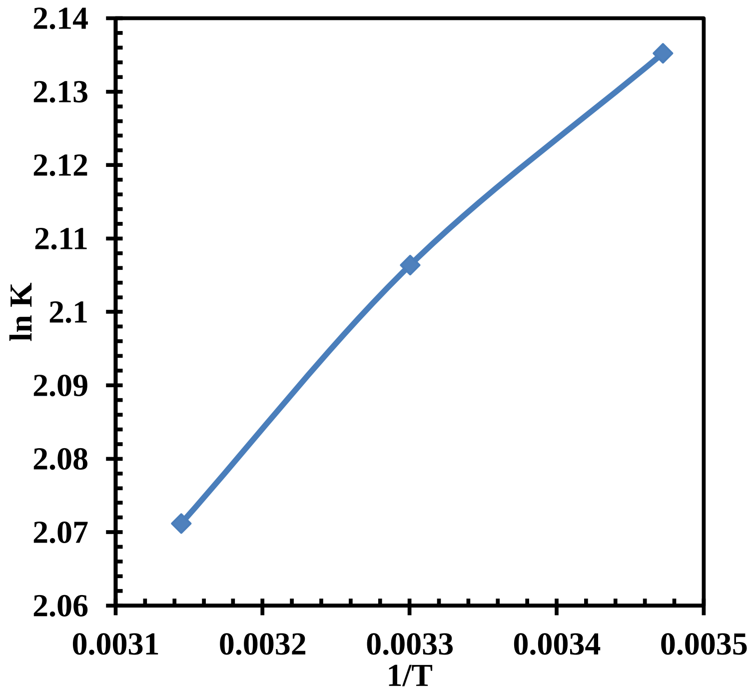


Figure 5.16. ln K vs 1/T at different temperatures for pyridine loaded BFA system (t= 1 h, Co = 100 mg/l, m =7 g/l).

Slope and intercept obtained from this equation were used for the determination of ΔH^o and ΔS^o, (which gives the idea of randomness or can say the degree of freedom). Here the value of ΔG^o was found to be negative which is the only criteria for the feasibility of reaction and this minus sign also indicate that the was spontaneous while the value of ΔH^o, which was negative, indicated the exothermic behavior of adsorption process of pyridine removal with the help of BFA.

Exothermic nature of pyridine removal process in adsorption on the BFA surface was due to the libration of heat when the adsorbate molecules came on the adsorbent surface and get stability by losing energy and making bond and this step would be dominating in the adsorptive removal process of pyridine removal by BFA, to fulfill the exothermic nature of process.

6 CONCLUSIONS

In the study of pyridine removal, from prepared aqueous solution by using BFA as an adsorbent, it was found that the BFA was overall the best adsorbent in the removal efficiency, availability and economical point of view, because our country generate huge amount of BFA and producers suffered with the disposal problems of it so that it was found to be best adsorbent for the application in large scale plant. In the batch study of the pyridine removal, it was found that removal efficiency was higher at the pH range 4.5 to 6 while the highest removal of observed at the natural pH, the doze of adsorbent 7g/l was found from the optimization result for 100 mg/l batch sample of pyridine with very low contact time (1 hr) required because most of the adsorption was taken place within 15 min. of contact and after the study of kinetics of the process it was found that the adsorption process involved in the study followed the pseudo 1st kinetics while after using different isotherm model, the data obtained from experiment was best fitted by R-P isotherm model equation. The thermal parameters were also evaluated and the value of ΔG^o was found to be negative which indicate feasibility of the process while the negative value of the enthalpy change indicates the exothermic nature of the adsorption process. The overall removal was found to be 94.67% which represent the effectiveness of the process.

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