

REMOVAL OF PYRIDINE BY ADSORPTION

A DISSERTATION

*Submitted in partial fulfilment of the
requirements for the award of the degree*

of

MASTER OF TECHNOLOGY

in

CHEMICAL ENGINEERING

(With Specialization in Industrial Pollution Abatement)

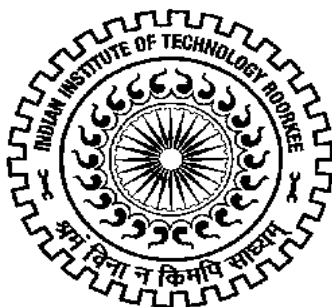
By

LAVINGIA GAURAVKUMAR SURESHKUMAR

Enrollment No. 11515007

Under esteem guidance of

Dr. SHISHIR SINHA



**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE – 247 667 (INDIA)
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DECLARATION

I hereby declare that the work being presented in the seminar report entitled “**Removal of pyridine by adsorption**” 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.

LAVINGIA GAURAVKUMAR SURESHKUMAR

Enrolment No. 11515007

Date: 14th June, 2013

CERTIFICATE

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

Dr. SHISHIR SINHA
Associate Professor
Department of Chemical Engineering
Indian Institute of Technology, Roorkee
Roorkee

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LAVINGIA
GAURAVKUMAR
SURESHKUMAR
Enrol. No. 11515007
M. Tech 2nd YEAR
IIT Roorkee

ABSTRACT

As we all know that pyridine is one of the most important aromatic compound in pharmaceutical and pesticides industry. Many important compounds which are derived from pyridine like 2-picoline, 3-picoline, 4-picoline and quinoline have very wide applications, but these compounds are also have injurious effects when exposed to the environment directly. Although the extent of harmfulness is always depends on the mode of contact to the person, but we cannot ignore the harmful effects in fertility and nervous system etc. so the removal of these compound are always necessary. In the present study the removal of pyridine was taken as an objective. There are many methods which can be directly applied for the removal of pyridine up to permissible level. Among these methods adsorption was found to be one of the best methods for removal of pyridine because of its economical operative cost and easily handling steps. For this purpose PAC was chosen due to its greater surface area, so the batch study was performed and it was also found that the removal of pyridine was higher at its natural pH, while the optimize dose of PAC for removal was found to be 6g/l and time of contact was 4hr, which give 95% removal at 30oC for 100ppm pyridine concentrated solution. From the kinetic study of the obtained data the kinetic was found of pseudo 1st order and the isotherm experiment results indicate that the obtained data was best fitted Hill isotherm model equation.

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1 INTRODUCTION

1.1 General Introduction

As we all know that air and water are the most important matters required for sustainability and healthy growth of all living beings on earth. Our natural sources are needed to be conserved and preserved for this purpose. Waste discharges in both gaseous and liquid form from domestic and industrial activities, and from various urban utilities agglomerates into the atmosphere, thus affecting the air and water quality. The rapid industrialization with the use of the various types of raw materials for the production of final product is resulting in waste discharge with various inorganic and organic components. These components have different physico-chemical, thermal and toxic characteristics. The indiscriminate, somewhat reckless and ill-treated waste discharges affect the quality of natural resources and therefore the water and air as well. Chemical, petrochemical and agro-based chemical industries are the sources of various pollutants. Several of these industries are the sources of generating toxic materials and hazardous waste. The waste emanating from such industries find their way into natural sources in various material states viz., solid, liquid, vapour or gas thereby adversely affecting the environment.

Toxic in wastewater often pass through effluent treatment plant (ETPs) which are not designed to remove them. They can also interfere with the operation of ETPs. It is therefore, necessary to properly reduce or minimize the pollution load at the source and then treat the wastewater either at the source or at the treatment facility (end of pipe, EOP treatment). Similarly many toxics are released into the atmosphere via the air source. In an industry many pollutants are present in the air stream that comes out through the chimney or stacks following various stages of industrial processes. Industrial processes like painting unit, thermal treatment units or many other units and processes where fumes or vapor or smoke is generated are the prime source of gaseous pollutants from industry. There was not much attention being paid to the serious implementation of regulatory rules regarding control of gaseous pollutants in industry till recently. Due to this tendency of ignorance even the treatment methods of gaseous pollutants did not receive much attention till now. But now due to serious efforts by different national and international regulatory agencies and also because of the serious problem of global warming, attention has now been diverted towards removal of gaseous pollutants coming out of industry. The minimization of toxicity at source can be achieved by following the rules of the pollution regulating agencies regarding the

limiting pollutant discharges to the atmosphere via gaseous and water streams. The reduction of the load at the source can be achieved by minimizing the use and/or spillage and the proper inventory control of the toxics, proper and adequate treatment prior to toxics discharge, recycling and reuse or waste by products, changes in the manufacturing Processes-both the use of raw materials and the unit operations. There are some organic compounds which when present in wastewater streams and/or air, are a cause of major emission concern as they are considered to be toxic and hazardous to various target organisms including human beings.

1.2 Different methods for removal of pyridine

1.2.1 Absorption

Absorption removes the waste contaminant with a scrubbing solution. The contaminant enters a large contactor where the gaseous pollutants get scrubbed by the scrub solution and contaminants are removed. Efficient gas-liquid mass transfer may be accomplished by using packed or bubble columns. Sometimes venturi contactor also used to achieve better removal efficiencies. Extent of removal depends on the affinity between the solute and the solvent. Various solvents are widely used as scrubbing solution common among them is water. pH should be adjusted according the user requirements to yield better efficiencies. Regeneration of scrubbing solution can be attained by removing the gaseous pollutants by treating it at higher temperatures. The desorbed pollutants can be incinerated to reduce pollution load.

1.2.2 Adsorption

In Adsorption process removal is attained by surface reaction between adsorbent and adsorbate. Numerous adsorbents are used worldwide to treat contaminated waste waters. Two types of adsorption can be found in literature namely, physical and chemical adsorption. Physical adsorption is low energy phenomena and can be reversible. Vander wall and molecular forces play a major role in the attachment of adsorbate to adsorbent. Major advantage of adsorption process is its simplicity, easy adaptability, ability to remove wide range of contaminants and less operating cost.

1.2.3 Condensation

Waste contaminants that are concentrated and have a high boiling point may be partially recovered by simultaneous cooling and compressing of the gaseous phase. This technique is only economical for concentrated vapor. Applicability of this method resides with the reuse of vapors condensed. Practically separation of vapors is very tedious and expensive as the industrial

vapors are not pure and mixture of various contaminates. In that case only incineration of condensed vapors should be carried out. Usually condensation is used along with conventional techniques in order to reduce the emissions.

1.2.4 Membrane Separation

Membrane separation system can be used to transfer VOCs from gaseous phase to liquid phase. In this process, gaseous vapors are compressed and condensed prior to membrane separation. As membrane process is a pressure driven process, higher flow rates are achieved by maintaining higher inlet gas pressures (310-1400 kPa). Some portion of the organic contaminants will be removed by condensing the vapors prior to membrane treatment. Further the contaminant laden solution is fed through membranes made of polyethylene and polypropylene which are hydrophobic and micro porous in nature. The membrane retards the flow of contaminants through it by allowing only air/water. Contaminant free stream is collected. The major problem regarding membrane separation process is sludge handling. The Contaminants produced during membrane separation causes secondary pollution if they are not properly treated. Recycling and incineration can be seen as feasible options for dealing contaminants. In this process gas permeation and reverse osmosis are the techniques used solvent recovery. Hydrocarbon mixture, Gasoline etc. can be separated effectively using aromatic poly membrane [Khan et. al.2000].

1.2.5 Incineration

Thermal and catalytic oxidations are widely used and effective treatment process for waste streams. Thermal oxidation involves the combustion of pollutants at temperatures of 700 to 1400°C. Catalytic oxidation allows process temperature between 300 to 700°C. Catalysts such as platinum, palladium, rubidium etc. Oxidation is the most widely used secondary technique, but costs are high for low concentration pollutant vapors because of the need for large amount of fuel. Regenerative or recuperative heat system is often used as an attempt to reduce these fuel operating costs. Production of nitrogen oxides and some dioxins is also possible during oxidation. In general this technology is more suitable for concentrated stream with moderate flow rates.

1.2.6 Biodegradation

Biological methods are among the commonly used techniques for removing organic compounds. Adaptability to different conditions and less cost makes this process most feasible. This process works biologically by degrading the contaminants by microbial action at near ambient conditions.

The treatment is carried out at ambient temperature and it does not generate secondary waste stream. In case of gaseous contaminants, degradation occurs when the contaminants are transferred from gaseous to liquid phase. Various energy sources are used for maintaining the microbial population in the medium. VOC acts as energy source for the microbes and gets consumed by microbes. This biological technology is also a desirable method for the cleaning up of subsurface and ground water, when they are contaminated by pyridine or its derivatives as pyridine degrading microorganisms have been found to grow in this place too [Thomas and Ward 1989]. Immobilized phase degradation experiments have yielded much more improved results than suspended phase ones [Bettman and Rehm 1985, Westmeier and Rehm 1987, Hallas et al. 1992, Ferschl et al., 1991, Rhee et al., 1996]. [Mohan et al. 2003] used *Pseudomonas* (PI2) to treat pyridine laded waste waters. The growth parameters of *Pseudomonas* (PI2) under aerobic conditions were studied to evaluate their effect on removal process. Gas chromatography was used to estimate the pyridine concentration. Various operating parameters such as dissolved oxygen, biomass growth and consumption were studied. This process successfully utilized *Pseudomonas* (PI2) to remove pyridine from aqueous solutions. Wide range of contaminants including organic (phenol chlorinated hydrocarbons, polyaromatic hydrocarbons and highly halogenated hydrocarbons) and inorganic compounds (hydrogen sulfide and ammonia) can be treated using biological methods. Major problem regarding this method are sludge generation, microbial contamination, maintaining microbial population and unknown degradation mechanism.

1.2.7 Biotrickling Filters

In biotrickling filter contaminants are adsorbed in a free liquid phase prior to biodegradation by either suspended or immobilized microorganisms. For biotrickling filters suspended microbes fixed to an inorganic packing material and suspended microbes in the water phase degrade the adsorbed contaminants as they pass through the reactor. Biotrickling filters can be operated in both co-current and counter current fashion. As the water is recirculated, nutrients, acids or bases may be added by the operator to regulate the environment for optimal pollutant removal. Biotrickling filters are governed by many of the same phenomena as biofilters. Most importantly a biotrickling filter reactor must host a thriving microbiological population while avoiding conditions that promote excessive biomass growth and clogging conditions. Rock, plastic

packing, polyurethane foam etc. were successfully used as packing materials in biotrickling filters.

1.3 Pyridine and its characteristics

1.3.1 Pyridine

Pyridine is an organic compound which is amphiphilic, volatile, toxic and colorless. It is sometimes called as azine or azabenzene and got a molecular radius of 0.3 nm. It is mainly released from chemical industries which deal with paints, resins, textile effluents, drugs, distilleries etc. [Kirk and Othmer, 1982; Yates,1984; Kumar et.al.,1995;Mall et.al.,2003;Lataye et.al., 2006]. Oil refinery wastes contain azine concentrations about 20-100 mg/l. Pyridines are also used as a catalyst in pharmaceutical industries. Secondary pollution can be caused due to pyridine by its derivatives i.e. quinoline, picoline and pyridine etc. High solubility in water and less degradability makes this as a potent pollutant. At a pyridine concentration of 0.82 mg/l in wastewater, unpleasant odor is detectable [Baker, 1963]. However, the vapor concentration may be as low as 7 µg/l. Pyridine demands neither BOD nor COD. Serious health effects of pyridine includes, dizziness, gastrointestinal upset, headache, nervousness, insomnia, nausea, liver and kidney damage, frequent urination and anorexia.[Lewis,2004]. As pyridine is highly toxic and carcinogenic its removal is prime motive of industries. Various treatment methods which are discussed in previous section are available for pyridine treatment. Most common and cost effective process among them is adsorption.

1.3.2 Sources of Pyridine

a. Natural sources:

Pyridine ring is inherently present in many natural compounds. They are found most commonly in organic compounds which are important for performing important biological tasks. Pyridine and its derivatives can be found in DNA, RNA, ATP, GTP and in certain vegetables, like artichokes, cocoa and coffee. It is used as electron carrier in DNA and RNA.

b. Anthropogenic sources:

Various industries such as pharmaceuticals, dyes, industrial solvent manufacturing, pesticides coal processing, chemical manufacturing etc use heterocyclic compounds with nitrogen source as a very important constituent as waste.

Pharmaceutical industries manufacture various products ranging from antiseptic to HIV and tuberculosis treatment drugs. Processes which are used to produce these important and valuable medicines may lead to the generation of pyridine and its derivatives [Sims et.al. 1986, Sims and Loughlin 1989, Fetzner 1998]. Coal tar, coke and tar-based chemicals are the major products that are produced in coal processing industry. Production of these products involves use of following process-coal carbonization, liquification and gasification. However, these processes contribute to significant pyridine release in to the atmosphere [Fetzer 1998, Sturener et.al. 1982, Pereira et.al.1983]. Dye manufacturing industry and chemical manufacturing industries are the other major sources of pyridine discharge. Dye is known to produce a very high amount of highly toxic and odorous waste discharge which is very injurious to human health.

1.3.3 Properties of Pyridine

Physical properties of pyridine are as follows: molecular weight: 79.10 (g/mol); solubility and vapor pressure at 20-25 °C are 300 (mg/l) and 20 mm Hg respectively. It has a diffusion coefficient (cm²/s) of 0.091 and 7.6×10^{-6} respectively in air and water. It has an aromatic structure with nitrogen atom. It is cyclic and stable with 6- π -electrons. The electropositive nature of carbon rings in pyridine is due to the nitrogen ring which is highly electronegative. It has a refractive index and dipole moment of 1.5012 and 2.37 at 20 °C. The physical and chemical properties of pyridine are given in the table.x.

Table 1.1 Properties of pyridine

Property	Corresponding value
Molecular formula	C ₅ H ₅ N
Standard enthalpy of formation in liquid and gaseous phase (kJ/mol)	100.2 and 140.4 respectively
Enthalpy of fusion at melting point (kJ/mol)	8.28
Enthalpy of vaporization at boiling point	35.09

(kJ/mol)	
Solubility	Soluble in water, alcohol
Boiling point (°C)	115.2
Melting point (°C)	-41.6
Flash point (°C)	21
Threshold limit value	5 ppm

1.3.4 Harmful Effects of Pyridine

According to pyridine is explained on above that pyridine is toxic and odorous. All human being is release to very low quantity of pyridine in the air, water and food. Most of the workers who make higher level of chemical to be exposed in air and water but this chemical is suggested that it may be damage the liver. The National Priorities List identified this chemical at least 11 of 1,416 found by NPL list. Pyridine is break down after several months or years into the other compound in the air and for water it may take for a few days to break down in other compounds so it is taking less time to remove from water. Soil particle sticks by pyridine.

Pyridine is very harmful for the human being so there is some causes occure by pyridine like people breathe when it is released into the air from smoke of cigarettes and from hot coffee. People who live near the hazardous waste sites where pyridine exists may be exposed by air contaminated breathing or drinking water contaminated. There is a very short information available about the harmful effects of pyridine. Liver damage is the main problem by pyridine. There was seen harmful effect in rats and mice that were given by pyridine. This effect was for a unknown period of time length. Irritation on skin and eye were seen during the experiment on rabbits when pyridine was placed on their skin or eyes.

1.4 Adsorption fundamentals

1.4.1 Adsorption

Adsorption is a surface phenomenon. It is used as a separation process where a species present in a fluid phase is transferred to the solid phase and gets attached to the solid surface of the bulk fluid is lesser than the fluid-solid species concentration [Tien,1994]. In an adsorption process, molecules or atoms or ions in the fluid phase get concentrated species on the surface of solid is called the adsorbate, and the porous solid material is known as an adsorbent.

The mechanism of adsorption process is very simple due to the required driving force for the process of reduction in interfacial surface tension in between the fluid and solid adsorbent due to the environment around the surface atoms so that they have unbalanced forces.

1.4.2 Adsorption Diffusion Study

Studies carried out by [Boyd et al.(1947) and Reichenberg(1953)] with regard to relation among adsorption and film diffusion have created the foundations of sorption kinetics. The rate of adsorption in kind of adsorption process is influenced heavily by the mass transfer between solute or adsorbate and adsorbent particle. Hence it becomes absolutely aqueous solution for removal of the solute for the study of the rate, i.e., gets adsorbed by the adsorbent, in industrial uses to apply the solid particles to apply the order. It is also necessary to identify the step that governs the overall removal rate in the adsorption process in order to interpret the experimental data. There are four steps for the adsorption of fluid from the bulk of fluid.

1. From the bulk of the fluid solute is transported to the external film of fluid surrounding the adsorbent particle (assumed to be very fast in agitated system)
2. Then the adsorbate diffuses from external bulk fluid layer adjacent to the adsorbent to the external surface of the adsorbent particle (film diffusion; the resistance could be neglected for properly mixed/agitated vessels)
3. Adsorbate is diffused gradually from the pore mouth of the adsorbent particle through the pores to the immediate vicinity of the internal adsorbent surface (pore, surface and molecular diffusion)
4. Finally the adsorbate of the adsorbent is adsorbed onto the interior surface of the adsorbent.

In overall sorption of the solute from the bulk fluid phase to the internal surface of an adsorbent as the above mentioned steps play a very key role. The transport resistance of the adsorbate from the bulk stage to the surrounding film of the outer part or the surface it can be small and we can neglect that stage.

1.4.3 Factors Affecting Adsorption

There are several factors which affect the adsorption of a substance on an adsorbent [Manual for laboratory practice in physical chemistry for students of pharmacy, 2007]. The most important of them are:

- Contact time or residence time: The longer the contact time, the more complete the adsorption would be.

- Surface area of the adsorbent: Large surface area implies a greater adsorption capacity
- Degree of adsorbate molecule of ionization: ionized molecules are less extent as compared to the neutral molecules.
- Particle size of the adsorbent: Similar sizes of the atom reduce the first diffutional and limits the mass transfer i.e. the adsorbate penetration of the inside of adsorbent (equilibrium is achived more easily during the full adsorption capacity can be utilized).
- pH: Degree of ionization of any species is affected by the pH solution. This, in turn, affects adsorption.

These are the important factors which significantly affect the adsorption process for pyridine removal from aqueous solution.

2 LITERATURE REVIEW

2.1 Biological removal of pyridine

Pyridine and its derivatives can be removed or degraded by using biological methods of treatment. The critical review on the biological treatment of pyridine and its derivatives has been discussed in this section.

In the study carried out by **Mathur et al. (2008 a)**, two bacterial strains, *Shewanella putrefaciens* and *Bacillus sphaericus*, were able to utilize pyridine and they two were not affected from biofilters. They both were checked through biochemical based check. In in liquid medium, *Shewanella putrefaciens* degraded pyridine to 500 mg L⁻¹ within 140 hour, whereas the *Bacillus sphaericus* degrades 500 mg L⁻¹ pyridine only practically 75% of it in more than 150 hours. So they concluded *Shewanella putrefaciens* used pyridine is much better carbon and energy source than *Bavillus sphaericus*.

In the study by **Mathur and Majumdar (2008 b)**, *Shewanella putrrfaciens*, as a new strain was used for the biofiltration of pyridine, this pyridine was overloaded with air stream in corncob. This corncob mostly filled with biotrickling and pass through a filter. In the biotrickling pass, which pass through a filter. *Shewanella putreciens* exhibited highest deduction 100% at less than the inlet absorption 0.03 g m⁻³ and this was more than 93% at average inlet absorption of 1.748 g m⁻³. In second one the clear bed residence time is 160sec. The alimination capacity of biotrickling filter was maximum when 102.34 g m⁻³ h⁻¹ biotrickling filter have the pyridine load of 119.62 g m⁻³ h⁻¹ with clear bed residence time 5 sec in phase VII. The elimination capacity from 100% exchange line was different and from phase I to VIII it varied from 0.257 to 10.166%. After kinetic study it had been that maximum removal rate is 0.24 g m⁻³ h⁻¹ and saturation constant was 6.44 g m⁻³ with correlation coefficient $R^2 = 0.9939$ and standard source error was 23.94% of pyridine.

In the study by **Mudliar et al. (2008)**, they reported subtraction of pyridine in a rotary rope bioreactor with removal efficiency of 85%. The society used for this purpose was *Pseudomonas pseudoalcaligenes*-KPN inaccessible from garden soil.

2.2 Physico-Chemical Removal of Pyridine

Pyridine and its derivatives can also be removed by using physico-chemical methods of treatment. The critical review on the physico-chemical management of pyridine along with its derivatives has been discussed in this section.

Layate et al. (2006) studied the adsorption of pyridine on low cost adsorbent which is available easily and abundantly. The authors studied the adsorption of pyridine from aqueous solution. For the study they used BFA in batch adsorption system. The effect of BFA was noted from the influence of various parameter like pH, dose of adsorbent, time of contact and the initial concentration i.e. 50-600 mg dm⁻³. When they used the BFA dosage of 25 kg m⁻³ at normal temperature they saw the 99% removal of pyridine which had a lower concentration less than 50 mg L⁻¹ and 95% removal when the concentration about 600 mg L⁻¹. They also studied the adsorption kinetics and equilibrium. Using different adsorption equilibrium such as Langmuir, Freundlich, Redlich-peterson and Terkin isotherm equation, they resulted Langmuir equation give the best equilibrium sorption data. They also conducted adsorption of pyridine was endothermic in nature. They also studied the desorption of pyridine using ethyl alcohol and 0.1 N H₂SO₄ respectively.

Layate et al. (2007) reported the use of BFA and RHA as adsorbent for the removal of pyridine and its derivative α -picoline. This BFA and RHA is the agriculture waste and it is used of a fuel in the boiler/furnaces. The burnt carbon BFA and RHA was used to remove the pyridine and its derivatives. These agri-wastes have excellent meroporous structure and very high affinity towards a large number of solutes in aqueous solution and wastewaters. They used the burnt ash which was activated carbon as an adsorbent and this adsorbent remove pyridine and picoline. The adsorptivity order was maximum for BFA and minimum for RHA in the application of pyridine and its derivative.

Mohan et al. (2005) studied the use of activated carbon which was developed from coconut shell to adsorb. Pyridine derivatives 2-picoline, 3-picoline and 4-picoline from the aqueous solution. The developed carbon were called as SAC. They used of adsorbent at different temperature, pH and solid/liquid ratio. They also utilized carbon at different pH range. They applied Langmuir and Freundlich isotherm and they saw Langmuir isotherm. This Langmuir isotherm follow the pseudo second order rate kinetics. They also concluded that ATSAC overall capacity was much higher than SAC.

Mohan et al. (2004) developed different carbons such as FAC, ATSAC, FAC activated carbon derived from acid treated coconut fiber and two types of ATSAC was prepared from the activated carbon derived from acid treated coconut shell and coconut fibers and this activated carbon is used in the adsorption study. These activated carbon was used for the lower range of pyridine concentration (1-100 mg L⁻¹). They studied in adsorption of Freundlich and Langmuir adsorption and found that Langmuir isotherm give the better result. They found the effective diffusion coefficient D_i , increasing with temperature in the range of $45.27 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ for all the adsorbents. The activation range for FAC, SAC,ATSAC and ATFAC was found to be 3.66, 5.34, 18.73 and 26.18 kJmol⁻¹ respectively. They concluded that temperature range 10 and 25°C, these was adsorption occur and at 40°C occurrence of film diffusion mechanism held. They also concluded at conc. 25 and 50 mg L⁻¹ the particle diffusion was the adsorption control while at $\leq 50 \text{ mg l}^{-1}$ it was film diffusion controlled.

Diez and Amalvy (2003) studied the interaction of pyridine and its different derivatives with the silica surface, the derivatives studied was 2-vinylpyridine and 4-vinylpyridine. Both the derivative less strongly interacts with silica cluster than pyridine. The 2-vinylpyridine exhibits larger interaction energy than 4-vinylpyridine. The interaction with silica devices is due to hydrogen bond between the nitrogen atom and the silica cluster which has hydroxyl group and also a very weak hydrogen bond is former.

Tadjeddine et al. (1999) have investigated the geometry of the adsorption of pyridine on gold crystal electrode. This electrode developed by in situ DFG in different aromatic ring in spectral range. They are used also of free electron laser. On the adsorption of the pyridine on nitrogen lone pair, the molecules flame got filtered, the potential depend of the vibrational modes which showed the evidences of a reorientation of the molecules of the molecules around the potential of zero charge.

Niu et al. (2002) developed a technique with high-area carbon cloth electrodes, these electrodes have quasi-3-dimensional surface and these electrodes coupled with UV-spectrophotometric technique. They also seemed kinetic for quantitatively monitoring the adsorption desorption processes. They also studied the convention of pyridine to PyH^+ , which decreases the removal efficiency. The reaction takes place in non buffered electrode range. Solution due to the change in the pH out it eliminated in HOA+NaOA buffer (pH 6.8) solution. The anodic polarization is helpful to rapid and complete removal of pyridine.

Bludau et al. (1998) studied the sorption and adsorption of pyridine. They studied this, into and out of ZSM-5, silicate and mordenite. They measured the sorption and desorption through the IR-bands intensity changes. At high temperature 525-575 K, the diffusion coefficient $D = 1 \times 10^{-12}$ and $D = 6 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ for H-MOR at 525 K and H-ZSM-5 at 575 K respectively. The rate determining step was the slow transport of pyridine in the micropores. The values were found for the kinetics of popularity both the Brominated centers. Isothermic heat of adsorption of pyridine in Li-ZSM-5 and Na-ZSM-5 were much much higher than for benzene.

Stern et al. (1997) reported batch ozonation and biological treatment method for the removal of 3-Methylpyridine (MP) and 5-ethyl-2methylpyridine (EMP). They found that 90% methyl pyridine was removed. 5 moles of ozone were needed per mole of MP removed. EMP was initially oxidized much faster but the reduction of DOC only 5% when EMP was removed by 90%. 4 moles of ozone were required to remove one mole of EMP.

Kumar et al. (1995) reported the adsorption of toxic and odorous pyridine on activated carbon in batch and column system. The batch study was performed in the initial concentration range of 50-250 mg dm^{-3} of pyridine. At an initial concentration of 200 mg l^{-1} , data represented by both the Freundlich and Langmuir model.

Akita and Takeuchi (1993) reported that the sorption of pyridine can be best represented by Langmuir isotherm on strong acid ion-exchange resin and Freundlich isotherm adsorption can be used for sorption of pyridine on both weak acid ion-exchange resin (200C) < weak acid ion-exchange resin (IRC-50) < porous resin (XAD -4). The monolayer adsorption capacity reported in the study is 4.47 mg g^{-1} for pyridine.

Martin et al. (1992) studied the adsorption of pyridine, formic acid, and acetic acid. They studied these samples adsorption on different samples like MgO, MgO₃ and MoO₃/MgO samples. These MgO, MgO₃ and MoO₃/MgO samples calcined at a specific temperature 773 K or 1600 K by FTIR spectroscopy. They also found that pyridine got sorbed on the lewis sites on the surface of magnesia developed by molybdena. They had shown the physisorption at the bands at 1442 and 1598 cm^{-1} .

Zaki et al. (1989) studied the adsorption of pyridine onto ceria surface and found that the IR spectrum has a unique band at 1534 cm^{-1} . The characteristic bands of pyridine bonded to lewis state at this band. The frequency range of band 1439-1550 cm^{-1} , at band occur at $\geq 1631 \text{ cm}^{-1}$ indicates the banded pyridine formation to frosted site. The pyridine adsorption capacity was

largely modified due to doping of ceria with Na^+ , Al^{3+} and Cr^{+3} ions. They revealed different disparate impacts on the acid/base properties of the different surface. They also concluded that lewis acid and sites of at least two different acidity through with two graphs of on. At high-temperature calcinations of ceria. Weakens the surface acidity and it improves the chemical reactivity of basic sites.

Zhu et al. (1998) used Rundle spent shale for the adsorption of pyridine from dilute aqueous solution. They reported that Rundle-Lurgi spent shale adsorbs a consider amount of pyridine at a specific pH 8. They also developed adsorption of pyridine from aqueous solutions, they used solution onto the L-4 Langmuir type of two plateau.

Lub and Baker (1997) also studied the desorption of pyridine from loaded clay in aqueous solution which was the function of pH, time, number of stages of desorption with transfer to fixed volumes of the solution. They also kaolonite desorption. For kaolonit no pyridine desorption occurred at pH 9 after the initial pyridine release in 17 min. They also studied monomorillonite this monomorillonite of time. At pH 1 both clays gave significant pyridine desorption. Pyridine desorption was much slower than sorption at different pH and clay pyridine ratio. The content of desorption was directly related to numbers of stages and volumes of different solution.

3 OBJECTIVES

The present adsorption study was the removal of pyridine from synthetic wastewater using powdered activated carbon as adsorbent.

The characterization of adsorbent was done like Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), BET surface area, thermogravimetry analysis (TGA), Fe-SEM and EDX.

The adsorption study included optimization of various parameters like pH, dose, time and isotherm.

The kinetic study was done to determine the pseudo 1st or 2nd order kinetics. The isotherm study also done to optimize various isotherms.

4. MATERIALS AND METHODS**4.1. Adsorbent selection**

Selection of adsorbent was the most important step for the removal of pyridine from its aqueous solution by adsorption process, Surface area and pore size parameter were the most important parameters for selection of adsorbent in adsorption process for removal of possible impurities, the diameter of pores in activated carbon was in the range of 10 to 10000 Å. If the pore size diameter was found to be greater than 1000 Å and the surface area in case of activated carbon was found to be in the range of 500 to 1500 m²/g with the help of literature. Due to the various application in the adsorption field the commercially grade activated carbon, It is manufactured up to the range of millimeter particle size. It was also found from the literature that the pore size was more important factor in comparison to surface area [Bystrzejewski et al., (2010)]. So that the adsorption capacities of activated carbon of different surface area were not much different. From the literature it was found that PAC had the much larger surface area than the other adsorbents like RHA, BFA, GAC etc. and it can be directly dissolved in the contaminated solution for the removal but the main problem attach with the PAC that after adsorption it should be removed from the residual solution by either filtration or centrifugation process before the disposal step. So that PAC was taken for the adsorptive of removal of pyridine in batch study. For this purpose the PAC was purchased from local Roorkee market.

4.2 Characterization of adsorbent

Characterization of adsorbent was one of the most important step for present study of pyridine removal. The characterization of adsorbent involve different techniques for the determination of adsorbent characteristic like morphological analysis with scanning electron microscope (FE SEM), Fourier transform infrared spectroscopy (FTIR) analysis for determination of chemical compound present in the adsorbent, ultimate analysis, proximate analysis, TGA-DTA-DTG analysis to examined of adsorbent at thermal decomposition process of constant rate, BET surface area to find out the pore size and surface area of blank and loaded adsorbent.

4.2.1 Proximate Analysis

First of all, the small of adsorbent was grounded finely and then kept into the silica crucible for the determination of moisture content, for this sample was firstly weighed and then kept in the oven for 1h, and at 105°C., when the one hour passed away then weight the sample again to find out the moisture content which was nothing but the difference of initial weight and final weight. After this study the sample was heated upto 750°C in a muffle furnace for 2h and weights the residue sample to find out the ash content present in the adsorbent. In for volatile content sample was put at 925°C for 7 min.

4.2.2 Ultimate analysis

Ultimate analysis was carried out of both loaded and blank adsorbent samples, this analysis was performed for the determination of major chemical compound present in the adsorbent samples, these major adsorbent included C, H, S, N with their percentage in both samples.

4.2.3 Brunauer-Emmett-Teller (BET) surface area

BET- surface area by using micromeritics ASAP 2020 was performed for the determination of BET surface area, pore volume of blank and loaded PAC. Basically it provide the textural characteristics of adsorbent samples, in this method nitrogen was used for the adsorption purpose at 77.15 K to determine the specific surface area and Barrett, Joyner and Halenda (BJH) adsorption/desorption surface area of pores, single point total pore volume and the cumulative BJH adsorption/desorption pore volume of pores ($17 \text{ \AA} < d < 3000 \text{ \AA}$) was observed.

4.2.4 Scanning Electron Microscopic analysis

SEM was used to examine the morphology of the adsorbent samples, the scanning electron microscope (SEM) micrographs were taken using LEO, model 435 VP, England. In the process of morphology test, the samples were firstly coated with the gold to raise the conductivity of the adsorbent sample for proper results, for this purpose Sputter Coater, Edwards S150, was used for the coating purpose, then the SEMs were taken at various magnification.

4.2.5 EDAX

The qualitative elemental composition of the PAC before and after treatment with pyridine was determined using an Energy Dispersive X-ray (EDAX) analyzer/spectrometer (Model ECON-149-10, country) and with the help of this study the various compounds present in the adsorbate samples were evaluated.

4.2.6 Fourier transform Infra red (FTIR) spectral analysis

FTIR spectrometer is a technique for the determination of functional group present in the adsorbent samples. For this study Thermo Nicolet, Model Avatr 370 was used. Pellet (pressed-disk) technique has been used for this purpose. The sample was mixed with KBr (IR spectroscopy, grade) thoroughly and pellet was made by using a special mold provided to make pellet under the pressure of 15 ton. The spectral range was from 4000 to 400 cm^{-1} .



Figure 4.1 TGA Analyzer



Figure 4.2 FTIR Analysis



Figure 4.3 Oven

4.3 Batch Study

Batch study was undertaken for the optimization of process parameters like pH value, contact time and adsorbent dosage for the adsorbent and to extract design parameters like rate constants and isotherm constants. Considering the requirement of the sample for the analysis of the pyridine, 100 ml of the sample volume was taken for each experiment (in distilled water) were taken in 250 ml Stoppard conical flask. Experiments were conducted with adsorbent namely activated carbon. The solution of pyridine was agitation speed of 150 rpm at a fixed temperature i.e. 30°C, when the experiment was completed, each solution was filtered and centrifuged for the removal of spent adsorbent. Percentage removal of pyridine can be estimate from the following formula:

$$\text{Percentage Removal} = 100 \frac{(C_o - C_e)}{C_o}$$

$$\text{Amount of adsorbed pyridine/gm of solid, } q_e = \frac{(C_o - C_e)V}{w}$$

4.3.1 Set-up for pyridine removal in batch system

All the experiments on pyridine removal were conducted in batch system. For adsorptive removal of pyridine, the batch system consists of 100 ml flask in which adsorption was carried out. The agitation was performed in an incubator cum shaker. At a time maximum 10 batch system could be agitated.

4.3.2 Adsorption as a physical process

4.3.2.1 Adsorption

Adsorption is a surface phenomenon. It is used as a separation process where a species present in a fluid phase is transferred to the solid phase and gets attached to the adsorbent if the species concentration is higher than bulk fluid concentration [Tien, 1994]. In an adsorption process, molecules or atoms or ions in the fluid phase get concentrated species on the surface of solid is called the adsorbate, and the porous solid material is known as an adsorbent.

4.3.2.2 Preparation of synthetic pyridine solution

Synthetic pyridine solution was prepared by mixing 1ml pyridine in 1 liter of distilled water that is 1000ppm solution of pyridine. Then the solution which was prepared was converted to 100ppm solution of pyridine with the distilled water dilution.

4.3.2.3 Calibration of UV spectrophotometer (UV)

Calibration of instruments is very essential to get reliable data in the experiments. Calibration of UV was done as per the instruction manual provided by the manufacturer using standard solutions of respective pyridine. The main concept behind the calibration curve is to relate the concentration with absorbance of the pyridine solution and for this firstly the value of λ_{\max} was find out which was 256 nm and then find out the absorbance of different known concentrations and draw the calibration curve which was shown in figure().

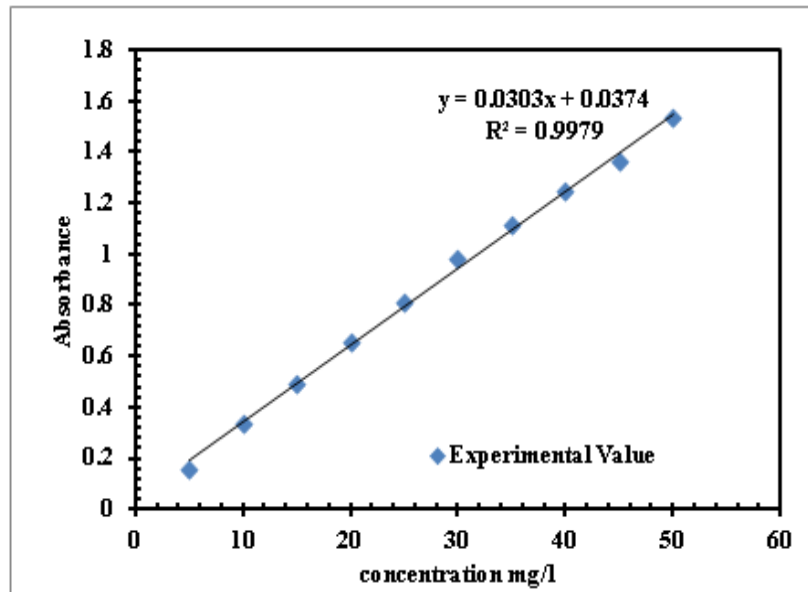


Figure 4.4 Calibration curve of pyridine sample

4.3.3 Factors controlling the adsorption process

4.3.3.1 Effect of pH

To find the effect of pH, experiments were conducted at different concentration of pyridine. The tests were conducted at different pH's of solution ranging from 2 to 10 pH for initial concentration of 100 mg/L of pyridine at 30°C in shaker for 180 rpm speed for 6hr. Basically it was found from the literature that the removal of adsorbate was in most cases at its natural pH so that one sample of natural pH was also kept for the experiment.

4.3.3.2 Effect of adsorbent dosage

To find the optimum adsorbent dosage, analysis was done at the different amount of the adsorbent ranging from 0.1 to 20 g/L with initial adsorbate concentration 100 mg/L of pyridine at 30°C in shaker for 180 rpm speed for 6hr. it was found that on increasing the temperature the rate of adsorption also increase rapidly due to more active sites availability but after some quantity of doze increment in removal was found to be very less so that after obtaining the result the optimum doze was selected.

4.3.3.3 Contact time and kinetic study

Time of contact is also very important factor for the adsorptive study it was found that at the time of contact the removal was found to be very high due to highly available active sites present on the surface of adsorbent but on increasing the active sites or pores covered with pyridine so that the adsorbate had to diffused into the bulk of the adsorbent for adsorption, so that rate of removal

after some time was very low, for this reason the optimization of contact time was also very important factors. For this study 250 ml flasks were used for with working volume of 100 ml, 6g/l of adsorbent in different flasks of pyridine. Flasks were shacked in an orbital shaker under temperature controlled conditions (30°C) at a uniform stirring speed of 150 rpm. Flasks were withdrawn at different time intervals (15min to 10 h), the contents of the flask were clean, centrifuged and supernatant was analyzed.

To study the kinetics of adsorption of pyridine various kinetic models, like pseudo-first order, pseudo-second order were analyzed.

4.3.3.4 Adsorption Isotherms

In the adsorption process commonly when temperature increasing the adsorption process are decreasing so most of time this adsorption process is exothermic process. while in some cases on increasing the temperature, the bonds near the edge of surface sites are breaking which generates more active sites for adsorption so that rate is increase in some cases.

Different adsorbate-adsorbents exhibit different types of equilibrium relationship [Qi and Schideman, (2008)]. It has been found that for most important cases of the wastewater treatment the equation takes either the form of a Langmuir isotherm or Freundlich isotherm. Both of these isotherms are explained in the subsequent sections.

4.3.3.4.1 Langmuir Isotherm

The Langmuir isotherm adsorption model is belongs to the homogeneous adsorption and also a two parameter isotherm.

It is semi-empirical isotherm derived from kinetic mechanism. It is based on four assumption:

1. Adsorbed molecules don't interact with each other.
2. ONLY monolayer adsorption is taking place.
3. Adsorbent surface do not migrate by adsorbate surface.
4. Adsorbent surface is uniform in terms of energy of adsorption.

The Langmuir isotherm is given by the following equation:

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

Where Q_e is the amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium, Q_m is the amount of adsorbate adsorbed per unit amount of adsorbent required for monolayer

adsorption (limiting adsorbing capacity) K_A is the constant, related to enthalpy of adsorption and C_e is the concentration of adsorbate solution at equilibrium.

4.3.3.4.2 Freundlich Isotherm

The Freundlich isotherm doesn't indicate when coverage of adsorption limit reaches sufficient to fill a monolayer. The heat of adsorption declines in magnitude with an increase in extent of adsorption in many instances. This decrease in the heat of adsorption is logarithmic, implying that the adsorption sites are distributed exponentially with respect to the adsorption energy [Losso et al., (2002)]. The equation describing such isotherm which is given by:

$$Q_e = K_F C_e^{\frac{1}{n}}$$

Where K_F and n are constant and C_e is the concentration of adsorbate solution at equilibrium.

Thus a plot between $\ln Q_e$ and $\ln C_e$ gives a straight line if the adsorbate and adsorbent are following Freundlich isotherm.

The Freundlich equation is found to be small concentration range for dilute solution. [Qi and Schideman, (2008)]. Adsorption taking place at strong solute concentration is indicated by a low 'n' value.

5 RESULT AND DISCUSSION

5.1 Ultimate analysis

This test was performed for the determination of major component present in the blank and loaded adsorbent PAC. From the result it was found that the %C.

Table 5.1 shows the results of ultimate analysis

Elements	Blank PAC (%)	Loaded PAC (%)
C	80.99	84.03
H	0.888	0.838
N	0.532	0.732
S	0.00	0.00
Initial weight	3.1180	4.1190

5.2 TGA-DTA-DTG analysis

Thermo gravimetric analyses of blank and loaded adsorbent were shown in the figures 5.1 and 5.2 the line at the bottom (blue line) represent the TGA analysis of the adsorbent. It was clear from the figure that in case of blank adsorbent no mass loss occurred till 27°C while at increasing temperature up to 85 °C 6.2% of loss in mass was observed in TGA study. On increasing the temperature up to 409 °C slight decreases in mass was observed which only 3.1% was in the blank adsorbent sample so no decomposition in GAC was observed till this temperature. On increasing the temperature up to 503°C the rate of loss in mass was increased that is 9.7% while the huge change was observed from increases in temperature 503 to 554°C. The loss was observed 77.4%. so it was clear that the main decomposition was taken place in the temperature range 503 to 554°C. After increasing the temperature up to 920°C only 0.1% loss was observed in the mass of adsorbent. Green line in the figure represents the DTA (Differential thermal analysis). The decomposition energy in this process of combustion of blank adsorbent was represented by the peak shown in graph which was 8.23 J/mg. and also represents the exothermic nature of the process. In this figure pink line also observed with a peak, the significance of this pink line was to provide the information of major mass loss rate obtain in what temperature range, and it is clear from the graph that at temperature 537°C the rate of decomposition was 3.94 mg/min

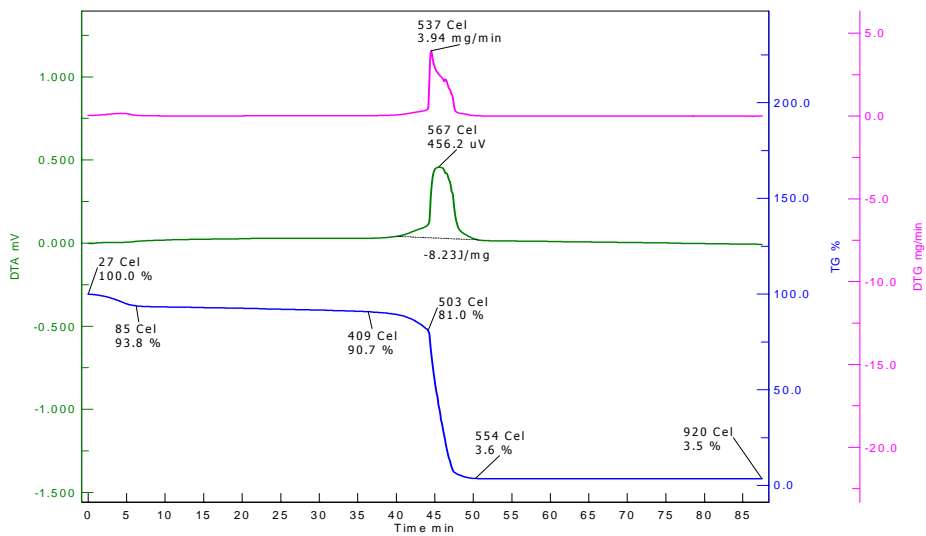


Fig 5.1 Before adsorption thermal Oxidation of GAC

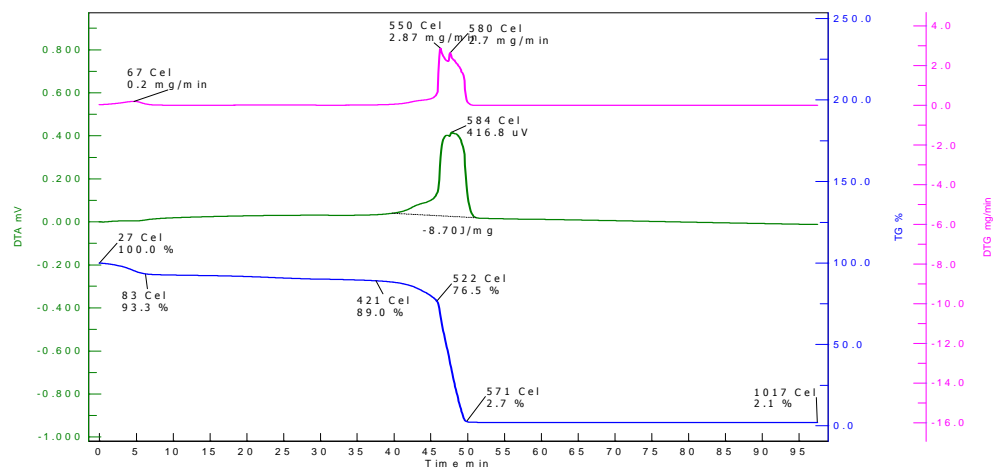


Fig 5.2 after adsorption thermal Oxidation of GAC

The plot of TGA study of loaded GAC was shown in figure (5.2). It was clear from the figure , As observed in this study of blank adsorbent the blue line followed the same path because till 27°C there was no loss in mass taken place, on increasing the temperature till 83°C some mass loss was taken place that was 6.7% while on increasing the temperature upto 421°C only 4.3% loss was observed so the rate of decomposition was very less till 421°C, on increasing the temperature 522°C the rate was slightly increased so the mass loss was 12.5% obtained from this temperature to 571°C the huge loss in mass is observed and 73.9% mass loss taken place while

increasing the temperature till 1017°C only 0.5% loss was observed so mass loss was increased in case of loaded GAC due to the fact that some pyridine was filled in the pore of GAC which increased the mass loss in thermal decomposition process. The green line represent the DTA analysis was shown in the figure had the peak at 584°C, the energy of decomposition process was 8.7 J/mg. pink line indicate that at 550°C the rate of decomposition of GAC was highest that was 2.87 mg/min.

5.3 SEM and EDX analysis

The SEM's of the blank and loaded GAC are shown in figure () and figure () respectively. The texture surface of GAC before and after treatment is revealed by these figures. The elemental composition of GAC was determined using EDX analyzer. It is found from the EDX analysis that GAC mainly contained carbon and oxygen. The relative weight percentages of elements in blank and loaded GAC are presented in table (). Figure () displays the EDX spectra of blank GAC while figure() displays the EDX spectra of loaded GAC. Both of these were found to contain about 91% of carbon and 8% of oxygen by weight. The picture shown in the table represent the SEM of the blank and loaded GAC, it was clear from the pictures that in case of blank GAC large number of pores available at the surface while it was filled with adsorbate in case of loaded GAC. EDX analysis results were shown in table 5.2.

Table 5.2 EDX analysis results

Element	Blank adsorbent		Loaded adsorbent	
	Wt %	At %	Wt %	At %
C	90.51	92.92	91.69	93.67
O	8.82	6.80	8.21	6.30
S	-	-	0.1	0.04
Al	0.07	0.03	-	-
Si	0.37	0.16	-	-

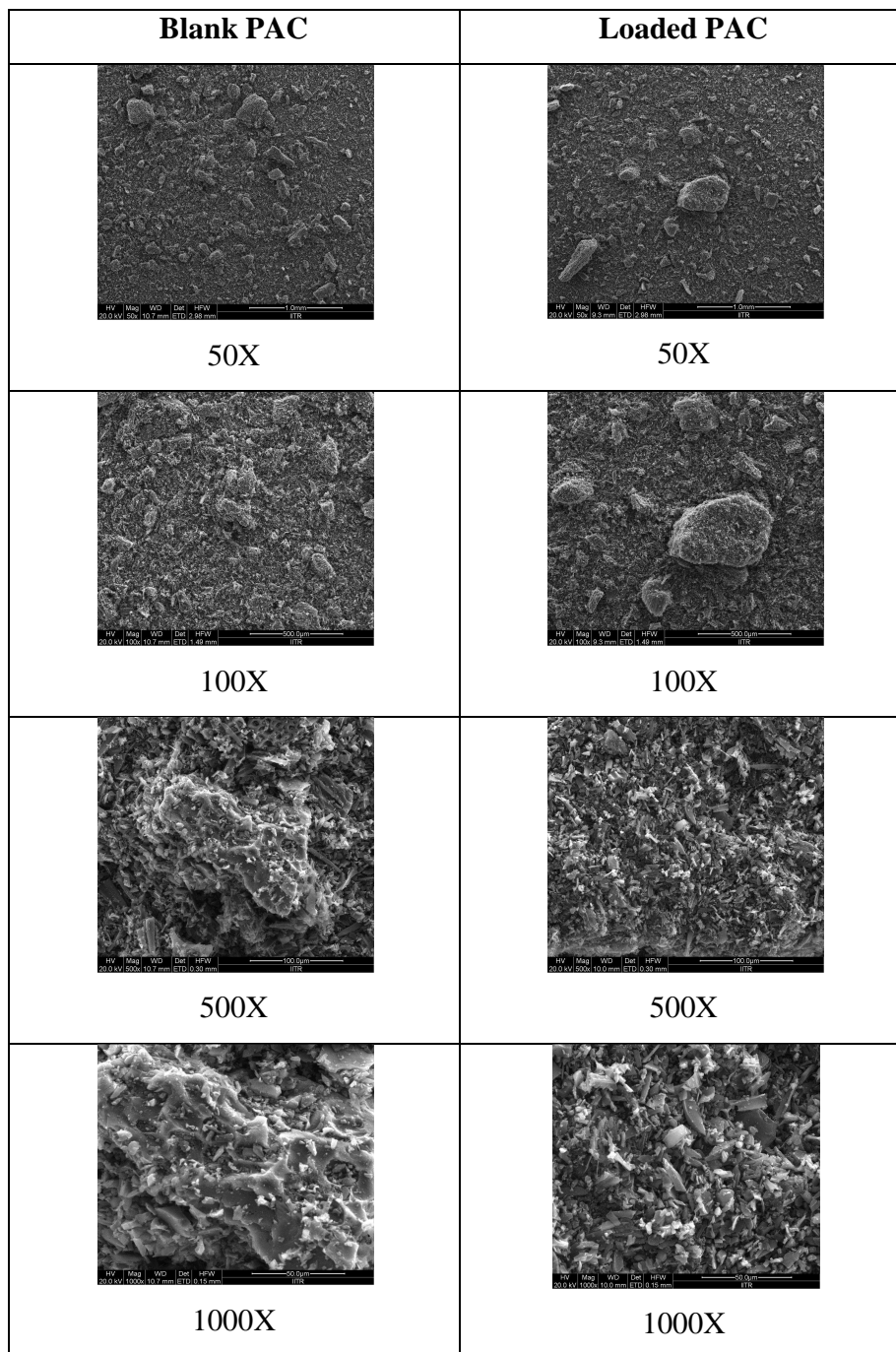


Figure 5.3 SEM analysis

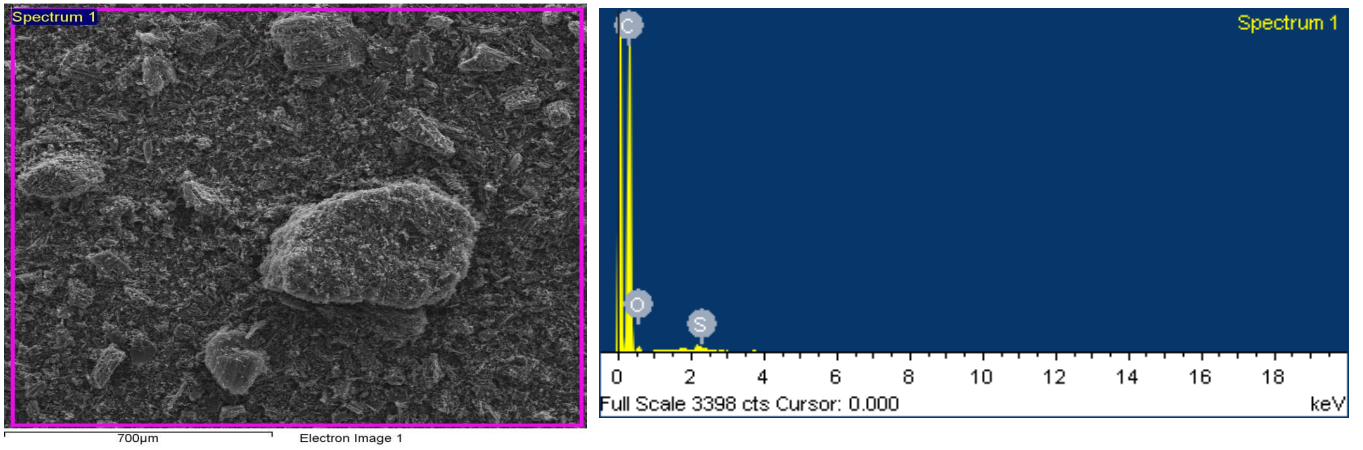


Figure 5.4 EDX analysis of blank PAC

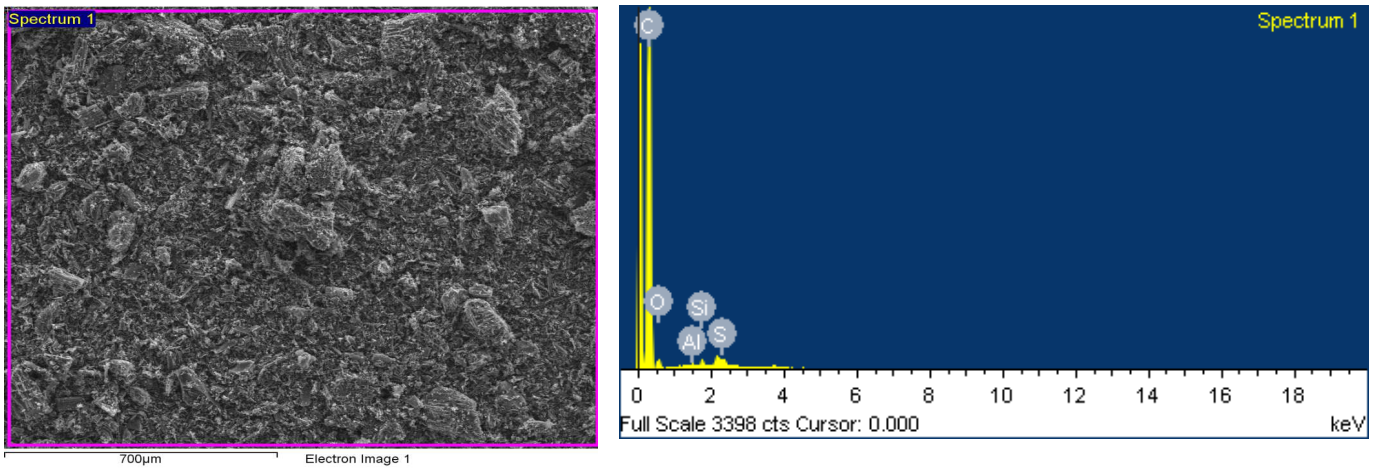


Figure 5.5 EDX analysis of loaded PAC

5.4 BET surface area

The BET surface area of PAC was found to be 784.7 m²/g.

5.5 XRD analysis

- XRD pattern shown in gives the idea of components present in compound. It actually predicts the degree of crystallinity in the sample.
- The higher the number of high intensity peaks, higher is its crystallinity. The graph shows only few peaks, GAC is non crystalline, amorphous in nature.

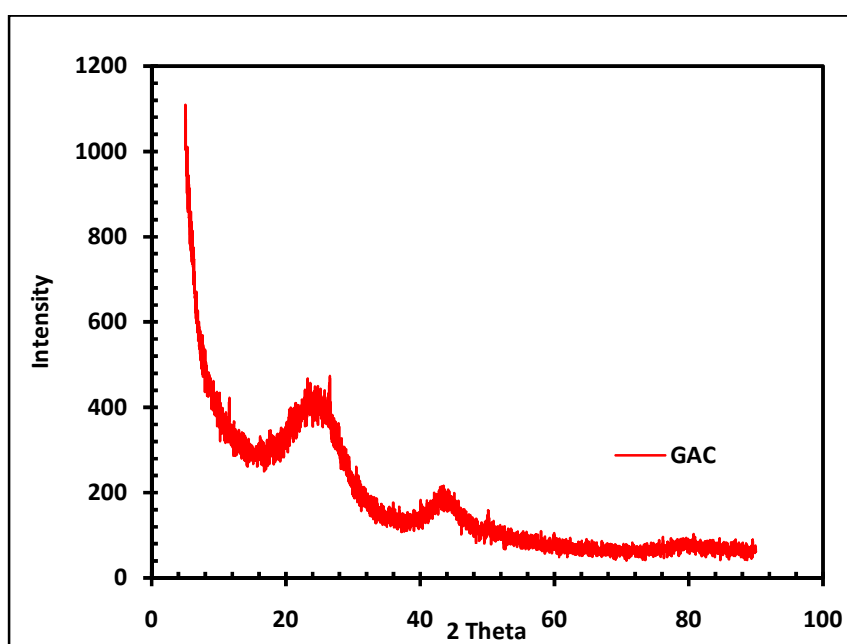


Figure 5.6 XRD analysis

5.6 Batch study

5.6.1 Effect of pH

The pH of the test solution plays a major role in the adsorption process as it affects the ionization and surface charge of contaminants and adsorbent. At the low pH, rate of removal of pyridine was low due to the fact that at low pH pyridine had less tendency to migrate toward PAC surface, because this surface positively charged. At increase the pH the rate of removal also increases and did not change significantly in the range 4 to 7. It was also found that the removal was maximum at neutral pH.

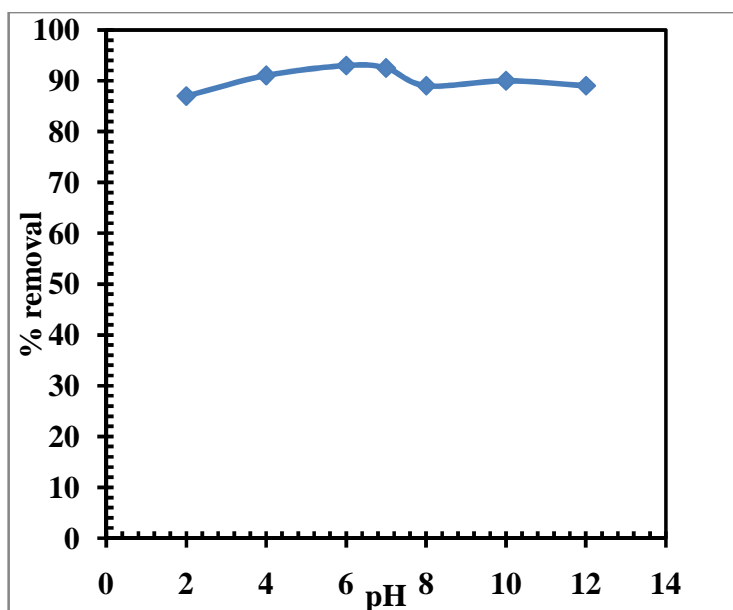


Figure 5.7 Removal of pyridine at different pH ($C_0=6\text{g/l}$, $T=303\text{K}$).

5.6.2 Effect of Adsorbents Dosage (w)

Effect of adsorbent dose on the removal of pyridine with the help of PAC was observed in this experiment, for this experiment the different parameters were taken as concentration of pyridine solution was taken 100mg/l , at the temperature of 303K and kept it in shaker for 8hr for this study different doses of batch were prepared these dose were varies from $0.1 - 20\text{g/l}$ at their natural pH. It was clear from the literature that the increment in dose gives result in higher removal of pyridine because of greater number of active sites presents in large amount of adsorbate, but as shown in figure (5.8), after some amount the removal was not significantly changed with dose, so after that dose the increment was worthless, so that value of dose considered as the optimum dose, from figure it was clear that on the dose amount 6g/l the removal was 96.66% , while the removal was increasing very slowly after again increment in adsorbent dose, so that for this study optimum dose was considered as 6g/l for the study of adsorptive removal of pyridine with PAC.

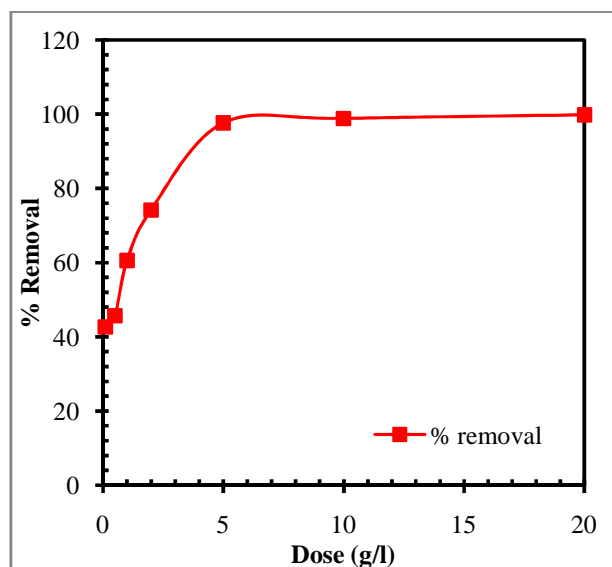


Figure 5.8 Effect of dose on Pyridine removal

5.6.3 Effect of Contact Time and Kinetic study

Figure 5.8 shows the pyridine removal by PAC due to the effect of contact time. the experiments were done using the solution of Pyridine having $C_o = 100$ mg/l, dose = 6 g/l, temperature 303K at different contact timings varying from 30min to 480 min. the incubator shaker was operated with a speed of 180rpm.

Pyridine removal increases rapidly with time up to $t = 240$ min, after that only slight change in removal % was observed. Considering this fact optimum time for adsorption process was taken as 240min.

Kinetic study

Experimental kinetic data were analyzed using Pseudo first and second order models. Experimental kinetic data was obtained for concentrations of 100 and 200 mg/l for different time intervals. It was clear from the figure 5.9 that the removal efficiency for 100 mg/l is more compared to 200 mg/l. Further kinetic study was performed to determine nature of the adsorption process. Pseudo-first kinetic model fitted adequately for 100 and 200 mg/l. Elevated removal efficiencies for 100 mg/l can be attributed to the fact that active sites are freely available for 100 mg/l compared to 200 mg/l. As the concentration increased from 100 to 200 mg/l degeneration of adsorbent occurred and removal efficiencies decreased. Figure 5.10 shows the predicted and experimental kinetic data for first order model.

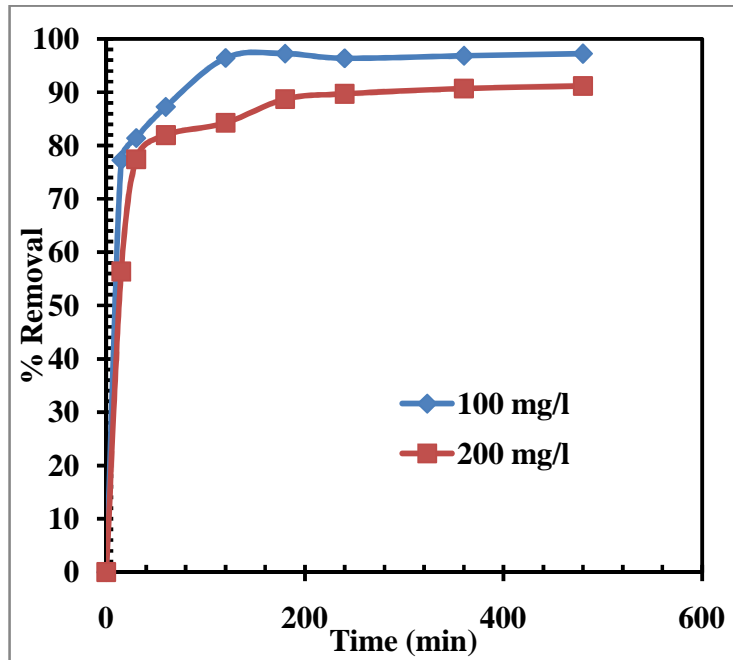


Figure 5.9 Effect of contact time on Pyridine removal

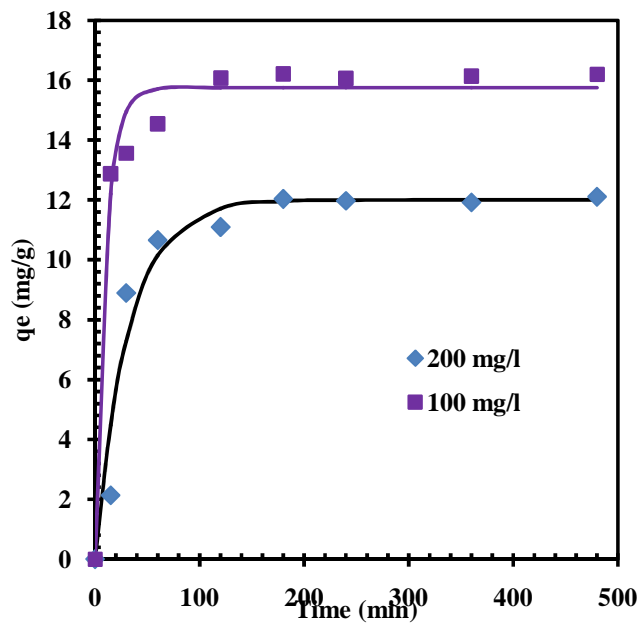


Figure 5.10 Kinetic data for 100 and 200 mg/l. Points represent experimental and line represents line

Table 5.3 Kinetic data for 100 and 200 mg/l

C_o = 100 mg/l	
1st order kinetics	
k (min ⁻¹)	0.067
q _e (mg/g)	29.40
R ²	0.823
2nd order kinetics	
k (min ⁻¹)	0.0038
q _e (mg/g)	30.93
R ²	0.820
C_o = 200 mg/l	
1st order kinetics	
k (min ⁻¹)	0.031
q _e (mg/g)	12.01
R ²	0.952
2nd order kinetics	
k (min ⁻¹)	0.003
q _e (mg/g)	13.34
R ²	0.925

5.6.4 Adsorption isotherm

Table 5.4 Isotherm constants for three different temperatures (288, 303, 318 K)

Isotherms	Parameters	BFA		
		Temperature (K)		
		288	303	318
Langmuir $q_e = \frac{Q_o b C_e}{1 + b C_e}$	Q _o	142.6658	142.8534	271.2853
	b	0.025	0.01823	0.004905
	R ²	0.953	0.921555	0.973687
Freundlich $q_e = K_F C_e^{1/n}$	K _F	9.44	6.805811	2.495685
	1/n	0.539	0.583514	0.780682
	R ²	0.981	0.954861	0.97501
Redlich-Peterson $q_e = \frac{K_R C_e}{1 + a_R C_e^g}$	a _R	4409.967	6047.93	15905.01
	K _R	41620.89	41163.08	39693.6
	g	0.460081	0.41649	0.219308
	R ²	0.98091	0.954862	0.975012

<p style="text-align: center;">Hill</p> $q_e = \frac{Q_{sH} C_e^{nH}}{k_D + C_e^{nH}}$	k _d	4414.693	4414.693	4414.693
	q	4308.465	4308.465	4308.465
	n	1.009458	1.00944	1.009431
	R ²	0.989831	0.989753	0.991366
<p style="text-align: center;">Tempkin</p> $q_e = B_1 \ln K_T + B_1 \ln C_e$	K _t	0.338185	0.389125	0.285707
	B1	27.84773	22.28075	19.62459
	R ²	0.931476	0.845337	0.819743

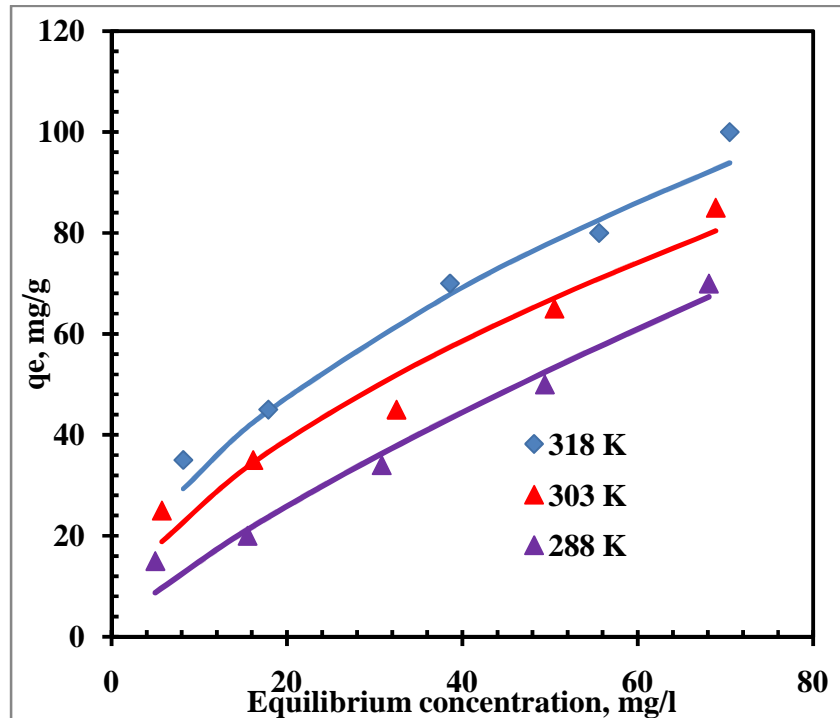


Figure 5.11 Isotherm data for three temperatures (288, 303, 318 K). point represents experimental value and line represents theoretical values.

The isotherm study was carried out to evaluate the best fitting model for the experimental adsorption equilibrium data. Various isotherm models i.e. Lagmuir, Freundlich, Redlich-Peterson, Hill, Temkin using Microsoft Excel solver. It is evident from the above table that the equilibrium data fitted adequately with the Hill isotherm. The parameters were optimized by maximizing R^2 using fore mentioned software.

6 CONCLUSIONS

As we all know that pyridine is one of the most important aromatic compound in pharmaceutical and pesticides industry. Many important compounds which are derived from pyridine like 2-picoline, 3-picoline, 4-picoline and quinoline have very wide applications, but these compounds are also have injurious effects when exposed to the environment directly. Although the extent of harmfulness is always depends on the mode of contact to the person, but we cannot ignore the harmful effects in fertility and nervous system etc. so the removal of these compound are always necessary. In the present study the removal of pyridine was taken as an objective. There are many methods which can be directly applied for the removal of pyridine up to permissible level. Among these methods adsorption was found to be one of the best methods for removal of pyridine because of its economical operative cost and easily handling steps. For this purpose PAC was chosen due to its greater surface area, so the batch study was performed and it was also found that the removal of pyridine was higher at its natural pH, while the optimize dose of PAC for removal was found to be 6g/l and time of contact was 4hr, which give 95% removal at 30oC for 100ppm pyridine concentrated solution. From the kinetic study of the obtained data the kinetic was found of pseudo 1st order and the isotherm experiment results indicate that the obtained data was best fitted Hill isotherm model equation.

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