DESULFURIZATION AND DENITROGENATION OF LIQUID FUELS BY MODIFIED ACTIVATED CARBON

A DISSERTATION
Submitted in partial fulfillment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Industrial Pollution Abatement)

By
SHELAKA GUPTA

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE-247667 (INDIA)
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CANDIDATE'S DECLARATION

I hereby declare that the work being presented by me in this dissertation entitled **"DESULFURIZATION AND DENITROGENATION OF LIQUID FUELS BY MODIFIED ACTIVATED CARBON"** in the partial fulfillment of the requirements for the award of the degree of Master of Technology in Chemical Engineering with specialization in "Industrial Pollution Abatement" submitted to the Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, is an authentic record of my original work carried out under the guidance of **Dr. V.C. Srivastava**, Assistant Professor, Department of Chemical Engineering, IIT Roorkee. The matter embodied in this project report has not been submitted for the award of any other degree.

Date: 14 June, 2013 Shelaka Gupta
Place: Roorkee Enrol. No: 11515020

CERTIFICATE

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

(**V. C. Srivastava**)
Assistant Professor,
Department of Chemical Engineering
Indian Institute of Technology, Roorkee
Roorkee-247667

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(Shelaka Gupta)
Enrol. No: 11515020

ABSTRACT

In the present study, nickel loaded activated carbon (Ni/AC) was synthesized and characterized by various techniques. It was further used for the adsorption of nitrogenous compound (N) (represented by quinoline) and sulfur compound (S) (represented by dibenzothiophene (DBT)).

Various methods like X-ray diffraction, Fourier transform infrared (FTIR) spectroscopy, energy dispersive and scanning electron microscopy, thermo-gravimetric analysis etc. were used for physico-chemical characterization of Ni/AC before and after the adsorption of N and S. FTIR spectra of Ni/AC indicated the presence of various types functional groups on its surface. Thermo-gravimetric analysis exhibited the thermal stability of Ni/AC up to 400 ^{o}C temperature.

The influence of various factors like loading, adsorbent dose, time and temperature on the adsorption of N and S from model fuel by Ni/AC were investigated. Equilibrium time for N and S was found to be 6 h and 9 h, respectively. The optimum adsorbent dose was found to be 20 g/l. It was found that adsorption of N and S followed pseudo-second-order kinetics. The adsorption of N and S was best represented by Redlich-Peterson isotherm.

Taguchi's method (L_{27} orthogonal array) was used to optimize various parameters for the removal of N and S simultaneously from model fuel using Ni/AC. The effect of various parameters like initial adsorbate concentration ($C_{o,i}$), adsorbent dose, temperature and contact time on the adsorption of N and S has been studied at three levels to see their effect on q_N, q_S and q_{tot}. It was found that the adsorbent dose is the most significant factor while the interaction between $C_{o,i}$'s is also significant.

For the binary system containing both S and N**,** equilibrium adsorption data was obtained ($C_{o,S}$ = 1.56-23.43 mmol/l, $C_{o,N}$ = 3.57-53.57 mmol/l, T= 303 K, t = 9 h, m = 20g/l). It was found that the adsorption capacity of Ni/AC was higher for N than that for S. For binary component system containing S and N, extended Freundlich isotherm best represented the isotherm data at 30 ^{o}C.

Table of Contents

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

$1/n$	heterogeneity factor, dimensionless
a_R	constant of Redlich – Peterson isotherm, 1/mg
β_T	Tempkin isotherm constant related to the heat of adsorption, kJ/mol
AC	lab grade activated carbon
C_o	initial concentration of adsorbate in solution, mg/l
C_e	equilibrium liquid phase concentration mg/l
C_S	adsorbate concentration in the solution
h	initial sorption rate, mg/g min
I	constant that has given idea about the thickness of boundary layer, mg/g
k_f	rate constant of pseudo-first-order adsorption model, min^{-1}
k_{id}	intra-particle diffusion rate constant, mg/g $\text{min}^{1/2}$
k_S	rate constant of pseudo-second-order adsorption model, g/mg min
K_F	constant of Freundlich isotherm, $(\text{mg/g})/(1/\text{mg})^{1/n}$
K_L	constant of Langmuir isotherm, 1/mg
K_R	constant of Redlich-Peterson isotherm, 1/g
m	mass of adsorbed per liter of solution, g/l
q_e	equilibrium solid phase concentration, mg/g
$q_{e,cal}$	calculated value of solid phase concentration of adsorbate at equilibrium, mg/g
$q_{e,\exp}$	experimental value of solid phase concentration of adsorbate at equilibrium, mg/g
q_m	maximum adsorption capacity of adsorbent as per Langmuir isotherm, mg/g
q_t	amount of adsorbate adsorbed by adsorbent at time t, mg/g
R	universal gas constant, 8.314 J/K mol
t	time, t
T	absolute temperature, K
V	volume of the solution, I
ΔG^o	Gibbs free energy of adsorption, kJ/mol

ΔH^o	enthalpy of adsorption, kJ/mol
a_{ij}	competition coefficients of component i by component j, dimensionless
a_R	constant of Redlich- Peterson isotherm, l/mg
$C_{o,i}$	initial concentration of each component in solution, mg/l
K_i	individual extended Langmuir isotherm constant of each component, l/mg
$q_{e,i}$	equilibrium solid phase concentration of each component in binary mixture, mg/g
$q_{e,cal}$	calculated value of solid phase concentration of adsorbate at equilibrium, mg/g
$q_{e,\exp}$	experimental value of solid phase concentration of adsorbate at equilibrium, mg/**g**

Greek symbols

β	constant of Redlich-Peterson isotherm ($0<\beta<1$)
β_i	constant in SRS model for each component, dimensionless
$\eta_{L,i}$	multicomponent (competitive) Langmuir adsorption constant of each component, dimensionless
$\eta_{R,i}$	multicomponent R-P adsorption constant of each component, dimensionless.

CHAPTER-1

INTRODUCTION

Energy production has become a crucial issue these days. About 82% of the energy required for the production of goods and services comes from fossil fuels and half of it comes from petroleum. Gasoline, diesel and jet fuel which forms the major portion of petroleum is used as transportation fuel (Srivastava, 2012). The US Environmental Protection Agency and government of many countries have issued new regulations for the production and use of eco friendly fuels with less content of aromatics and sulfur (Song et al., 2003). The USEPA has directed 15 ppm of sulfur emission limit in diesel fuel while Europe has also stressed EU changeover to 10 ppm in transportation fuel. Diesel fuel is derived from crude oil and sulfur present in crude oil causes emission of particulates and soot. Soot results in the emission of black fumes which contribute to air pollution. Sulfur compounds present in diesel produce SO_x and in addition to this also poison catalyst which are used in catalytic convertors (Kim et al., 2006). Nitrogen concentration in the oil is very low but nitrogen compounds interfere in the desulfurization process. So removal of nitrogen compound becomes very essential.

In India Bharat Stage specifications (BS-1V) are been followed since April 2010 in thirteen major cities which requires the sulfur level to be lowered from 350 ppm (BS-III) to 50 ppm (BS-IV) while the rest of country is still following BS-III. Due to these stringent regulations worldwide refiners are getting new challenges to meet these requirements and reduce aromatic content in the fuel.

Table 1.1 Sulfur standards in India (Source: www.unep.org).

Region	Year	Sulfur standard
	1995	10000 ppm, Cetane no: 45
Delhi, some cities	1996	5000 ppm
Delhi	1998	2500 ppm
Delhi	1999	500 ppm
All over nation	2000	2500 ppm, Cetane no:48
Delhi, some cities	2001	500 ppm
Selected areas	2005	350 ppm
All over nation	2010	350 ppm
Selected areas	2010	50 ppm

The new regulations which control the sulfur emission are beneficial for the environment but are very difficult to meet due to economical and operational challenges (Babich and Moulijn, 2003).

The requirement for ultra deep desulfurization contains lot of technical problems. Factors which affect the degree of desulfurization include presence of nitrogen and other aromatic compounds, process parameters, source and quality of feed, type of sulfur compound, etc. Some sulfur containing molecules like 4, 6-DMDBT, DBT, etc. are difficult to remove by HDS and in order to achieve the stringent regulations refiners need to remove these. Another challenge for the refiners is to produce high quality diesel from low quality feed. Lot of research work is being done to find out how to improve the catalyst performance for hydrotreating processes and to develop alternative techniques.

Diesel is a mixture of many hydrocarbons. The sulfur and nitrogen compounds present in it upon combustion forms SO_x and NO_x. In addition to these CO, CO_2 and particulate matter is also released. SO_x mainly contain SO_3 which dissolves in water to form H_2SO_4. These particulate matter and oxides degrade the air quality and affects human health.

Diesel fuel contains many sulfur compounds and these can be divided into two categories. One includes benzothiophenes which may be alkyl substituted and other includes DBT. It has been found that BT’s and their alkyl substituted compounds are easier to desulfurize in comparison to DBT’s. Further alkyl DBT’s which include 4-MDBT, 4, 6-DMDBT are even more difficult to remove due to their low reactivity. It has been suggested that due to steric hindrance offered by DBT to the catalyst surface they become difficult to desulfurize. If the level of sulfur has to be reduced to a very low value it is necessary to remove the alkyl substituted DBT’s also which cannot be removed by HDS process. In the following section there is a brief description of the type of technologies used and developed for the removal of N and S compounds from diesel fuel.

1.1. REMOVAL OF SULFUR COMPOUNDS FROM DIESEL

Various techniques that are used for desulfurization are oxidative desulfurization (Zhang et al., 2012; Chika et al., 2006; Zhao et al., 2008; Gui et al., 2010), adsorptive desulfurization (Liu et al., 2008; Dasgupta et al., 2013) biodesulfurization (Olmo et al., 2005; Andaloussi et al., 2003), etc. which are discussed below.

1.1.1. Hydrodesulfurization

At present hydrodesulfurization which is a high temperature (300-450 ^{0}C) and high pressure (3-5MPa) process and uses $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$ as catalysts is used as the industrial process for the removal of sulfur from diesel in the form of H_2S. The HDS process is suitable for removing thioles, sulfides and lighter thiophenic compounds but not for sulfur compounds containing substituted alkyl groups. The diesel fuel mainly contains polycyclic aromatic sulfur heterocycles (PASH’s) like trimethyl-benzothiophenes (TMBT’s), dibenzothiophenes (DBT’s) and extracts (Liang et al., 2006).In low diesel sulfur fuels the compounds present are dibenzothiophene (DBT), 4-methyl-dibenzothiophene (4MDBT), 4,6-dimethyl-dibenzothiophene (4,6-DMDBT), 2,3,5-trimethyl-benzothiophene (2,3,5-TMBT), 2,3,7-trimethyl-benzothiophene (2,3,7-TMBT). These compounds remain in the fuel even after HDS because of the hindrance offered by the substituted alkyl group present in the sulfur compounds in the interaction between the active sites of the catalyst and the sulfur (Thomas, 2008).

1.1.2. Oxidative desulfurization

In this process low temperature (50°C) and atmospheric pressure are employed. With the help of oxidants like ozone (Zaykinaa et al., 2004), nitric acid (Tam et al., 1990), H_2O_2 and photocatalyst (Matsuzawa et al., 2002), H_2O_2 and HCOOH (Grobas et al., 2007), H_2O_2 and acetic acid (Shahrani et al., 2007), etc. sulfides present in the fuel are oxidized in such a way that there is no C-S bond breakage and only the sulfur of the molecule gets oxidized to sulfones as shown in the Figure 1.1. The oxidized compounds have high polarity and can be adsorbed easily. The oxidized compounds can also be separated by distillation or extraction.

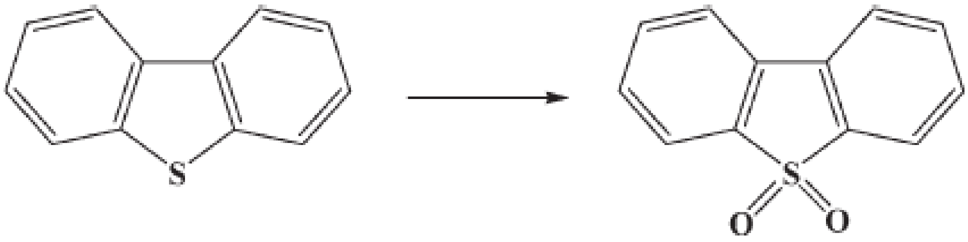


Figure 1.1 Oxidation of DBT to sulfone.

Catalysts like molybdenum/tungsten oxides (Collins, 1994), Mo/γ- Al_2O_3(Gutierrez et al., 2008), V_2O_5 supported on silica, alumina, etc. (Caero et al., 2008) are used in oxidative desulfurization. Oxidative desulfurization can be carried out in many other ways like radiations which covert sulfur compounds into sulfones (Zaykina et al., 2002), by UV light photooxidation (Hirai et al., 1996).

Oxidative desulfurization has two drawbacks. Oxidants sometime produce side reactions due to which quality of fuel decreases. Secondly the type of solvent used for extraction may lead to removal of useful olefins, etc. from the fuel. Moreover the catalysts used are toxic in nature. Despite all the disadvantages ODS needs low temperature and pressure and doesn't require H_2 thereby reducing the cost as compared to HDS.

1.1.3. Biodesulfurization

It is an eco friendly method of removing sulfur compounds from diesel. In this method microorganisms capable of decomposing DBT as energy source are separated from their habitat. Bacterial species like *Pseudomonas* (Grossman et al., 1999), *Pseudomonas delafieldii* (Guobin et al., 2006), *Rhodococcus* spp (Farland et al., 1998), *Gordona, Bacterium* (Akbarnejad et al., 2006), etc. are capable of using DBT as energy source. BDS has got advantage of less cost, high quality products and less production of green house gases. But the process has been of limited use due to slow degradation and it becomes difficult to keep the bacteria alive.

1.1.4. Adsorptive Desulfurization

In this process the adsorbents selectively adsorb the sulfur compounds present in the fuel. It is divided into two types reactive adsorption and physical adsorption based on the separation mechanism. This is discussed in brief in Chapter 2.

1.2. DENITROGENATION OF FUEL

Presence of nitrogen compound in the refinery streams inhibits the removal of DBT and other sulfur compounds. This is because sulfur and nitrogen compounds both compete for the same catalyst sites but nitrogen compounds show strong adsorptive strength. So it becomes necessary to remove the nitrogen compounds. The degree of inhibition depends on the concentration and type of nitrogen compounds. It has been found that by decreasing the nitrogen content HDS reactivity increases (Yang et al., 2004).The nitrogen compounds produce NH_3 during hydrocarbon reforming which acts as poison to the catalyst as well as in the fuel cells.

There are different types of nitrogen compounds present in the diesel. Non-heterocyclic compounds (aliphatic amines and aniline), heterocyclic compounds which are six member and are basic (acridine and quinoline) and five member heterocycles which are non-basic (Carbazole and indole). Among these basics are the strongest inhibitors (Stanislaus et al., 2010).

Hydrodenitrogenation has been used for the removal of nitrogen compounds in presence of H_2 at high pressure and high temperature (Almarri et al., 2009; Maldonado et al., 2004) but it is very costly and energy intensive process. Also in HDN the nitrogen can be removed only after the hydrogenation of heterocycles which results in higher consumption of nitrogen and is also responsible for slowing down the process.

Various other methods are used for the denitrogenation of fuels like solvent extraction using ionic liquid such as 1-Butyl-3-methylimidazolium chloroaluminate (III) (Gao et al., 2005), 1-butyl-3-methyl-imidazolium chloride (Xie et al., 2008), etc., extraction by membranes (Matsumoto et al., 2006) and adsorption (Kim et al., 2006) which has a benefit of not using H_2 gas and can be carried out at ambient temperature thus reduces the cost of the process as compared to HDS. Adsorption can also be used to remove the nitrogen compounds and a lot of work has been done in which adsorbents like silica gel, activated alumina, copper zeolites, etc. have been used. Recently metal organic framework (Ferey, 2008; Jhung et al., 2012) have been used for adsorptive denitrogenation.

1.3. OBJECTIVE OF THESIS

Only scarce work in the literature has been found on the use of Ni based adsorbents for the denitrogenation and desulfurization of liquid fuels. Moreover, no work has been reported on the use of Ni loaded activated carbon (Ni/AC) for the simultaneous denitrogenation and desulfurization of liquid fuel. The following aims and objectives have been set for the present work in view of the literature review and the necessity for developing a process for desulfurization and denitrogenation.

1. To prepare and characterize Ni/AC for various physiochemical and analytical properties. These characteristics include X-ray diffraction (XRD), Fourier transform infra red spectral (FTIR) analysis, scanning electron microscopic (SEM), Brunauer–Emmett–Teller (BET) surface area and Thermo gravimetric (TG) analysis.

2. To study the feasibility of using Ni/AC as an adsorbent for the individual as well as simultaneous removal of quinoline (Nitrogenous compound) and dibenzothiophene (DBT, Sulfur Compound) from model fuel.
3. To find out the best fit of mono component adsorption isotherm models (i.e., Freundlich, Langmuir and Redlich-Peterson (R-P)) for single component system.
4. To gather experimental data for binary system so as to study the effects of various parameters on adsorption using Taguchi's method.
5. To gather equilibrium adsorption data for binary system and to find out the best fit multicomponent adsorption isotherm model for representing the isotherm data.

CHAPTER-2

LITERATURE REVIEW

In this chapter literature review on the adsorptive removal of nitrogen and sulfur compounds from diesel fuel is presented. Both these compounds are unwanted and must be removed from the fuel. Various adsorbents have been used in the literature and some of these have been discussed below.

2.1. DESULFURIZATION BY ADSORPTION

Refinery streams containing organosulfur compounds are passed through the adsorbent bed so as to selectively adsorb the sulfur compounds. The nature of interaction depends on the nature of sulfur compounds and hence adsorption by desulfurization can be classified into two classes: desulfurization by physical adsorption and desulfurization by reactive adsorption.

2.1.1. Desulfurization by Physical Adsorption

In this the sulfur molecule gets attached to the surface of the adsorbent but doesn't reacts with it chemically and can be regenerated. Various adsorbents have been developed such as adsorbents based on activated carbon (Sano et al., 2004), alumina (Srivastav and Srivastava, 2009) zeolites (Yang et al., 2003), reduced metals (Ma et al., 2005), (Ma et al., 2005), etc. which have high sorption capacity, easy regenerability but still efforts are being made to have better performance so that they can also adsorb 4, 6-DMDBT which are difficult to treat by hydrodesulfurization.

2.1.1.1. Studies based on activated carbon: Activated carbon has been used as an adsorbent in wastewater treatment as it has high surface area and high porosity. Haji and Erkay (2003) synthesized, characterized and used carbon aerogels as adsorbent for the removal of DBT from n-Hexadecane. It was found that CA with larger pore size had higher adsorption capacity and the adsorbent was capable of adsorbing DBT over naphthalene.

Sano et al. (2005) integrated HDS process with adsorption using ACF bed so as to reduce sulfur content in hydrodesulfurized straight run gas oil (HDS-SRGO) to less than 10 ppm. The used adsorption bed of ACF was also used in the pretreatment of SRGO before it entered the HDS unit. It was found that ACF showed high performance.

In many studies activated carbon has been modified by incorporation of metals on its surface and treatment with different acids which has shown an increase in the removal efficiency of DBT's. The reason for this increase is believed to be π-complexation of sulfur molecule with the metal and also because of oxidation (Srivastava, 2012).

Cao et al. (2008) loaded silver on commercial carbon in different amount. Different characterization tests like XRD, SEM and FTIR were carried out in order to study the chemical properties of the sample before and after adsorption. It was found that π-complex was formed between silver and sulfur and better results were obtained for higher loading.

Selvavathi et al. (2009) loaded Ni on activated carbon and also used two modified activated carbon treated with HNO_3 as the adsorbent to remove 4-methyldibenzothiophene (4-MDBT), dibenzothiophene (DBT) and 4,6-dimethyl-dibenzothiophene (4,6-DMDBT) from diesel oil. They found that the two modified activated carbon had better removal efficiency as compared to Ni loaded activated carbon.

Seredych and Bandosz (2010) investigated three activated carbon derived from a polymer loaded with Fe and Cu as adsorbents for removal of DBT and 4,6-dimethyl-dibenzothiophene (4,6-DMDBT). XRD, SEM, etc. were carried out before and after adsorption. It was concluded that due to the presence of Cu and Fe selectivity for DBT and 4,6-DMDBT increased as compared to naphthalene due to changes in the volume of micropore. The Fe and Cu/CuO species first oxidized the sulfur compounds and then the oxidized product was adsorbed on the carbon surface.

Fallah and Azizian (2012) studied the adsorption of BT, 4,6-DMDBT and DBT onto activated carbon cloths and also on modified ACC. Modification was done by treatment with HCl, $HNO_{3,}$ NaOH, $H_2SO_{4,\ etc}$. Adsorption study was done with both kinetic and equilibrium point of view. The experimental data was fitted to Langmuir, Freundlich curves. It was concluded that HNO_3 treated ACC showed highest removal efficiency. Regeneration of ACC was also studied.

Seredych et al. (2012) incorporated oxygen, sulfur and phosphorous atoms into the polymer derived activated carbon and studied the removal of DBT and 4,6-DMDBT from model fuel. It was concluded that phosphorous loaded carbon showed highest selectivity when phosphorous was present in the form of pyrophosphates and P_2O_5. It was suggested that in case of phosphorous adsorption mechanism was also different as it doesn't allow oxidation of the sulfur compounds and also phosphorous being a bulky group was present in pores of larger size where the molecules were adsorbed by dispersive forces. The adsorbent was thermally regenerated because of its stable surface and also due to physical adsorption.

2.1.1.2. Studies based on activated alumina: Activated alumina being crystalline in nature has oxygen vacancies on its surface and its surface can be modified easily either by treatment with HCl or HNO_3 or with alkaline.

Etemadi and Yen (2007) compared the morphological structure of nanoparticles alumina and acidic amorphous alumina and also studied the effect of calcination on the alumina particles with the help of SEM. They found that adsorption capacity of nanoparticles alumina was higher although their surface area was lower as compared to amorphous alumina. It was concluded that because of surface irregularities, more topological traps and absence of crystallanity nanoparticles alumina had higher adsorption capacity.

Srivastav and Srivastava (2009) reported the use of activated alumina (Al_2O_3) as adsorbent for the removal of DBT from n-hexadecane. The optimum dose was found to be 20g/l. Langmuir adsorption isotherm showed best fit for the equilibrium data. It was suggested that the carbon oxygen functional groups present on the surface of alumina were responsible for the adsorption of sulfur compound.

Sarda et al. (2012) prepared different adsorbents by varying Ni/Cu loading on activated alumina and ZSM-5 so as to remove sulfur compounds from diesel. To further improve their removal efficiency H_2O_2 was used as oxidizing agent. It was concluded that sulfur removal depends on the amount of loading, type of support and nature of metal. It was found that 10%Ni/Al_2O_3 showed higher removal as compared to Cu/Al_2O_3 and Ni/ZSM-5. 90% of sulfur was removed using Ni/Al_2O_3. Using 10%Ni/Al_2O_3 fixed bed experiment were carried out and effect of bed height, flowrate and oxidizing agent on the removal were analyzed. The adsorption capacity was found to be 496mgS/kg.

2.1.1.3. Studies based on Zirconia: Zirconia has been used for isomerization (Watanabe et al., 2005), hydrocarbon alkylation (Wang et al., 2007), etc. It has been used by many researchers for the removal of thiophene from n-heptane and n-octane (Wang et al., 2009) and its adsorptive properties were also found to be good.

Baeza et al. (2008) used Cu loaded zirconia for separating thiophenes from a model fuel having initial sulfur concentration of 2000 ppm dissolved in n-octane. It was concluded that as the percentage loading of Cu increased removal efficiency also increased and was found to be maximum for 3%Cu loading. The adsorption capacity was found to be 0.49 mmol/g of the adsorbent.

Kumar et al. (2011) prepared different zirconia samples (dried zirconia, sulfated and calcined zirconia at 893K and calcined zirconia at 893K) and used these for the desulfurization of model fuel (DBT dissolved in iso-octane). The adsorption system reached equilibrium state after 22 h and optimum adsorbent dose was found to be 20 g/l for the system. They also fitted the adsorption equilibrium data and BET adsorption isotherm was found to have best fit.

2.1.1.4. Studies based on Zeolites: Zeolites have high surface area, stable structure and metal cations that can be exchanged. Zeolites are basically aluminosilicates of metals like Na, K and Ca. SiO_4 and Al_2O_3 are the primary units of zeolites which are arranged in a polyhedral structure. In order to remove thiophenic compounds via π complexation d-block elements like Ag^{2+}, Cu^{2+}, etc. are introduced into zeolites. Several adsorbents have been reported which show high adsorption capacity for sulfur compounds including thiophenes and 4,6-DMDBT via π-complexation.

Maldonado et al. (2005) studied desulfurization of gasoline, jet fuels and diesel by using sorbents formed by ion exchange of zeolites with Cu^{2+}, Zn^{2+} and Ni^{2+} using different techniques. They carried the adsorption test using fixed-bed. It was found that desulfurization performance of sorbents followed the order $Cu^{+} > Ni^{2+} > Zn^{2+}$. Cu(I)-Y was found to be the best sorbent and the equilibrium adsorption capacity was found to be 0.395 mmolS/g for jet fuel and 0.278 mmol S/g for diesel.

Maldonado et al. (2006) removed sulfur and nitrogen compounds from diesel, gasoline and jet fuel with the help of π-complexation sorbents which contained Cu^{+}, Pd^{2+}, Ag^{+}, Ni^{2+} metal cations and these metal cations formed π bond with the thiophenes or pyridine rings. For denitrogenation and desulfurization of diesel fixed bed of CuY zeolite was used. The sorbents showed high selectivity for sulfur and nitrogen compounds as compared to other aromatics. Regeneration of sorbent was carried in two ways either by heating in air at 350^{o}C or by ultrasound assisted desorption.

2.1.1.5. MOF (metal-organic framework) based adsorbents: From the above studies it has been concluded that π complex based adsorbents can selectively remove thiophene but for this a porous support is required for high dispersion. MOF’s are a good choice because they have high porosity ranging from microporous to mesoporous pores (Stock and Biswas, 2012). Lot of work has been done on the use of MOF's for the removal of sulfur compounds from both gaseous and liquid phase.

Achmann et al. (2010) investigated many MOF for removal of sulfur from fuel. The model fuel consisted of tetrahydrothiophene and thiophene. They found that Cu containing MOF (copper benzene-1,3,5-tricarboxylate) showed maximum removal efficiency by reducing 78% sulfur content in thiophene and 86% in THT. It was found that most of the removal took place during the initial 60min.

Brieva et al. (2011) found that adsorption of DBT on MOF's at ambient temperature is higher as compared to Y-Zeolites. They also concluded that adsorption was higher for Cu (C300) and Al (Al00) containing MOF than Fe (F300) MOF. MOF's were also regenerated at the end of the experiments. It was also concluded that some of the adsorbed sulfur of regenerated MOF was converted to S(VI) form.

Khan and Jhung (2012) evaluated Cu^+ loaded MOF's for the adsorption of benz othiophene (BT). It was found that the adsorption capacity increased with Cu^+ loading till Cu/Fe ratio of 0.07 and the increase in Q_0 was about 14% as compared to MIL-110-Fe without Cu^+. It was concluded that although due to Cu^+ loading the surface area decreases but increase in Q_0 may be due to the increased π complexation of Cu^+ with BT.

2.1.1.6. Ni based adsorbents: Ma et al. (2005) conducted adsorptive desulfurization of gasoline at a temperature of 25-200°C under atmospheric pressure over Ni-Al adsorbent. It was found that the adsorbent was highly selective and had high capacity for desulfurization of gasoline. They also concluded that at room temperature olefins inhibited desulfurization but by increasing the temperature performance was increased. On the basis of experimental result it was shown that C-S bond cleavage was responsible for the adsorption of S compound on the sorbent.

2.1.2. Reactive Adsorption

This method combines the advantages of both adsorption and catalytic technologies. It can remove stable sulfur compounds like thiophene and a low concentration can be achieved. In this the sulfur compounds react with the sorbent in presence of H_2. S-Sorb process was developed by the Conoco Phillips Petroleum Company that used various sorbents for the removal of S compounds from gasoline oil by reactive adsorption (Khare et al., 1995).

Landau et al. (2008) performed adsorptive desulfurization of gasoline (22 ppmw) in a fixed bed reactor of Ni/Al-SiO_2 at 503K. It was seen that by adding 3wt% ethanol to gasoline the adsorption capacity increased to 2wt% (mass of sulfur per unit mass of adsorbent). They suggested three ways of improving sorbent capacity: (i) Ni_3C was formed which had higher reactivity for sulfur compounds as compared to metallic Ni, (ii) carbon deposit was reduced in presence of H_2 and (iii) presence of H_2 formed during the dehydrogenation of EtOH leads to the formation of Ni_3S_4 and changes the mode of desulfurization from chemisorption to fast reactive adsorption.

Zhang et al. (2010) studied the effect of structure of ZnO on desulfurization activity so as to understand thiophene reactive adsorption on Ni/ZnO. Firstly they synthesized ZnO and then with the help of incipient impregnation they prepared Ni/ZnO. It was found that the size of Ni/ZnO varied with calcination temperature. It was concluded that ZnO played an important role in the removal of S as it got converted into ZnS during adsorption process. It was also found that ZnO particles having small crystal particles with large surface area showed exhibited good adsorption.

Bezverkhyy et al. (2009) used Ni/SiO_2 in a fixed bed reactor as sorbent for the removal of thiophene. Reaction took place in presence of H_2 at 280-360^oC and thiophene pressure was 10-40 mbar. It was found that H_2S was present in the reaction mixture from the beginning and the catalytic activity of adsorbent decreased as NiO converted to Ni_2S_3. It was concluded that there is no direct interaction between thiophene and Ni/SiO_2. At first thiophene gets desulfurize and then the H_2S formed reacts with Ni. As the adsorption process continued, H_2S amount decreased and its partial pressure dropped to some equilibrium value. Because of this it was suggested that system achieved steady state. It was also concluded that the stability of Ni particles in presence of S compounds was due to the catalytic reaction involvement.

Zhang et al. (2012) used Ni/ZnO (5wt% NiO) as adsorbent in a fixed bed reactor for the removal of thiophene in model gasoline. With the help of impregnation technique different size of ZnO particles were prepared and characterized by XRD, TEM, etc. It was concluded that as the size of ZnO particles decreased adsorption capacity of Ni/ZnO increased. It was suggested that removal capacity of Ni/ZnO for S was higher for small ZnO particles due to higher dispersion of Ni.

2.2. ADSORPTIVE DESULFURIZATION AND ADSORPTIVE DENITROGENATION

Nitrogen compounds present in diesel feedstock act as strong inhibitors for desulfurization. The main nitrogen compounds present in diesel include carbazole and indole which accounts for 75% of total nitrogen composition and rest is quinoline (Laredo et al., 2002). Different adsorbents have been used for the removal of N compound from model oil e.g. activated alumina (Almarri et al., 2009), molecular sieves (Zhang et al., 2010), activated carbon (Wen et al., 2010), etc.

Kim et al. (2008) studied adsorptive desulfurization and denitrogenation using three adsorbents namely activated carbon, Ni/SiO_2-Al_2O_3 and alumina using model diesel fuel containing indole, quinoline, DBT, 4,6-DMDBT, naphthalene, 1-methyl naphthalene. It was found that activated carbon showed highest selectivity among the three adsorbents and it was due to hydrogen bonding which is responsible for desulfurization and denitrogenation. In case of Ni/SiO_2-Al_2O_3 direct interaction exists between Ni and S. On the other hand for alumina it was suggested that acid-base interaction and electrostatic potential leads to desulfurization.

Almarri et al. (2009) studied the removal of N compound (indole and quinoline) along with sulfur compounds (4,6-DMDBT and DBT) using seven different samples of activated carbon and three different samples of activated alumina. They found that nitrogen compounds were removed more by activated carbon than by activated alumina. They concluded that with the increase in oxygen concentration of activated carbon removal capacity of N compound increased and functional groups containing oxygen determined the removal of sulfur and nitrogen compounds.

Koriakin et al. (2010) removed N compounds from residue diesel of HDS process by preparing and using mesoporous Li modified silica adsorbents in batch experiments conducted at 45^0C. It was found that the adsorbents showed higher affinity for N compounds than S compounds. They also regenerated the adsorbent by using organic solvent.

Table 2.1 Literature review on adsorption of S and N compounds on different adsorbent.

Process	System	Adsorbent	Model oil	S and N compound	Initial Conc (S_0)	Optimum conditions & Result	Reference
Adsorption	Fixed bed	Cu(I)-Y and Ni(II)-zeolites	Gasoline, diesel		335 and 297.2 ppmw	Max. removal for Cu(I)-Y Q_0 = 0.167and 0.143 (mmolS/g)	Maldonado et al., 2005.
Adsorption	Fixed bed	Cu(I)Y zeolite	n-octane	Benzene, thiophene, BT, DBT, Carbazole, quinoline, fluorine, naphthalene, phenanthrene	PAH= (1.6 mmol/l), Nitrogen compd (1.6 mmol/l). S=100 ppmw	C_e = 0.1 ppm	Jayaraman et al., 2006
Adsorption	Fixed bed reactor	Cu loaded on zirconia	n-octane	Thiophene	2000 ppm	T = 180^0C, Q_0 = 0.3 mmol/gm.	Baeza et al., 2008.
Adsorption	Fixed bed	Activated carbon, alumina, Ni/SiO_2-Al_2O_3		Indole, quinoline, DBT, 4,6DMDBT, Naphthalene, 1-methyl naphthalene	687 ppmw (S), 303 ppmw (N)	T = 25^0C, Q_0 = 0.223 mmolS/g, Q_0 = 1.067 mmolN/g.	Kim et al., 2008.
Reactive adsorption	Fixed bed reactor	Ni on mesoporous silica.	Diesel		11.7 ppmw	T = 200^0C, Ni conc = 30%,, Removal = 99%	Park et al., 2008.
Adsorption	Batch reactor	Ce/Ni-Y zeolites	n-octane	DBT	500 ppm	T = 25^0C, t = 2 h, Removal = 54%, Q_0 = 11 mg/g.	Wang et al., 2009.
Adsorption	Batch	Activated carbon Activated alumina	Decane, n-tetradecane	DBT, 4,6-DMDBT, quinoline, indole	16.4 mmol/l(N) .015 mol/l(S)	Activated carbon Q_0 = 0.8 (mmolN/g) and Activated alumina Q_0 = 0.34 (mmolN/g) =0.05 S/g)	Almarri et al., 2009
Adsorption	Batch system	Activated alumina	n-hexane	DBT	500 ppm	t = 24 h, dose = 20 g/l, T = 30^0C	Srivastav and Srivastava, 2009.

Reactive adsorption	Packed bed	Polymer derived carbon with Cu and Fe loading	Decane and hexadecane	DBT, 4,6-DMDBT, Naphthalene, 1-methyl naphthalene	20 ppmw	T = 25^0C,P = 1 atm,	Seredych and Bandosz, 2010.
Adsorption	Batch	Mesoporous molecular sieve (Si-Zr)	Diesel		16.5 mmol/l(N), 0.011 mol/l(S)	0.66 (mmolN/g) 0.02 (mmolS/g)	Koriakin et al., 2010
Adsorption	Batch	Activated carbon	Do-decane	Carbazole, indole, quinoline, DBT	18 mmol/l(N) 0.018 mmol/l(S)	1.19 (mmolN/g), 1.12 (mmolS/g)	Wen et al., 2010
Adsorption	Batch	Zirconia	Iso-octane	DBT	1000 ppm	T = 30^0C, t = 22 h, Dose = 20 g/l	Kumar et al., 2011.
Adsorption	Fixed Bed	Activated carbon	Diesel	DBT 4,6-Me$_2$DBT	500 ppm	T=75^0C, removal = 90%	Bu et al., 2011
Adsorption	Batch system	Modified activated carbon cloth	n-heptane	BT, DBT, 4,6-DMDBT	450 ppm	T = 30^0C t = 40 min, % removal = 90%	Fallah and Azizian, 2012.
Adsorption	Batch and Column	Ni/Cu loading on ZSM-5 and activated alumina	Diesel	BT, DBT, 4-MDBT, 4,6-DMDBT	325 ppmw	T = 27^0C, P = 1atms Adorption capacity(Column adsorption)=496 mgS/Kg Removal=90% (Ni/Al$_2$O$_3$)	Sarda et al., 2012.
Adsorption	Batch reactor	Metal organic framework	2,2,4 trimethyl pentane	DBT	1724 ppm	T=31^0C, higher adsorption on Cu and Al MOF as compared to Fe MOF.	Brieva et al., 2012.
Adsorption	Batch system	Cu loaded MOF	n-octane	BT	5000-50 µg/g.	T=25^0C,t=24h, Q_0= 154mg/g	Khan and Jhung, 2012.
Reactive Adsorption	Fixed bed reactor	Ni/ZnO	n-heptane	Thiophene	500 ppm	T=280^0C, Q_0=84mg /g Removal=100%	Zhang et al., 2012
Adsorption	Batch	Ni$_2$P/SBA15	Paraffin	Carbazole, indole, quinoline, DBT	999.9 (ppmwN), 761.60 (ppmwS)	q_e = 9.1mg/g (N)	Shahriar et al., 2012

CHAPTER-3

FUNDAMENTALS OF ADSORPTION

Adsorption is a surface phenomenon in which solute molecules may be in liquid or gaseous state adheres to a solid surface. The solid surface is known as adsorbent while solute molecule that adheres to its surface is adsorbate. Adsorption is a result of surface energy. Atoms present on the surface of the adsorbate are bond deficient as they are not surrounded by other atoms. This deficiency causes the solute molecule to stick to the adsorbent surface. The nature of binding depends on the type of interaction and based on this adsorption is classified into two categories. First is physisorption which is due to molecular or dipole forces and other is chemisorption in which molecule gets attached to the surface through a chemical bond.
(http://www.rpiedu/dept/chem-eng/Biotech-Environ/Adsorb/adsorb.htm)

3.1. ADSORPTION PROCESS

Adsorption rate depends on the rate of solute transfer from the bulk of the solution to the adsorbate surface. This transfer involves four steps. First is diffusion of the species through a stationary film that surrounds the adsorbent. Second is diffusion through macropores and in the third step through micro pores and lastly adsorption occurs at the appropriate site. Last step occurs very fast while second is the slowest. If the film thickness is very less than the main resistance is offered by diffusion step. The intraparticle diffusion model given by Weber and Morris is applied to competitive adsorption. The uptake of solute in a particle depends on fraction of diffusivity D and radius of the particle r. The plot of q_t against $t^{0.5}$ is multilinear (Allen et al., 1989).The first portion is instantaneous adsorption stage. The second stage where diffusion is rate controlled represents gradual adsorption stage and the third stage is equilibrium stage where diffusion slows down due to low concentration of solute (Ramachandran et al., 2011).

3.2. ADSORPTION KINETIC MODEL

Adsorption kinetics helps in studying the effect of contact time on adsorption rate. It also provides information on adsorption mechanism. Adsorption kinetics also helps in providing rate of adsorbate uptake which is required for finding optimum conditions (Alyuz and Veli, 2009).

3.2.1. Pseudo First Order Rate Equation

In order to describe the kinetic process of liquid-solid phase adsorption Lagergren (1898) presented a first-order rate. It is given below (Qiu et al., 2009):

$$\frac{dq_t}{dt} = k_f (q_e - q_t) \tag{3.1}$$

where, q_e is equilibrium adsorption uptake, q_t is adsorption capacity at time t and k_f is first order rate constant. Applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ gives

$$\ln\left(\frac{q_e}{q_e - q_t}\right) = k_f t \tag{3.2}$$

The above equation can be arranged as:

$$q_t = q_e[1 - \exp(-k_f t)] \tag{3.3}$$

This kinetic equation for adsorption is called pseudo first order equation so as to distinguish it from solution concentration.

3.2.2. Pseudo Second Order Rate Equation

The rate equation was given by Ho in 1995 by describing the kinetic process of adsorption for divalent metal ions on peat (Ho and Mckay, 1999).

The equation is given as:

$$\frac{dq_t}{dt} = k_s (q_e - q_t)^2 \tag{3.4}$$

where, K_s (g/(mg·min)) is the pseudo-second-order rate constant of adsorption, q_e is equilibrium adsorption uptake, q_t is adsorption capacity at time t.

Eq. (3.4) can be arranged as:

$$\frac{dq_t}{(q_e - q_t)^2} = k_s dt \tag{3.5}$$

Applying boundary conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$ gives

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_s t \tag{3.6}$$

It can also be written as:

$$q_t = \frac{t k_s {q_e}^2}{1 + t k_s q_e} \tag{3.7}$$

Eq. (3.7) is known as pseudo second order rate equation.

3.2.3. Intraparticle Diffusion Model

It was found that in many adsorption processes solution uptake varied proportionally with $t^{0.5}$ (Weber et al., 1963).

$$q_t = k_{id} t^{1/2} + I \tag{3.8}$$

where, I gives an idea about film thickness while k_{id} is the intra particle diffusion rate constant.

3.3. ADSORPTION ISOTHERMS

It is important to establish the right correlation for the equilibrium curves so as to optimize the adsorption system.

3.3.1. Mono-component Isotherm Equations

In order to describe the equilibrium characteristics of adsorption various isotherm equations like Langmuir, Freundlich, Redlich Peterson, etc. have been used. Freundlich isotherm is applicable for heterogeneous surfaces i.e. surface having sites of different affinities. According to this the sites with strong affinities are binded first and as the sites are occupied binding affinity decreases (Freundlich, 1906). According to this equation as the concentration of adsorbate increases the concentration of adsorbate on adsorbent also increases as it an exponential equation (Hamdaoui and Naffrechoux, 2007). The equation is given as:

$$q_e = k_f C_e^{1/n} \tag{3.9}$$

where k_f (mg/g(l/mg)$^{1/n}$) is defined as adsorption coefficient and represents amount of solute adsorbed per unit equilibrium concentration. Both k_f and n are Freundlich constants.

For monolayer sorption on the surface of an adsorbent having homogeneous sites Langmuir equation is valid (Langmuir, 1918). It is given as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad , \tag{3.10}$$

where, K_l is Langmuir constant and depends on the affinity of the sites and q_m (mg/g) is the amount of solute per unit weight of the adsorbent that forms a complete monolayer on its surface.

R-P isotherm can be applied for both homogeneous and heterogeneous surfaces and has three parameters (Redlich and Peterson, 1959). It is describes as follow:

$$q_e = \frac{K_{RP} C_e}{1 + (\alpha C_e)^{\beta}} \tag{3.11}$$

where, K_{RP} (1/g) and α (1/mg) are R-P isotherm constant, β is an exponent having value between 0 and 1. For high concentrations Eq. (3.11) reduces to Freundlich isotherm, Eq. (3.9) where $K_f = K_R/a_R$ and $1/n = (1-\beta)$ is known as heterogeneity factor. For β=1, Eq. (3.11) reduces to Eq. (3.10) i.e. Langmuir isotherm.

3.3.2. Multicomponent Isotherm Equatons

When more than one component is present in the solution then there is a competition for adsorption sites between the species as they interfere with each other. This leads to formation of complex equations for equilibrium. So relationship between quantity adsorbed of one species and concentration of other species are described by multicomponent adsorption isotherms (Aksu et al., 2002).

3.3.2.1. Non-modified Langmuir model: This multi-component isotherm predicts the amount of component (i) adsorbed per unit weight of the adsorbent ($q_{e.i}$) in the presence of other species at equilibrium (Nouri, 2002).

$$q_{e,i} = \frac{q_{m,i} K_{L,i} C_{e,i}}{1 + \sum_{j=1}^{N} K_{L,j} C_{ei}} \tag{3.12}$$

where, $C_{e,i}$ is the equilibrium concentration of component i in a mixture containing N components and $q_{m,i}$ and $K_{L,i}$ are model parameters derived from individual isotherm equations.

3.3.2.2. Modified Langmuir model: Sometimes the individual isotherm constants fail to predict the interactions between the components of the mixture. In order to make the model capable of predicting the complex adsorption system a correction factor was introduced to the non-modified model (Leitao and Serrao, 2005).The modified Langmuir model is given as:

$$q_{e,i} = \frac{q_{m,i} K_{L,i} (C_{e,i}/\eta_{L,i})}{1 + \sum_{j=1}^{N} K_{L,j} (C_{e,i}/\eta_{L,j})} \tag{3.13}$$

where, $q_{m,i}$ and $K_{L,i}$ are model parameters derived from individual isotherm equations and $\eta_{L,i}$ is correction parameter for component i and depends on the concentration of other species and is the characteristic of the species i. Its value is determined from the experimental data of multicomponent adsorption system.

3.3.2.3. Extended Langmuir isotherm model: It is assumed that the adsorption sites on the surface of adsorbent are uniform w.r.t. the energy of adsorption and all the ions (adsorbate species) present in the solution compete for the same sites. There is no interaction between the species (Butler and Ockrent, 1930). (Yang, 1987) extended the Langmuir equation for multicomponent system as:

$$q_{e,i} = \frac{q_{\max} K_i C_{e,i}}{1 + \sum_{j=1}^{N} K_j C_{e,j}} \tag{3.14}$$

where, $q_{\max}$ and K_i are Langmuir constants for maximum adsorption capacity of the adsorbents (mmol/g) and adsorptivity of the adsorbate (L/mmol) in single system, respectively.

3.3.2.4. Extended Freundlich isotherm model: For binary system Extended Freundlich model is given as (Kumar et al., 2011):

$$q_{e,1} = \frac{K_{f,1} C_{e,1}^{n_1 + x_1}}{C_{e,1}^{x_1} + y_1 C_{e,2}^{z_1}} \tag{3.15}$$

$$q_{e,2} = \frac{K_{f,2} C_{e,2}^{n_2 + x_2}}{C_{e,2}^{x_2} + y_2 C_{e,1}^{z_2}} \tag{3.16}$$

where, $K_{f,1}$, $K_{f,2}$, n_1 and n_2 are constants of single Freundlich equation while $x_1, x_2, y_1, y_2, z_1, z_2$ are parameters of extended Freundlich model for the two components.

3.3.2.5. Non-modified competitive Redlich-Peterson Model: The non modified competitive Redlich-Peterson model (Mckay and Duri, 1991) includes individual isotherm parameters and is given as:

$$q_{e,i} = \frac{K_{R,i} C_{e,i}}{1 + \sum_{j=1}^{N} a_{R,j} C_{e,j}^{\beta,j}} \tag{3.17}$$

where, $K_{R,i}$ (l/g), $a_{a,j}$ (l/mmol) are Redlich-Peterson isotherm constants for component i and β_i is dimensionless R-P isotherm constant for component i.

3.3.2.6. Modified competitive Redlich-Peterson isotherm equation: The competitive non-modified Redlich Peterson equation is modified by including an interaction factor η_i so as to account for the characteristic of each species which gives modified competitive R-P isotherm as follow (Srivastava et al., 2006):

$$q_{e,i} = \frac{K_{R,i}(C_{e,i}/\eta_{R,i})}{1+\sum_{j=1}^{N} a_{R,j}(C_{e,j}/\eta_{R,j})^{\beta,j}} \tag{3.18}$$

where, $\eta_{R,I}$ is estimated from competitive adsorption data.

3.3.3. Determination of Isotherm Parameters

The isotherm parameters of all multi component isotherms were found by minimizing sum square errors (SSE) by using Microsoft excel 2007. It has been used by many researchers (Ncibi, 2008; Luna et al., 2010). Here also SSE was minimized for the determination of parameters.

$$SSE = \sum_{i=1}^{N}\left(q_{e,calc} - q_{e,meas}\right)_i^2 \tag{3.19}$$

Here the subscript 'calc' and 'exp' stands for experimental and calculated data. $q_{e,i,}$ adsorption yield (Ad%) and total adsorption yield (Ad_{tot}%) are calculated using following relationship:

$$q_{e,i} = \left(C_{o,i} - C_{e.i}\right)\ V/w \tag{3.20}$$

$$Ad\% = 100(C_{0,i} - C_{e,i})/C_{0,i} \tag{3.21}$$

$$Ad_{tot}\% = 100\sum(C_{0,i} - C_{e,i})/\sum C_{0,i} \tag{3.22}$$

where, w is the mass of the adsorbent (g) and V is the volume of the solution (I).

3.4. THERMODYNAMICS STUDY

In order to differentiate physical and chemical adsorption heat of adsorption can be used. Gibb's free energy (ΔG) must decrease if the process is spontaneous. The second law of thermodynamics is:

$$\Delta G = \Delta H - T\Delta S \tag{3.23}$$

When the adsorbate to the surface of the adsorbent from the solution its entropy decreases as a result of this ΔS is negative and also entropy of the adsorbent remains unchanged. Hence for most of the adsorption ΔS is negative. From eq. (3.23) it is concluded that for ΔG to be negative

ΔH must be less than zero. So, for a process in which entropy decreases the process will be exothermic.

CHAPTER-4

MATERIALS AND METHODS

In this study, adsorption of nitrogenous compound (represented by quinoline) and sulfur compound (represented by dibenzothiophene (DBT)) onto nickel loaded activated carbon (Ni/AC) has been studied. Experimental details of the study have been presented in this chapter. These details include: batch study for adsorption and multicomponent adsorption study using Taguchi's method.

4.1. MATERIALS

Lab grade chemicals were used in this study. For adsorptive desulfurization and denitrogenation study, model fuel used was a mixture of quinoline and DBT dissolved in iso-octane. DBT was purchased from Spectrochem Pvt. Ltd. Mumbai, India. Quinoline and iso-octane (99.8%) were purchased from S.D. fine Chemicals, Mumbai, India. Iso-octane was used as a solvent. AC was purchased from S.D. fine Chemicals, Mumbai, India.

4.2. MODEL OIL

DBT and Quinoline in iso-octane were used for the preparation of model oil with different initial concentrations (C_o). For this preparation DBT was accurately weighed, quinoline was measured and dissolved in some amount of iso-octane. The final volume in the conical flask was made up by adding remaining required iso-octane. Fresh stock solution was prepared as required every day. The C_o was checked before the start of each experimental run accordingly. This model oil was used in adsorptive desulfurization.

4.3. PREPARATION OF ADSORBENT

AC of lab grade supplied by G.S. Chemical testing lab and allied industries was taken and washed with distilled water until it was free from ash. Then it was kept at 100 ^oC for 6 h for moisture removal. Washed AC was then treated with 30% HNO_3 and was again washed with distilled water unless the pH of the effluent became neutral (Guo et al., 2012). After this it was kept in the oven for 6 h so that the moisture is removed completely. The dried adsorbent then was treated for about 2 h by stirring with $Ni(NO_3)_2.6H_2O$ with different amount so as to obtain a loading of 1%, 2.5%, 5% and 10%. After loading it was again dried and then calcination was done at 200 ^oC, 400 ^oC and 600 ^oC for 3 h. The calcined adsorbent was then cooled under vacuum in the desiccator and was used for the removal of S and N compounds (Hernandez et al., 2010).

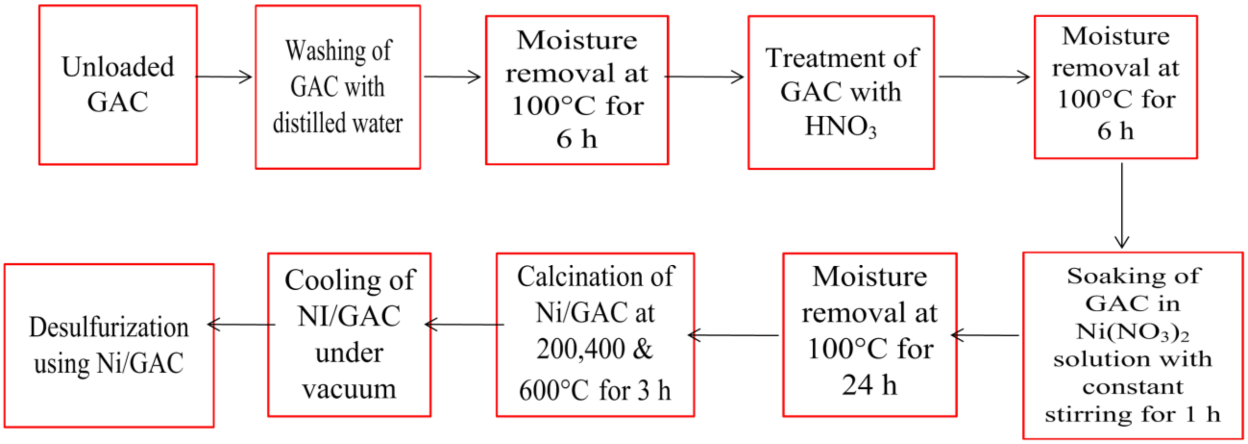


Figure 4.1 Preparation of nickel loaded activated carbon.

4.4. BATCH ADSORPTION STUDIES

In order to study the effects of various parameters like contact time (t), adsorbent dose (m) and temperature (T) on adsorption batch experiments were conducted. In a 100 ml conical flask 20 ml iso-octane was taken, some amount of DBT and quinoline were dissolved in it and required amount of adsorbent was added so as to prepare a solution of known concentration for each experimental run. In the orbital shaker (Remi Instruments, Mumbai) which is temperature controlled these flasks were agitated at a temperature of 30°C and at a constant shaking rate of 150 rpm. After 9 h the samples were withdrawn, filtered and saved for the analysis in Gas Chromatography Equipment (Netel (India) Limited).

4.4.1. Analysis of Quinoline and DBT

By using Gas Chromatograph (GC) containing flame ionization detector (FID) and having capillary column (length 30 m, internal diameter 0.53 mm, Film 0.88 µm) the concentration of N and S in the samples collected was determined. The injector temperature was set to 280°C and detector temperature was set to 300°C, respectively. The column temperature was started at 150°C for 3 min and was heated to 200°C at a rate of 10°C/min and stayed at 200°C for 2 min. The carrier flow (N_2) was 15 mL/min. 1 µL sample volume was injected for each GC-FID run. The sensibility (limit detection) is 2 ppm. The DBT in model sample was identified and analyzed by the standard samples.

Using the following relationship percentage removal of sulfur and nitrogen were calculated:

$$\% \text{ S or N removal} = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (4.1)$$

$$\text{Adsorption capacity} = \frac{C_o - C_e}{m} \qquad (4.2)$$

Where, C_o is the initial S and N concentration (mmol/l), and C_e is the equilibrium concentration (mmol/l).

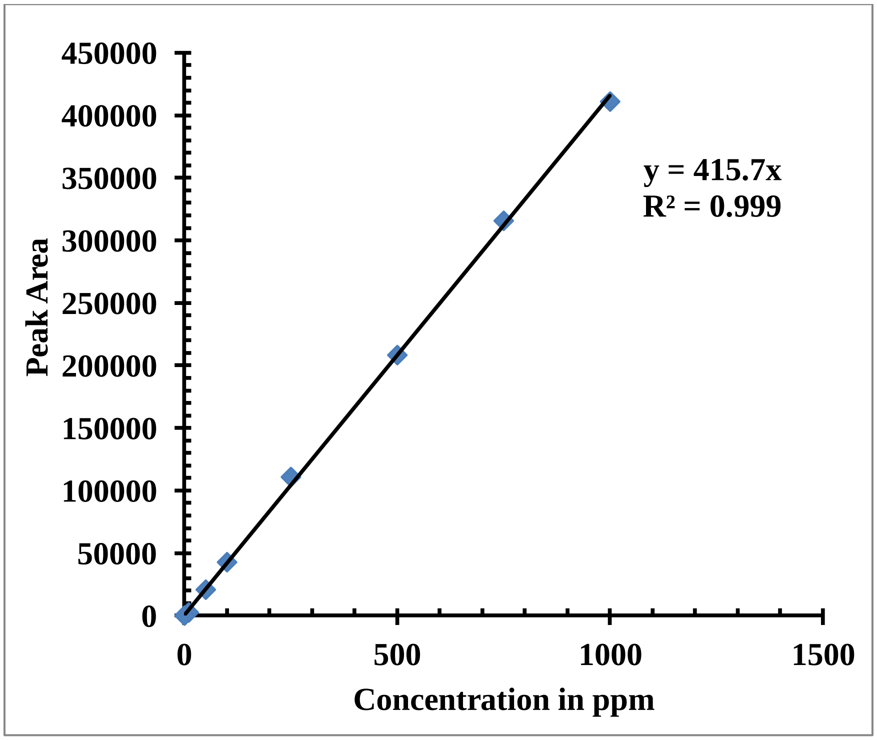


Figure 4.2 Calibration curve of dibenzothiophene.

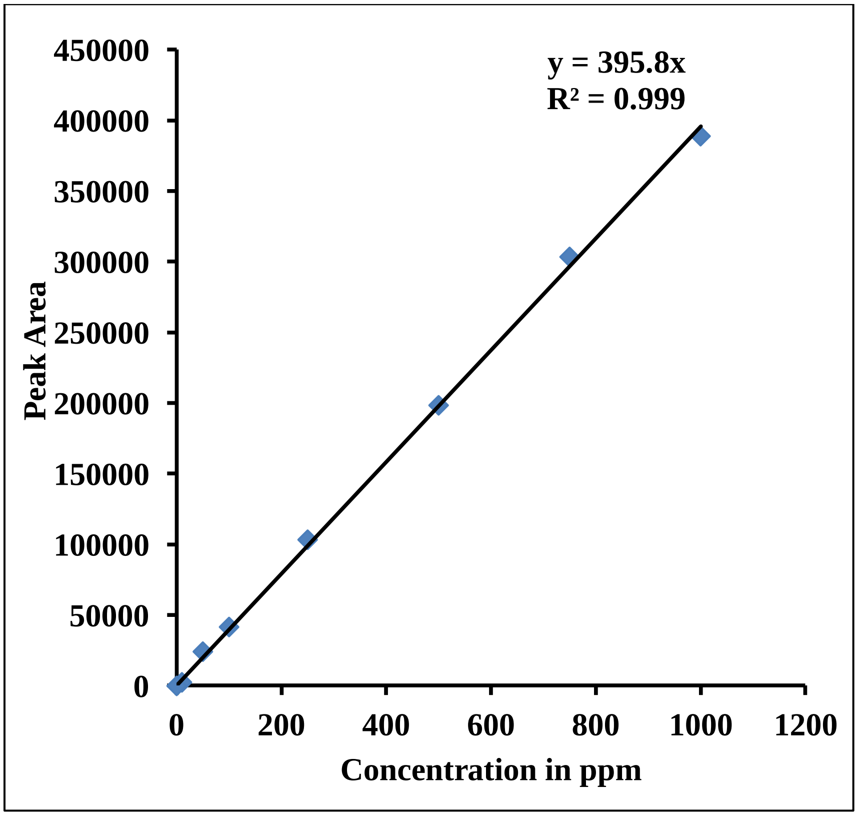


Figure 4.3 Calibration curve of quinoline.

4.5. ADSORPTION ISOTHERM EXPERIMENTS

For single component DBT and quinoline Ni/AC system was taken with initial concentrations of DBT and quinoline varied from 50 to 1000 ppm (viz., 50,100, 250, 400, 500, 600, 800 and 1000 ppm).

4.6. MULTI-COMPONENT ADSORPTION STUDY USING TAGUCHI'S METHOD

The Taguchi's method was developed by Genichi Taguchi and has been used to optimize the experimental variables as it minimizes time as well as cost of experiment(Chiang, 2005), (Zolfaghari et al., 2011). Taguchi's orthogonal arrays are used to show the effects of parameters. In the optimization of a process given steps should be followed for Taguchi's method (Phadke, 1989). First step is the identification of performance characteristics and selection of process parameters. Second is to decide how many process parameters are there and mutual effect of those parameters. Third is to select orthogonal array (OA) and parameters are assigned to it. After this experimental runs are taken according to the array arrangement. Then performance statistics are calculated. After this results are analyzed with the help of ANOVA. Finally optimized parameters are verified by confirmation experiments (Engin et al., 2008).

4.6.1. Experiment Design (Phase 1)

Firstly factors to be optimized were identified that affected the simultaneous removal of quinoline and DBT from iso-octane onto Ni/AC. The various factors to be optimized for the removal of sulfur and nitrogen from iso-octane were selected and ranges were decided based on the adsorbate removal using Ni/AC (Kumar et al., 2011; Srivastav and Srivastava, 2009). For the present study five process parameters were selected for experimental design based on the experience. The process parameters, their designations and level are given in Table 4.1. Two parameter interaction was studied between initial concentration of adsorbate i.e. $C_{o,S} \times C_{o,N}$ and $C_{o,S} \times C_{o,N}$ as the initial concentration of one adsorbate ($C_{o,i}$) affects the adsorption of other adsorbate in simultaneous adsorption.

In the second step matrix experiment was designed and data analysis procedure was defined. The appropriate OA was chosen as Taguchi provides many standard OA's. The selected OA must satisfy the following inequality:

Total degree of freedom required for the experiment ≤ Total degree of freedom (DOF) of the OA (Srivastava et al., 2007).

Table 4.1 Multi-component adsorption study parameters for the adsorption of S and N onto Ni/AC using Taguchi's OA.

Parameters			**Units**	**Levels**		
				0	1	2
A:	Initial concentration of S	$\mathbf{C_{0,S}}$	mmol/l	0	7.81	15.62
B:	Initial concentration of N	$\mathbf{C_{0,N}}$	mmol/l	0	17.86	35.71
C:	Temperature	**T**	(^{o}C)	15	30	45
D:	Adsorbent dose	**m**	(g/l)	2	10	18
E:	Contact time	**t**	(min)	60	360	660

Each parameter was further divided into three levels. With five parameters at three levels and two second order interaction the total DOF= 14 $\left[=5\times(3-1)+1\times4\right]$ since three level parameter has 2 DOF (no. of levels-1) and each two-parameter interaction has 4 DOF(2×2).

Therefore, L_{27} (3^{13}) OA (a standard 3 level OA) has been selected. The L_{27} array is shown in Table 4.2.

4.6.2. Experimentation Study (Phase 2)

For simultaneous removal of adsorbate batch experiments were performed by employing 27 trials with five process parameters in combination at three levels Table 4.2. The results obtained for each set as total amount of adsorbate adsorbed (q_{tot}) in mg per gm of ACC are shown in Table 4.2. For each experimental run 50 ml solution containing 25 ml each (viz. quinoline and DBT) adsorbate solution of known conc. was taken in a 100 ml stoppered conical flask with known amount of adsorbent. These flasks were agitated in a orbital shaker (Remi instruments, Mumbai) at 150 rpm maintained at 288 K, 303 K and 318 K. The samples were withdrawn after appropriate contact time and were analyzed for residual concentration.

The equilibrium adsorption uptake q_{tot} (mg/g) was calculated using the following relationship:

$$q_{tot} = \sum_{i=1}^{3} \left(C_{0,i} - C_{e,i} \right) / m \qquad (4.3)$$

where, $C_{0,i}$ is the initial adsorbate concentration (mmol/l), $C_{e,i}$ is the equilibrium adsorbate concentration (mmol/l) and m is the adsorbent dose (g/l).

4.6.3. Data Analysis and Performance Prediction (Phase 3)

The experimental data was analysed (i) to obtain the optimum conditions for adsorption, (ii) to identify the effect of individual parameters on adsorption (iii) to estimate q_{tot} at optimum conditions.

Taguchi has suggested many methods for analyzing the data and in this present study following methods have been used: (i) Plot of average response curves; (ii) ANOVA of data.

The plot of average response is a pictorial representation of the effect of parameter on the response and indicates the trend at each level of the parameter. It can be seen from the response curves that how the response varies with the change in levels of the parameter.

The optimal value of the response curve is measured as:

$$\mu = \overline{T} + (\overline{A_2} - \overline{T}) + (\overline{B_2} - \overline{T}) = \overline{A_2} + \overline{B_2} - \overline{T} \text{ (Srivastava et al., 2008)} \qquad (4.4)$$

where, $\overline{T}$ is the overall mean of the response and $\overline{A_2}$ and $\overline{B_2}$ are average value of response at second level of parameters A and B.

Table 4.2. Taguchi's L_{27} (3^{13}) orthogonal array for multi-component adsorption onto Ni/AC.

Exp. No.	1	2	3	4	5	6	7
	A	B	AxB	AxB	C	D	E
17	0	0	0	0	15	5	1
19	0	0	0	0	30	15	6
24	0	0	0	0	45	25	11
23	0	250	1	1	15	5	1
2	0	250	1	1	30	15	6
27	0	250	1	1	45	25	11
18	0	500	2	2	15	5	1
8	0	500	2	2	30	15	6
7	0	500	2	2	45	25	11
1	250	0	1	2	15	15	11
20	250	0	1	2	30	25	1
22	250	0	1	2	45	5	6
25	250	250	2	0	15	15	11
5	250	250	2	0	30	25	1
6	250	250	2	0	45	5	6
13	250	500	0	1	15	15	11
12	250	500	0	1	30	25	1
26	250	500	0	1	45	5	6
9	500	0	2	1	15	25	6
3	500	0	2	1	30	5	11
14	500	0	2	1	45	15	1
15	500	250	0	2	15	25	6
21	500	250	0	2	30	5	11
11	500	250	0	2	45	15	1
16	500	500	1	0	15	25	6
4	500	500	1	0	30	5	11
10	500	500	1	0	45	15	1

4.7 MULTI- COMPONENT ISOTHERM STUDY

For the multi-component study, binary mixture-Ni/AC system was taken. For each initial concentration of DBT (viz. 1.56, 3.12, 7.81, 15.62, 23.43 mmol/l), quinoline concentration was varied in the same range. The experiments were conducted at 303 K in the orbital shaker at a speed of 150 rpm. For each experimental run 10 ml of the adsorbate solution with some initial concentration C_o was taken in a 100 ml conical flask with 20 g/l adsorbent dose and was shaken for 11 h. The samples were withdrawn and analyzed for the residual concentration, C_e.

CHAPTER-5

RESULTS AND DISCUSSION

In this chapter, the results of the adsorption of nitrogenous compound (represented by quinoline) and sulfur compound (represented by dibenzothiophene (DBT)) onto nickel loaded activated carbon (Ni/AC) are reported and discussed. These results include characterization of the adsorbent, batch adsorption study of sulfur and nitrogen, and binary adsorption study of sulfur and nitrogen.

5.1. CHARACTERIZATION OF ADSORBENT:

X-ray diffraction for Ni/AC is shown in Figure 5.1. XRD analysis was carried out by using Phillips (Holland) diffraction unit (Model PW1140/90) with Cu as the target and Ni as the filter media. Radiation was maintained constant at 1.542 Å. Goniometric speed was maintained at 10°/min. Ni/AC before adsorption showed similar broad peaks at $2\Theta = 24^0$ and 44^0 which are indicative of amorphous carbons. The XRD patterns of Ni/AC after simultaneous DBT and quinoline adsorption (here-to-after referred as Ni/AC-SN) also indicates its amorphous state.

In accordance with the IUPAC classification pore size are classified as micro pores ($d < 20$ Å), meso pores (20 Å $< d <$ 500 Å) and macro pores ($d >$ 500 Å) (Srivastava et al., 2008). BET surface area analysis was performed using surface area and porosity analyzer (ASAP 2020, Micromeritics). Single point total pore volume after adsorption is 0.164 cm^3/g and before adsorption is 0.312 cm^3/g. BJH adsorption/desorption area of pores (17 Å $< d <$ 3000 Å) is 48.3 m^2/g and 37.6 m^2/g. BJH cumulative adsorption/desorption pore volume (17 Å $< d <$ 3000 Å) is 0.0337 cm^3/g and 0.0216 cm^3/g, respectively. AC has a high surface area of 591 m^2/g which decreases to 553.2 m^2/g for Ni/AC. This is due to the loading of Ni species onto AC in which loaded Ni may have blocked some of the microporous pores (Wang et al., 1998). The BET surface area of Ni/AC after simultaneous DBT and quinoline adsorption (here-to-after referred as Ni/AC-SN) further decreased to 302.4 m^2/g.

EDX of blank AC, Ni/AC and Ni/AC-SN was conducted shown in Figure 5.2. EDX analysis showed the presence of 86.83% C and 13.17% O in blank AC. While blank Ni/AC contained 88.22% C, 9.92% O and 1.87% Ni.

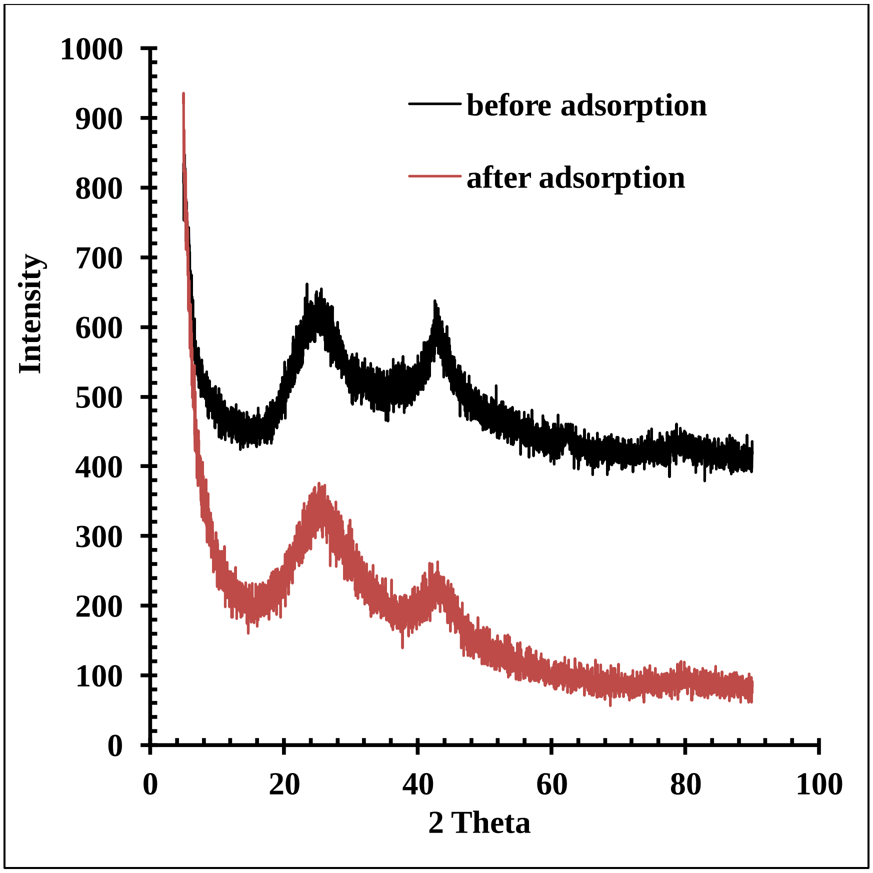
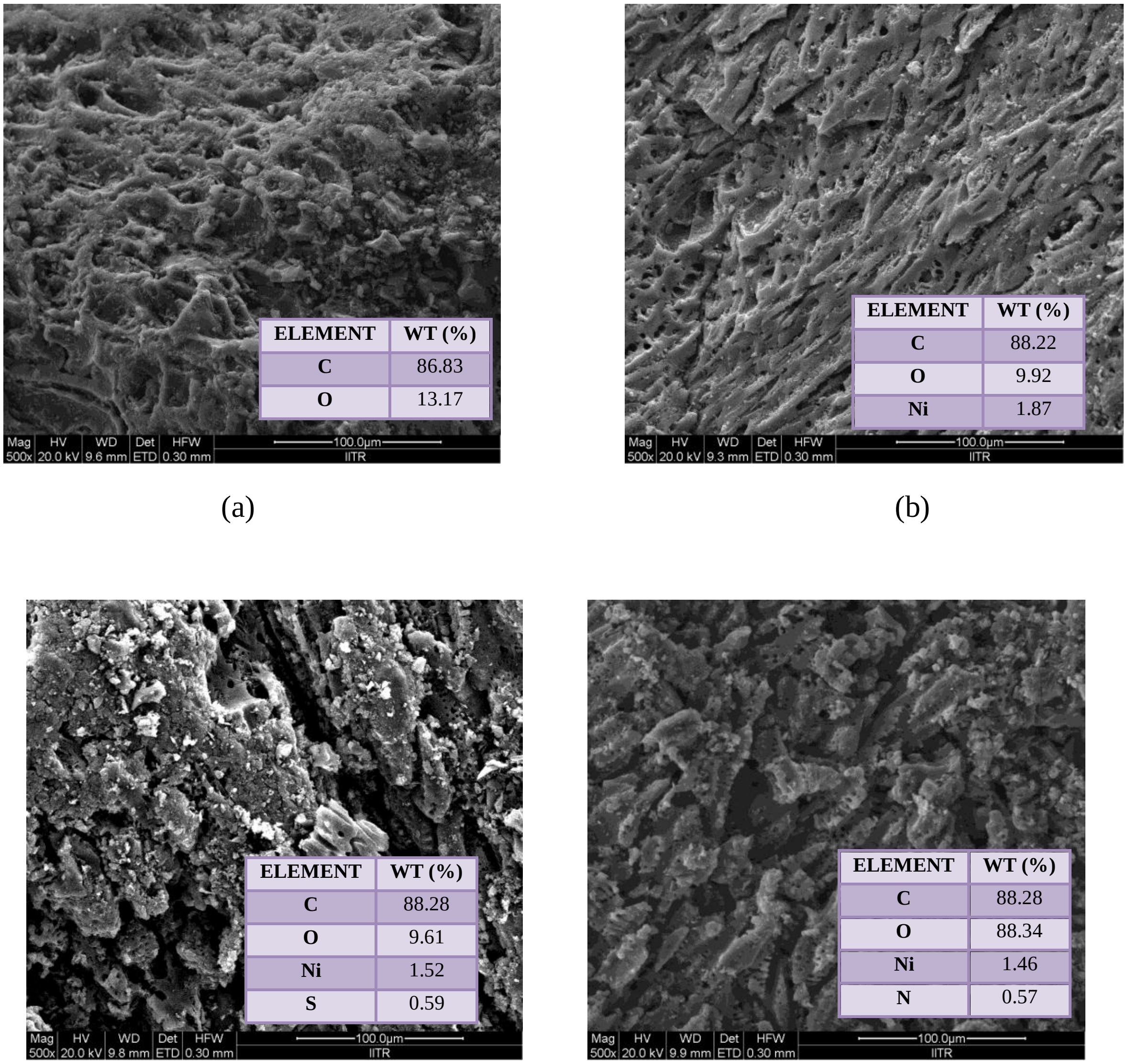


Figure 5.1 XRD pattern of Ni/AC before and after adsorption of N and S.

EDX analysis was also done after adsorption and showed 88.28% C, 9.61% O, 1.52% Ni and 0.59% S for sulfur loaded adsorbent (here-to-after referred as Ni/AC-S) while 88.34% C, 9.63% O, 1.46% Ni and 0.57% N for nitrogen loaded adsorbent (here-to-after referred as Ni/AC-N). The increase in C content after adsorption may be due to the loading of sulfur and nitrogen.

If possible it is necessary to dispose of the used Ni/AC or reutilize it for some useful purpose. This is essential due to the hazardous nature of the spent-AC. Thermogravimetry was performed to study the thermal degradation characteristics of DBT loaded Ni/AC. TGA, DTA, and DTG curves of the virgin and Ni/AC-SN at a heating rate of 10 K/min are shown in Figure 5.3 and Figure 5.4. Up to 400°C there is loss of water molecules and moisture. The weight loss was 18% for virgin-AC and 17.69% for Ni/AC-SN. Higher temperature drying (> 100°C) occurs due to loss of the surface tension bound water of the particles. Virgin Ni/AC and Ni/AC-SN do not show any endothermic transition between room temperature and 400°C, indicating no phase changes during the heating process. The weight loss increased between 400°C and 637 °C (77.46% weight loss) for virgin Ni/AC between 400 °C and 600 °C (80.8% weight loss).

In these temperature ranges, the virgin Ni/AC gets oxidized and loses its weight. The exothermic peak between 500–665°C represents degradation due to oxidation.



ELEMENT	WT (%)
C	86.83
O	13.17

(a)

ELEMENT	WT (%)
C	88.22
O	9.92
Ni	1.87

(b)

ELEMENT	WT (%)
C	88.28
O	9.61
Ni	1.52
S	0.59

(c)

ELEMENT	WT (%)
C	88.28
O	88.34
Ni	1.46
N	0.57

(d)

Figure 5.2 Fe-SEM images and EDX analysis of (a) Blank AC (b) Ni/AC (c) Ni/AC-S (d) Ni/AC-N.

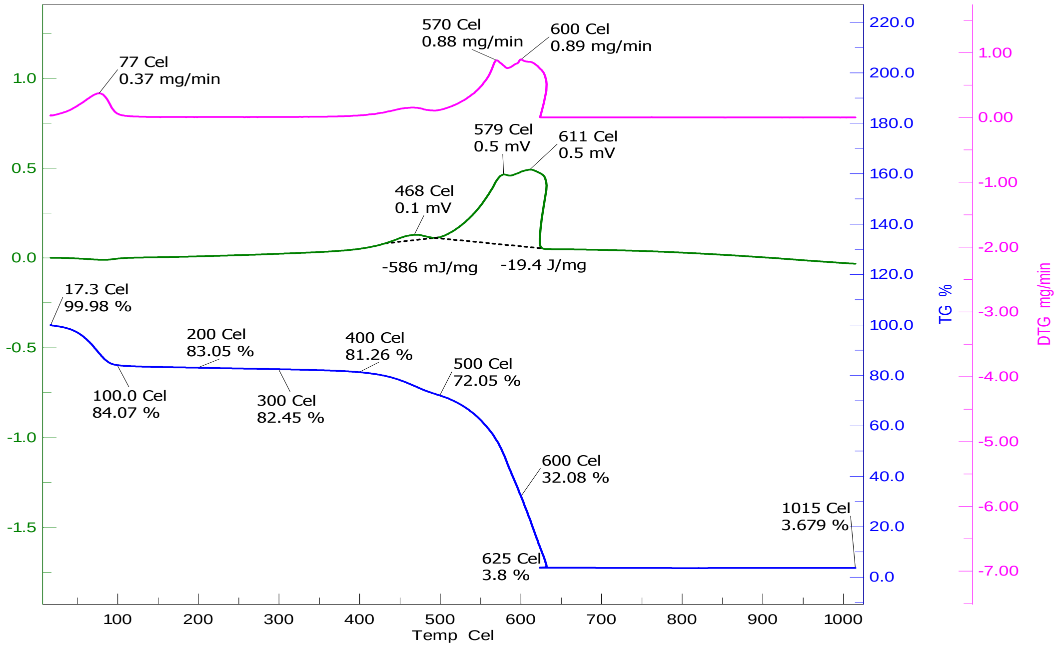


Figure 5.3 Differential thermal gravimetric and differential thermal analysis of Ni/AC before adsorption.

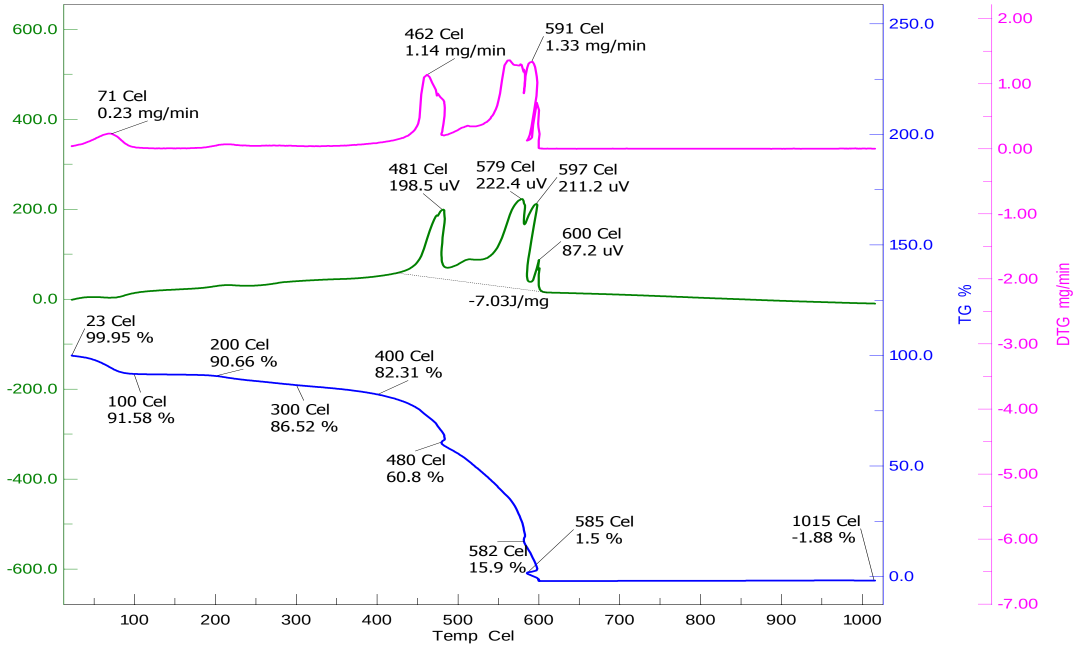


Figure 5.4 Differential thermal gravimetric and differential thermal analysis of Ni/AC after adsorption.

In order to understand the adsorption process it is important to have knowledge about the chemical structure of the adsorbent. The surface behavior and characteristics of the surface are influenced by the functional groups present on the surface of the adsorbent. Mostly carboxyl groups, carbonyl groups, phenolic hydroxyl groups and lactone group are the suggested functional groups. FTIR is a technique of identifying the functional groups responsible for the adsorption of S and N onto Ni/AC. FTIR of blank Ni/AC (Figure 5.5) shows a broad band at 3430.81 cm^{-1} that indicates the presence of free and hydrogen bonded OH group on its surface. At 1570 cm^{-1} the spectrum shows a broad band which indicates the presence of CO group due to aldehyde and ketone. The band around 1461 cm^{-1} may be due to carbonyl group which may be conjugated hydrocarbon bonded. At around 1200 cm^{-1} the spectra shows transmittance which may be due to –COH and Si-O-Si stretching or due to CC group vibration in lactones and also due to deformation of –OH group. The peak at around 750 cm^{-1} signifies SiH. It is seen that after adsorption there is a little shift in the peaks which may be accounted due to participation of functional groups in the process of adsorption. But the broad and weak bands do not provide relevant information about the mechanism of adsorption.

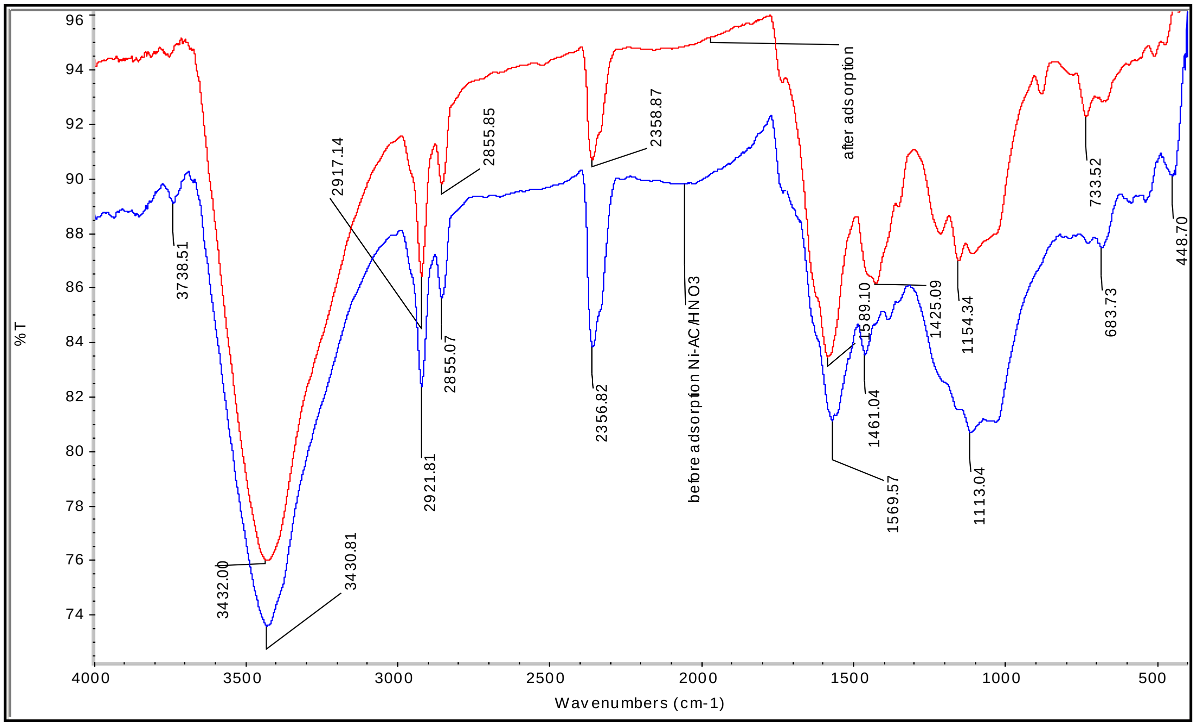


Figure 5.5 FTIR of Ni/AC before and after adsorption.

5.2. INDIVIDUAL ADSORPTION STUDY OF SULFUR AND NITROGEN

In order to study the effect of different parameters on adsorption batch experiments were performed. The effect of various parameters viz. time (t), adsorbent dose (m) and temperature (T) have been studied and are discussed in this section.

5.2.1. Effect of Loading

For single component system different percentage nickel loaded activated carbon were added in model fuel having initial concentration of $C_{o,S}$ = 15.62 mmol/l, $C_{o,N}$ = 35.71 mmol/l and these solutions around 100 ml in volume were kept in the orbital shaking incubator at 30^{o}C for 6 h. After 6 h the samples were withdrawn and analyzed using GC. It was found that 1% nickel loaded activated carbon calcined at 400 ^{0}C gave maximum removal in both the cases (Table 5.1).

5.2.2. Effect of Adsorbent Dose

The effect of dose (m) on the adsorption of S and N onto 1% Ni/AC was studied at T=303 K and $C_{o,S}$ = 15.62 mmol/l, $C_{o,N}$ = 35.71 mmol/l and the results are shown in Figure 5.8. The removal of S and N increased with an increase in m from 1 to 20 g/l. The removal remained unchanged for m >20 g/l. The increase in the adsorption with the Ni/AC dosage may be due to the availability of more adsorption sites and higher surface area. At about m = 20 g/l, the removal efficiency became almost constant for S and N removal by Ni/AC.

5.2.3. Effect of Time

It can be seen in the Figure 5.8 that the rate of S and N removal was found to be very rapid during the initial 60 min and after that the rate of removal decreased. It was found that the adsorptive removal of the S and N decreased after 9 h and 6 h of contacting with Ni/AC. This may be because a large number of vacant surface sites were available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Initially the pores of the adsorbent got saturated with solute molecules and after that the adsorbate molecules had to travel deeper into the micro-pores and faced larger resistance. As a result of this adsorption process slowed down after sometime.

Table 5.1 Effect of loading on removal (T=303 K, C_o = 15.625 mmol/l (S), t = 6 h).

Loading %	Calcination Temperature (^oC)	% Removal
1	200	25.65
1	400	42.22
2.5	200	22
2.5	400	33.23
5	200	26.2
5	400	29.6
10	200	13.27
10	400	15.49

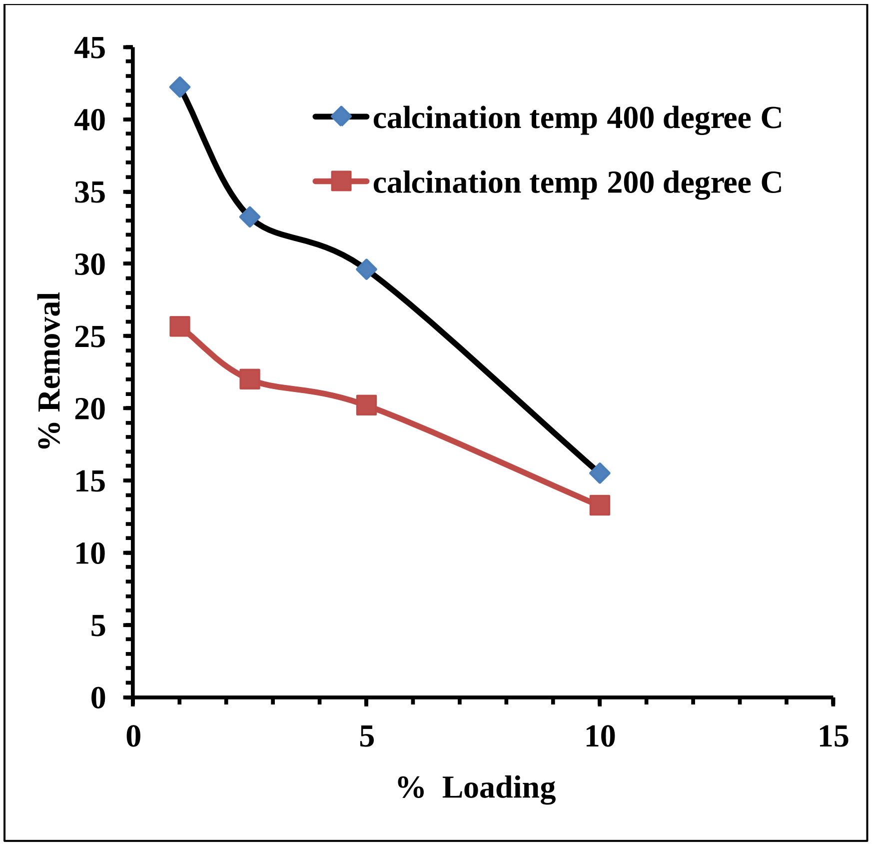


Figure 5.6 Percentage removal of sulfur versus % loading of Ni on activated carbon. ($C_{o,S}$ = 15.62 mmol/l, T = 303 K, t = 9 h).

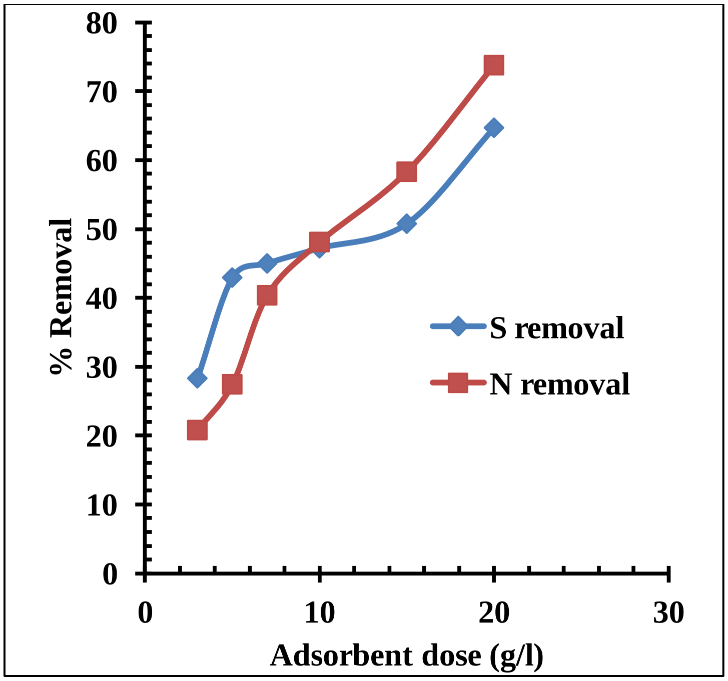


Figure 5.7 Effect of adsorbent dose on the removal of S and N.

($C_{o,S}$ =15.62 mmol/l, $C_{0,N}$=35.71 mmol/l, T=303 K, t=6 h (N), t=9 h (S)).

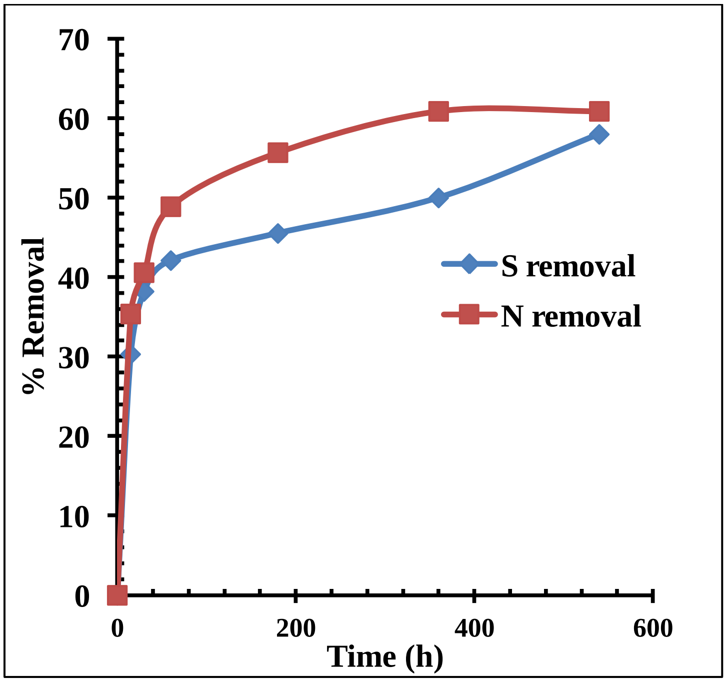


Figure 5.8 Effect of contact time on the removal of S and N.

($C_{o,S}$ =15.62 mmol/l, $C_{o,N}$ = 35.71 mmol/l, T= 303 K and m=10 g/l).

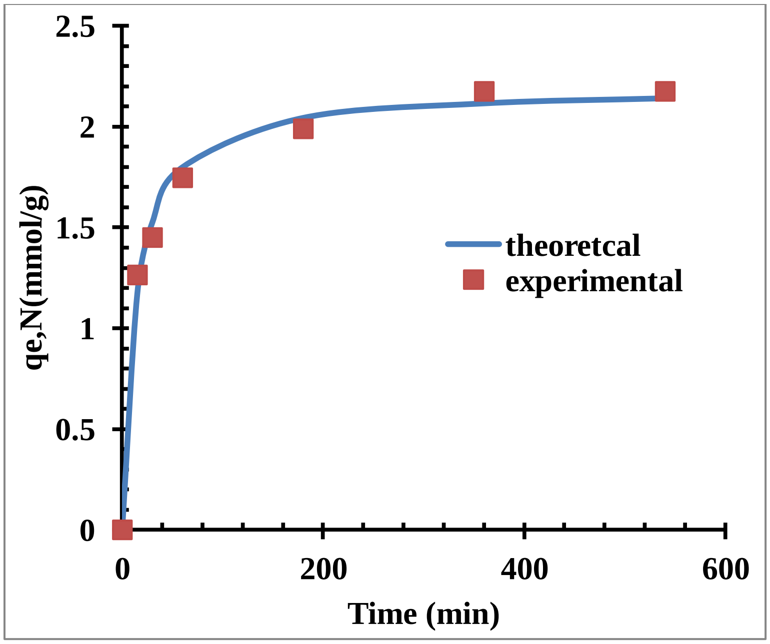
5.2.4. Adsorption Kinetics

5.2.4.1. Pseudo first order and second order model: Table 5.2 and Figure 5.9 shows the best fitting of pseudo 1st or 2nd order kinetics. S and N adsorption on Ni/AC at any instant (t) was studied by pseudo-first-order model and pseudo-second-order model.

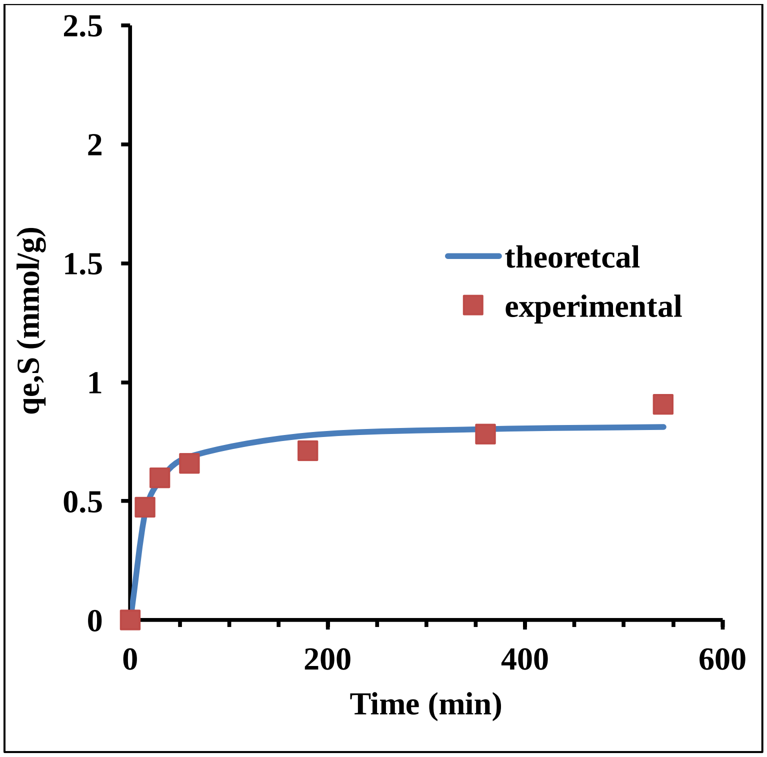
Table 5.2 shows the best fit values of kinetic parameters such as k_f, h, q_e and k_s along with the correlation coefficients, SSE and RMSE values for both pseudo-first order and pseudo second order models. The R^2 value for pseudo second order is higher than pseudo first order and hence it shows that the pseudo-second-order model best fits adsorption kinetic data for Ni/AC. Figure 5.9 shows the best fitting of the experimental value in the pseudo 2nd order kinetics for N and S. It is clear that the adsorption by Ni/AC follows the second- order – kinetics.

Table 5.2 Kinetic parameters for the removal of S and N by Ni/AC.

Sulfur (t = 9 h, C_0 = 15.625 mmol/l, m = 10 g/l, T = 30 °C).			
Pseudo 1st order		**Pseudo 2nd order**	
k_f (min^{-1})	0.05	k_s (g/mg min)	0.09
q_e (mg/g)	0.77	q_e (mg/g)	0.83
SSE	0.03	SSE	0.01
R^2 (non-linear)	0.94	R^2 (non-linear)	0.97
RMSE	0.02	RMSE	0.02
Nitrogen (t = 6 h, C_0 = 35.71 mmol/l, m = 10 g/l, T= 30 °C).			
Pseudo 1st order		**Pseudo 2nd order**	
k_f (min^{-1})	0.05	k_s (g/mg min)	0.03
q_e (mg/g)	2.05	q_e (mg/g)	2.19
SSE	0.12	SSE	0.02
R^2 (non-linear)	0.96	R^2 (non-linear)	0.99
RMSE	0.05	RMSE	0.02



(a)



(b)

Figure 5.9 Effect of contact time on the removal of (a) N and (b) S.

(t = 9 h, $C_{o,S}$ = 15.625 mmol/l, t = 6 h, $C_{o,N}$ = 35.71 mmol/l, m = 10 g/l).

5.2.4.2. Intraparticle diffusion model: Transfer of adsorbate molecule from the solution to the surface of the adsorbent is controlled either by film diffusion, surface diffusion, pore diffusion or adsorption. Intraparticle diffusion model suggests the possibility of intra-particle diffusion and is given as:

$$q_t = K_{td} t^{1/2} + I \qquad (5.1)$$

Where, I is the intercept and K_{td} is the intra particle diffusion rate constant (mg/g min$^{1/2}$). We can see in the Figure 5.10 and Figure 5.11 that graphs are not linear over the whole range of time which implies that more than one process is involved in adsorption and are controlling its rate. Slope of the two linear portions ($K_{id\ 1}$ and $K_{id\ 2}$) indicated the rate of adsorption. As the value of $K_{id\ 1}$ is higher than $K_{id\ 2}$ (Table 5.3) it suggests that the second linear portion is slower which may be due to low concentration of the adsorbate left in the solution. The intercept I indicates boundary layer thickness.

Table 5.3 Kinetic parameters for removal of S and N by Ni/AC. ($C_{0,S}$ = 15.625 mmol/l, $C_{o,N}$ = 35.71 mmol/l t=9 h, T = 303 K and m = 10 g/l).

Parameters	**S-Ni/AC adsorption system**	**N-Ni/AC adsorption system**
$K_{id\ 1}$	0.05	0.12
I_1	0.31	0.77
R^2	0.97	0.998
$K_{id\ 2}$	0.02	0.03
I_2	0.56	1.60
R^2	0.96	0.99

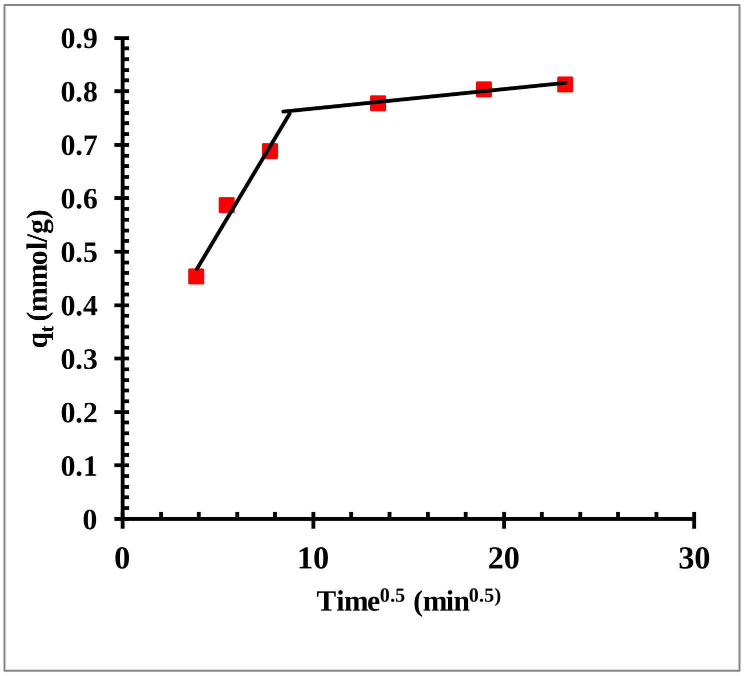


Figure 5.10 Weber and Morris plot for intraparticle diffusion of S onto Ni/AC. ($C_{o,S}$ = 15.625 mmol/l, T = 303 K and m= 10g/l).

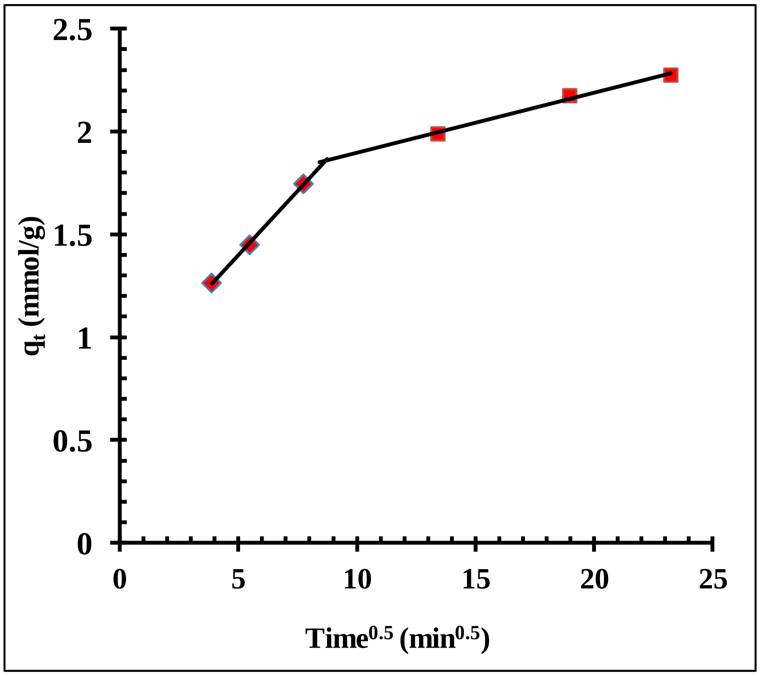


Figure 5.11 Weber and Morris plot for intraparticle diffusion of N onto Ni/AC. ($C_{o,N}$ = 35.71 mmol/l, T = 303 K and m= 10g/l).

5.2.5. Adsorption Equilibrium Study

5.2.5.1. Effect of temperature: As adsorption is an exothermic process it is expected that the adsorption capacity of the adsorbent should decrease with increase in temperature. But if the process is controlled by intraparticle transport pore diffusion the adsorption capacity will show an increase with increase in temperature because diffusion is an endothermic process. If the temperature increases then mobility of solute molecule increases and the retarding force on the molecule decreases as a result of which sorption capacity increases.

5.2.5.2. Single component adsorption isotherm modeling: Most commonly Freundlich and Langmuir equations are used isotherm study. For heterogeneous surfaces and at very low concentration Henry's law is valid. While Freundlich isotherm (Freundlich, 1906) is also used for heterogeneous surfaces but it does not approaches to Henry's law at low concentration. On the other hand Langmuir law (Langmuir, 1918) follows Henry's law at very low concentrations but is valid for homogeneous surfaces only. Redlich Peterson equation contains three parameters and it reduces to Henry's law at low concentrations while Freundlich law at very high concentration. Here three isotherm equations Freundlich, Langmuir and R-P equations have been used for fitting the data obtained from adsorption experiments of S and N onto Ni/AC. Sum of square error has been used to find out the best isotherm model for fitting experimental data.

The isotherm parameters and the value of correlation coefficient R^2 are given in the Table 5.4 and Table 5.5 for S and N. We can see from the Table 5.3 and Table 5.4 that R^2 value for R-P equation are closer to 1 as compared to other R^2 values obtained from other isotherm models. SSE value is also minimum for R-P model as compared to other isotherms. Hence R-P isotherm gives the best fit for the experimental data. The value of 1/n is less than unity for both S and N and it indicates that both are favorably adsorbed by Ni/AC at all temperatures. The equilibrium isotherm with the experimental data fit at different temperatures for S and N onto Ni/AC are shown in Figure 5.12 and Figure 5.13. It can be seen that at first when temperature was increased from $T = 288$ K to $T = 303$ K the adsorption capacity of the adsorbent increased but after this when temperature was further increased from $T = 303$ K to $T = 318$ K it decreased. As explained earlier that adsorption is an exothermic process so it is expected that the sorption capacity must decrease with temperature. But for $T \leq 303$ K it shows an increase which implies that both S and N adsorption onto Ni/AC may be diffusion controlled and diffusion is an endothermic process so removal efficiency increased (Kumar and Srivastava, 2012).

Table 5.4 Isotherm parameters for the adsorption of S on Ni/AC.

(t= 9h, $C_0 = 1.56$ mmol/l to 25 mmol/l, m=20 g/l).

<table>
<tr><td colspan="2">Freundlich</td><td colspan="2">$q_e = k_f c_e^{1/n}$</td><td colspan="2"></td></tr>
<tr><td>T(K)</td><td>K_f</td><td>1/n</td><td>R^2</td><td colspan="2">SSE</td></tr>
<tr><td>288</td><td>0.15</td><td>0.42</td><td>0.988</td><td colspan="2">0.004</td></tr>
<tr><td>303</td><td>0.25</td><td>0.58</td><td>0.998</td><td colspan="2">0.003</td></tr>
<tr><td>318</td><td>0.05</td><td>0.73</td><td>0.963</td><td colspan="2">0.009</td></tr>
<tr><td colspan="2">Langmuir</td><td colspan="2">$q_e = \frac{q_m k_l c_e}{1 + k_l c_e}$</td><td colspan="2"></td></tr>
<tr><td>T(K)</td><td>q_m</td><td>K_l</td><td>R^2</td><td colspan="2">SSE</td></tr>
<tr><td>288</td><td>0.55</td><td>0.31</td><td>0.992</td><td colspan="2">0.002</td></tr>
<tr><td>303</td><td>1.85</td><td>0.11</td><td>0.994</td><td colspan="2">0.017</td></tr>
<tr><td>318</td><td>1.18</td><td>0.03</td><td>0.973</td><td colspan="2">0.008</td></tr>
<tr><td colspan="2">Redlich Peterson</td><td colspan="2">$q_e = \frac{k_R c_e}{1 + a_R c_e^{\beta}}$</td><td colspan="2"></td></tr>
<tr><td>T(K)</td><td>K_R</td><td>a_r</td><td>B</td><td>R^2</td><td>SSE</td></tr>
<tr><td>288</td><td>0.29</td><td>0.98</td><td>0.78</td><td>0.993</td><td>0.001</td></tr>
<tr><td>303</td><td>22.92</td><td>87.75</td><td>0.42</td><td>0.998</td><td>0.002</td></tr>
<tr><td>318</td><td>67.30</td><td>1144.93</td><td>0.29</td><td>0.976</td><td>0.006</td></tr>
</table>

Table 5.5 Isotherm parameters for the adsorption of N on Ni/AC.

(t = 6 h, C_0= 3.57 mmol/l to 57.14 mmol/l, m = 20 g/l).

<table>
<tr><td colspan="2">Freundlich</td><td colspan="2">$q_e = k_f c_e^{1/n}$</td><td colspan="2"></td></tr>
<tr><td>T(K)</td><td>K_f</td><td>1/n</td><td>R^2</td><td colspan="2">SSE</td></tr>
<tr><td>288</td><td>0.16</td><td>0.47</td><td>0.996</td><td colspan="2">0.004</td></tr>
<tr><td>303</td><td>0.26</td><td>0.43</td><td>0.981</td><td colspan="2">0.036</td></tr>
<tr><td>318</td><td>0.21</td><td>0.44</td><td>0.996</td><td colspan="2">0.005</td></tr>
<tr><td colspan="2">Langmuir</td><td colspan="2">$q_e = \frac{q_m k_l c_e}{1 + k_l c_e}$</td><td colspan="2"></td></tr>
<tr><td>T(K)</td><td>q_m</td><td>K_l</td><td>R^2</td><td colspan="2">SSE</td></tr>
<tr><td>288</td><td>1.15</td><td>0.08</td><td>0.996</td><td colspan="2">0.007</td></tr>
<tr><td>303</td><td>1.41</td><td>0.13</td><td>0.995</td><td colspan="2">0.013</td></tr>
<tr><td>318</td><td>1.24</td><td>0.10</td><td>0.994</td><td colspan="2">0.012</td></tr>
<tr><td colspan="2">Redlich Peterson</td><td colspan="2">$q_e = \frac{k_R c_e}{1 + a_R c_e^{\beta}}$</td><td colspan="2"></td></tr>
<tr><td>T(K)</td><td>K_R</td><td>a_r</td><td>B</td><td>R^2</td><td>SSE</td></tr>
<tr><td>288</td><td>0.27</td><td>0.99</td><td>0.64</td><td>0.997</td><td>0.002</td></tr>
<tr><td>303</td><td>0.18</td><td>0.12</td><td>1</td><td>0.994</td><td>0.013</td></tr>
<tr><td>318</td><td>0.35</td><td>1.07</td><td>0.66</td><td>0.997</td><td>0.003</td></tr>
</table>

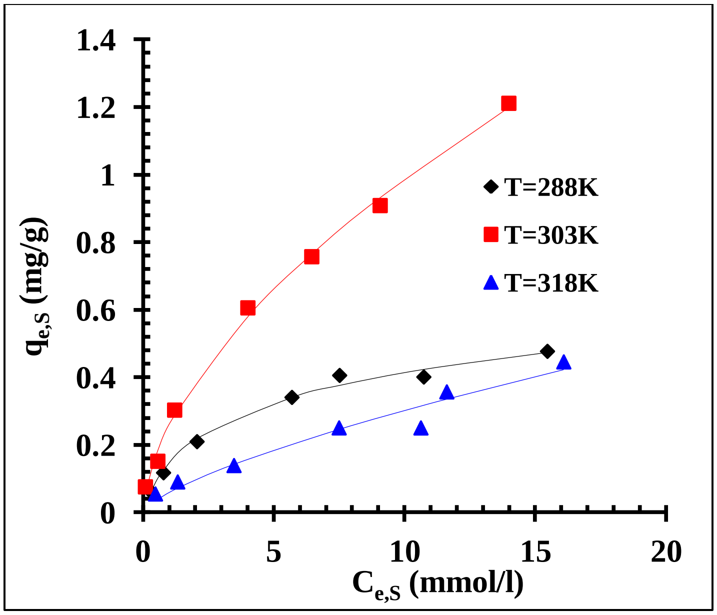


Figure 5.12 Mono-component adsorption isotherms for S at different temperature. (C_o = 1.56 mmol/l to 25 mmol/l, t = 9 h, m = 20 g/l).

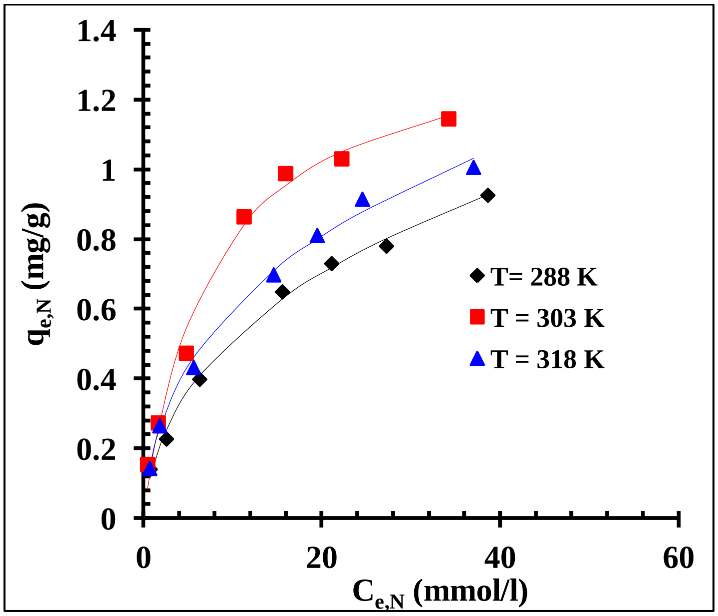


Figure 5.13 Mono-component adsorption isotherms for N at different temperature. (C_o = 3.57 mmol/l to 57.14 mmol/l, t = 6 h, m = 20 g/l).

5.2.6. Adsorption Thermodynamics

Classical Van' Hoff equation relates equilibrium constant with free energy change of the process:

$$\Delta G^0 = -RT \ln K_D \tag{5.2}$$

The entropy change and heat of adsorption at constant temperature are also related to Gibbs free energy according to the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{5.3}$$

The above two equations when combined gives:

$$\ln K_D = -\frac{\Delta G^0}{RT} = \frac{\Delta S^0}{R} = -\frac{\Delta H}{R}\frac{1}{T} \tag{5.4}$$

where, ΔG^o is free energy change (KJ/mol), ΔS^o is entropy change (J/mol K), ΔH^o is change in enthalpy (kJ/mol), R is universal gas constant (8.314×10^{-3} kJ/mol K), T is the absolute temperature (K) and $K_D=(q_e/C_e)$ is coefficient of linear adsorption distribution. Thus from the slope of the Van't Hoff plot $\ln K_D$ vs 1/T we can determine ΔH^o using the following equation:

$$\Delta H^0 = \left[R\frac{d\ln K_D}{d(1/T)} \right] \tag{5.5}$$

In the above equation ΔH^0 is isosteric heat with $q_e=0$ (Suzuki and Fujji, 1982). It is direct measure of the strength of bonding between adsorbate and adsorbent surface. The intercept of the plot between $\ln(q_e/C_e)$ and q_e gives K_D at $q_e=0$. From the Van't Hoff plot ΔH^o and ΔS^0 values have been obtained. We can see from the Table 5.6 and Table 5.7 that ΔS^0 values are positive for both S and N which suggests that randomness increases on the interface and the degree of freedom also increases of adsorbed species. ΔH^o values are positive which indicates the endothermic nature of the reaction whereas ΔG^o values are negative which indicate the feasibility and spontaneity of the adsorption process of S and N on Ni/AC.

Table 5.6 Thermodynamic parameters for the adsorption of S onto Ni/AC. (t= 9 h, C0= 1.56 mmol/l to 25 mmol/l, m = 20 g/l).

Temp (K)	K	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
288	5.90	-4.39	2.04	0.01
303	6.82	-4.52		
318	5.41	-4.64		

Table 5.7 Thermodynamic parameters for the adsorption of N onto Ni/AC. (t = 9 h, C_0 = 3.57 mmol/l to 57.14 mmol/l, m= 20g/l).

Temp (K)	K	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
288	5.30	-4.03	1.55	0.02
303	5.74	-4.32		
318	5.62	-4.61		

5.3. OPTIMIZATION OF PARAMETERS FOR BINARY ADSORPTION OF SULFUR AND NITROGEN

5.3.1. Multi-component Study Using Taguchi's Method

According to the test runs specified by L_{27} OA (Table 5.8) experiments were conducted for S and N adsorption onto Ni/AC. The average value of q_{tot} for each parameter at different levels is calculated from Table 5.9(a). It is observed that adsorption of both S and N is dependent on the parametric conditions.

Table 5.8 Taguchi's $L_{27}(3^{13})$ orthogonal array for three interactions and their assignment in column and the adsorption values for S and N system onto Ni/AC.

Exp. No.	A	B	AxB	AxB	C	D	E	R1
1	0	0	0	0	15	5	1	0.00
2	0	0	0	0	30	15	6	0.00
3	0	0	0	0	45	25	11	0.00
4	0	17.85	1	1	15	5	1	144.57
5	0	17.85	1	1	30	15	6	57.93
6	0	17.85	1	1	45	25	11	47.85
7	0	35.71	2	2	15	5	1	182.00
8	0	35.71	2	2	30	15	6	65.07
9	0	35.71	2	2	45	25	11	85.37
10	7.81	0	1	2	15	15	11	8.01
11	7.81	0	1	2	30	25	1	4.76
12	7.81	0	1	2	45	5	6	63.19
13	7.81	17.85	2	0	15	15	11	82.35
14	7.81	17.85	2	0	30	25	1	43.59
15	7.81	17.85	2	0	45	5	6	201.34
16	7.81	35.71	0	1	15	15	11	81.47
17	7.81	35.71	0	1	30	25	1	66.24
18	7.81	35.71	0	1	45	5	6	179.07
19	15.62	0	2	1	15	25	6	19.03
20	15.62	0	2	1	30	5	11	150.74
21	15.62	0	2	1	45	15	1	34.29
22	15.62	17.85	0	2	15	25	6	41.53
23	15.62	17.85	0	2	30	5	11	144.81
24	15.62	17.85	0	2	45	15	1	63.97
25	15.62	35.71	1	0	15	25	6	66.19
26	15.62	35.71	1	0	30	5	11	191.63
27	15.62	35.71	1	0	45	15	1	74.73
total								2099.72

5.3.1.1. Process parameters effects: The average value of q_{tot}, q_S and q_N for each parameter at levels 1, 2 and 3 along with interactions at these levels are given in Table 5.9(a), 5.9(b) and 5.9(c) for S and N adsorption on Ni/AC. Various parameters ($C_{0,i}$, T, m and t) affect the value of q_{tot}, q_S and q_N. The effect of concentration of one compound w.r.t other compound i.e. the interaction between the components has a significant effect on q_{tot} values. From Table 5.9(a) we see that adsorbent dose (m) has the greatest effect at level 1 on q_{tot} whereas $C_{o,N}$ has highest effect at level 2 and 3. Difference between level 1 and 2 (L2-L1) indicates the relative influence of the effect. The larger the difference stronger is the influence. It can be seen from the table that $C_{o.i}$ has a strong influence on q_{tot} than other parameters. q_{tot} increased with $C_{o,i}$ because of the increase in mass transfer driving force which resulted in the decrease of resistance to the adsorbate uptake.

Table 5.9(a) Average and main effect of q_{tot} values-raw data

Parameter	Raw data, Average value			Main effect (Raw data)	
	L1	L2	L3	L2-L1	L3-L2
A	64.75	81.11	87.44	16.36	6.33
B	31.11	91.99	110.20	60.88	18.20
C	69.46	80.53	83.31	11.07	2.78
D	139.71	51.98	41.62	-87.73	-10.36
E	68.24	77.04	88.02	8.80	10.98
AxB	68.72	80.00	84.58	11.28	4.58

From Table 5.9(b) we can see that adsorbent dose m has greatest effect at level 1 and $C_{o,i}$ at level 3 on q_s. We also found that the difference between level 1 and level 2 is highest for $C_{o,S}$ and hence it indicates that $C_{o,S}$ has stronger influence on q_s as compared to other parameters. Similarly from Table 5.9(c) we can see that at level 1 again adsorbent dose m has highest effect on q_N while at level 2 and 3 $C_{0,N}$ holds the largest effect. Again in case of q_N the difference between level 2 and level 3 is largest for $C_{o.N}$ which indicates that it has strongest effect as by increasing the concentration mass transfer driving force increases which reduces the resistance for adsorption.

Table 5.9(b) Average and main effect of q_S values-raw data

Parameter	Raw data, Average value			Main effect (Raw data)	
	L1	L2	L3	L2-L1	L3-L2
A	0.00	25.91	46.09	25.91	20.18
B	31.11	24.93	15.97	-6.19	-8.96
C	10.46	34.59	26.96	24.14	-7.63
D	49.44	14.53	8.04	-34.91	-6.49
E	12.11	22.88	37.01	10.77	14.13
AxB	20.45	23.54	28.02	3.09	4.48

Table 5.9(c) Average and main effect of q_N values-raw data

Parameter	Raw data, Average value			Main effect (Raw data)	
	L1	L2	L3	L2-L1	L3-L2
A	64.75	55.20	41.34	-9.56	-13.86
B	0.00	67.07	94.23	67.07	27.16
C	59.01	45.94	56.36	-13.07	10.42
D	90.27	37.45	33.58	-52.82	-3.87
E	56.13	54.16	51.01	-1.97	-3.14
AxB	48.27	56.46	56.56	8.19	0.10

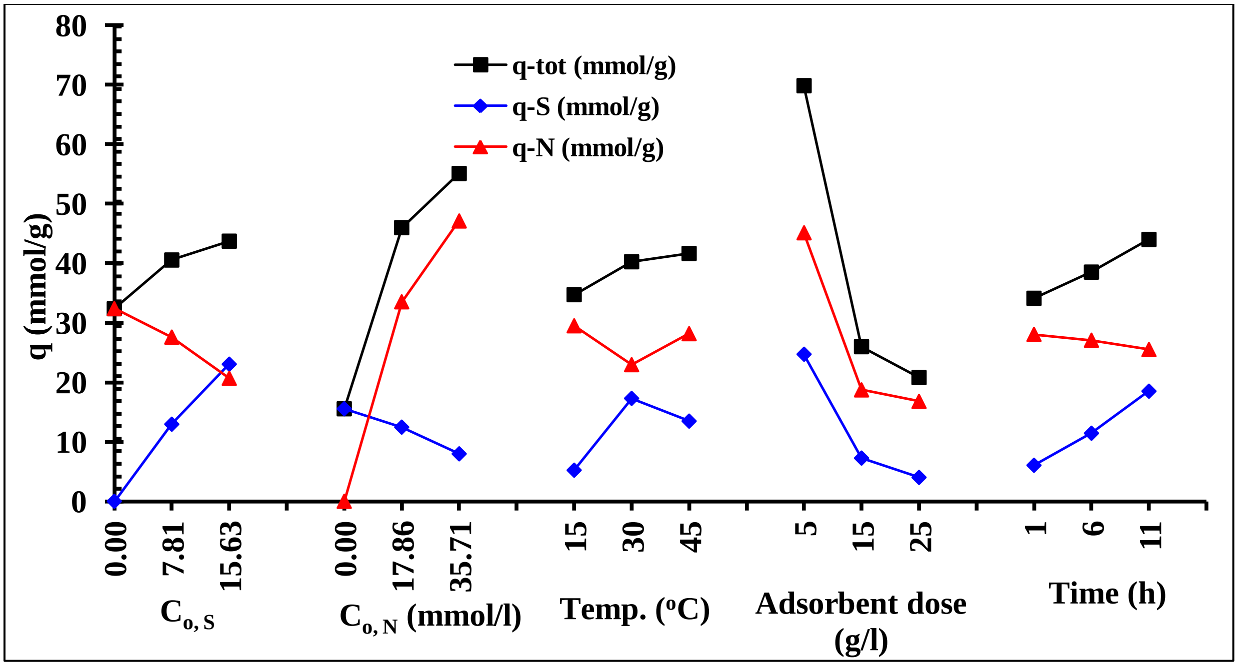


Figure 5.14 Effect of process parameters on q_{tot} for multicomponent adsorption of S and N onto Ni/AC.

The effects of parameters on q_{tot}, q_S and q_N for adsorption of S and N onto Ni/AC are given in the Figure 5.14. It can be seen from the graph that an increase in $C_{o,i,}$ T, and t from 1 to 2 and 2 to 3 resulted in an increase in q_{tot} value.

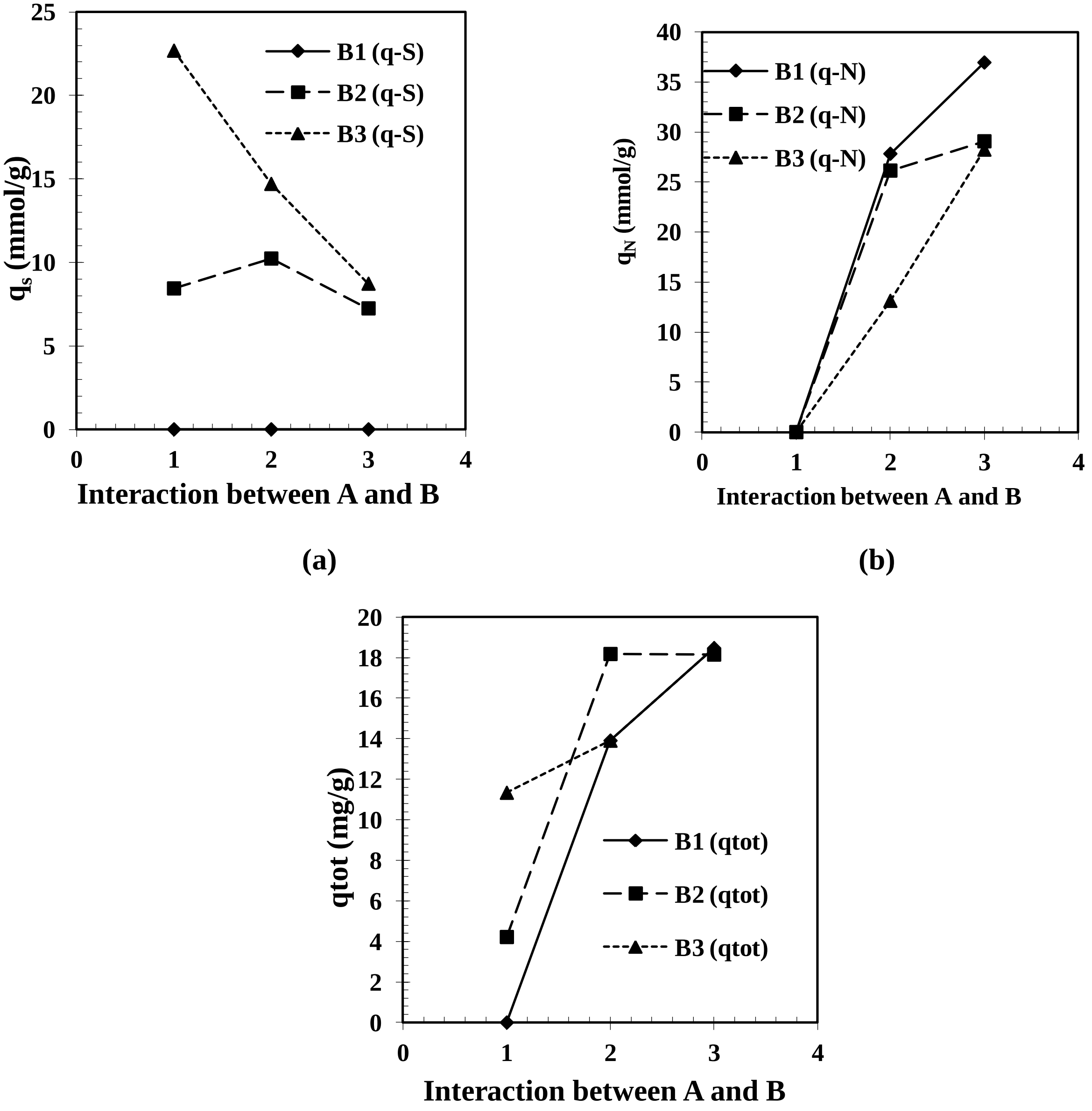
As adsorption is an exothermic process it is expected to decrease with increase in temperature. But it can be seen from the Figure 5.14 that an increase in temperature shows different pattern for q-S and q-N. It is observed that when temperature increases from T = 15°C to T = 30°C q_S increases but in this temperature range q_N decreases on the other hand when adsorption of S decreases for T ≥ 30°C q_N increases. This is because both S and N compete for the same adsorption site. So at first when sulfur is adsorbed more adsorption of N is less on the other hand when adsorption of S decreases N adsorption increases. But q_{tot} shows an increase with increase in temperature which suggests that the overall adsorption process is endothermic in nature and is diffusion controlled.

q_{tot} value increased with an increase in time from level 1 to 3. It can be seen in the Figure 5.14 that adsorption of S increases with contact time until equilibrium is achieved between adsorbate and adsorbent. Same is observed for N but in that case equilibrium is achieved much earlier. During the initial stages a number of vacant sites are available for adsorption but after sometime when the sites get occupied repulsive forces comes into play between the solute molecules. Further the S and N molecule have to travel deeper into the pores which results in higher resistance. As a result adsorption slows down in the later stages.

As far as adsorbent dose is concerned we can see that as m increases first from level 1 to level 2 and then from 2 to 3 the value of q_{tot} decreases. Mall et al (2005) have shown that with increase in m unit adsorption decreases although percent removal increases because of the availability of more sites for adsorption.

From Table 5.8 we can see that interaction between $C_{o,S}$ and $C_{o,\,N}$ $\left[\left(A \times B\right)\right]$ significantly affects the average value of q_{tot}. These interaction graphs are shown in Figure 5.15. Non- parallel lines in the graph indicate that interaction exists between the factors.

ANOVA results for raw data with desired response characteristics are given in Table 5.10 for multicomponent N and S adsorption onto Ni/AC.



(a)

(b)

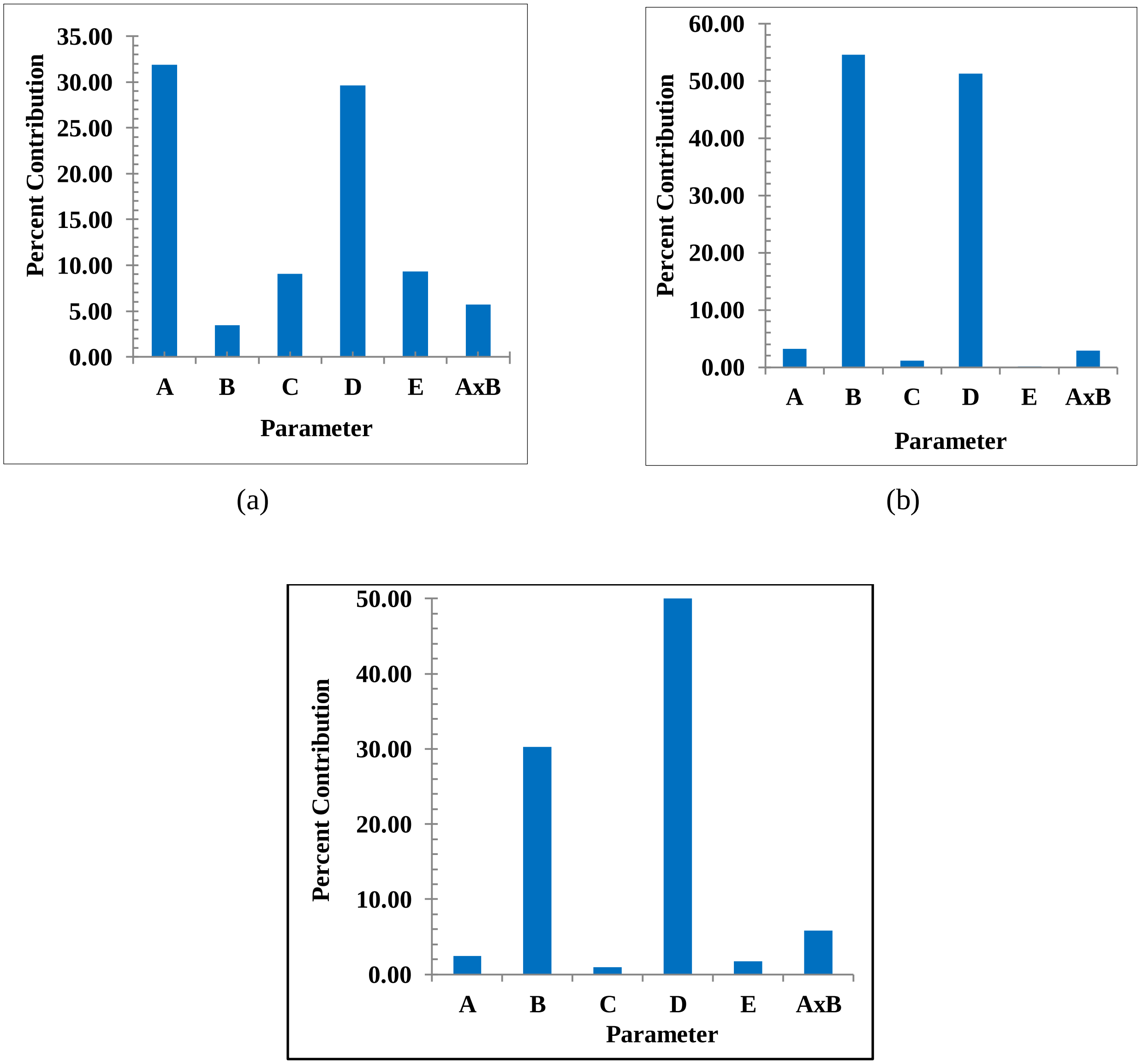
(c)

Figure 5.15 The interaction between A and B parameters at 3 levels on (a) q_S (b) q_N and (c) q_{tot} for multicomponent adsorption of S and N onto Ni/AC.

Table 5.10 ANOVA of q_{tot} for multicomponent adsorption of S and N onto Ni/AC.

q_{tot}					
	Sum of squares	**DOF**	**Mean square**	**% contribution**	**F-value**
A	616.51	2	308.26	308.26	6.22
B	7719.16	2	3859.58	3859.58	77.91
C	241.57	2	120.79	120.79	2.44
D	13068.30	2	6534.15	6534.15	131.90
E	442.22	2	221.11	221.11	4.46
$A \times B$	1487.07	4	371.77	371.77	7.50
Residual	1932.05	12	49.54	49.54	
Model	23574.84	14	11415.65	11415.65	230.43
Cor. total	25506.88	26	11465.19	11465.19	
q_N					
A	2493.98	2	1246.99	3.22	1.31
B	42345.66	2	21172.83	54.59	22.20
C	859.01	2	429.51	1.11	0.45
D	18052.50	2	9026.25	51.23	9.46
E	119.86	2	59.93	0.15	0.06
$A \times B$	2249.31	4	562.33	2.90	0.59
Residual	11447.08	12	953.92	14.76	
Model	66120.32	14	32497.83	85.24	34.07
Cor. total	77567.40	26	33451.76	100.00	
q_S					
A	9609.64	2	4804.82	31.88	17.48
B	1043.75	2	521.87	3.46	1.90
C	2739.39	2	1369.70	9.09	4.98
D	8925.57	2	4462.79	29.61	16.24
E	2807.52	2	1403.76	9.31	5.11
$A \times B$	1723.51	4	430.88	5.72	1.57
Residual	3297.89	12	274.82	10.94	
Model	26849.39	14	12993.82	89.06	47.28
Cor. total	30147.28	26	13268.64	100.00	

The level of factors can be controlled in a manner that higher or lower values produce the preferred results. Thus the level of factor which produces preferred result can easily be predicted. The percentage contribution of each factor for q_N, q_s and q_{tot} as desired response characteristic is shown in the bar graph Figure 5.16. It can also be seen that interaction between A and B also contribute significantly to raw data for simultaneous as well as individual adsorbate removal onto Ni/AC.



(a)

(b)

(c)

Figure 5.16 Percent contribution of various parameters for (a) q_S (b) q_N and (c) q_{tot} for multi-component adsorption of S and N onto Ni/AC.

5.3.1.2. Selection of optimal levels and estimation of optimum response characteristics: Greatest value of q_{tot} is considered to be optimal. After examining the response (Figure 5.14) of average value of q_{tot} optimum level of parameters were obtained and are given in Table 5.9. It is found that that at first level parameter D (m) and at third level parameter A, B ($C_{o,i}$), C (temperature) and E (time) have higher value of q_{tot}. Thus A3, B3, C3, D1 and E3 are the significant process parameters at their optimum level affecting the removal of S and N by Ni/AC.

The predicted optimum value of q_{tot} for Ni/AC is given by μ as calculated theory in chapter 3 and were found to be μ_{tot}=197.6 mmol/g, μ_S=102.234 mmol/g μ_N=149.326 mmol/g.

5.4 MULTI-COMPONENT ISOTHERM STUDY

Binary mixture of S and N were taken and simultaneous adsorption of both the components was measured. For each initial concentration of S 50, 100, 250, 500 and 750 initial concentration of N was varied from 50 to 750 ppm. From the Table 5.11 it can be seen that equilibrium uptake of N increased as its concentration was increased for each concentration of S. But uptake decreased as S concentration increased. Similar trend was observed for S also. At 53.57 mmol/l (750 ppm) concentration of N in presence of 23.4375 mmol/l (750 ppm) of S, q_e was 0.5469 mmol/gm while at 53.57 mmol/l concentration of N with no S present, $q_{e.}$ was 9897 mmol/g. On the other hand, for S at 23.4375 mmol/l (750 ppm) in presence of N 53.37 mmol/l (750 ppm), q_e was found to be 0.1795 mmol/g.

Table 5.11 Comparison of individual and total adsorption uptakes and yields found at different S concentrations with increasing concentration of N onto Ni/AC.

$C_{e,N}$	$C_{e,S}$	$q_{e,N}$	$q_{e,S}$	Ad_N%	Ad_S%	Ad_{tot}%
0.15	0.10	0.17	0.07	95.64	93.23	94.91
0.72	0.30	0.32	0.06	89.83	80.48	88.15
5.63	0.48	0.61	0.05	68.42	68.82	68.45
19.48	0.74	0.81	0.04	45.45	52.33	45.74
34.39	0.93	0.95	0.03	35.8	40.25	35.93
1.03	0.83	0.12	0.11	71.04	73.41	72.15
2.47	1.10	0.23	0.10	65.33	64.67	65.13
7.03	1.33	0.54	0.08	60.61	57.38	60.13
21.40	1.52	0.71	0.08	40.06	51.22	40.96
37.46	2.05	0.80	0.05	30.06	34.25	30.29
1.18	2.73	0.11	0.25	66.78	65	65.56
3.18	3.46	0.19	0.21	55.45	55.67	55.56
8.71	3.87	0.45	0.19	51.21	50.45	50.98
22.50	4.03	0.66	0.18	36.98	48.38	39.03
39.71	5.27	0.69	0.12	25.86	32.46	26.70
1.41	6.20	0.10	0.47	60.26	60.28	60.28
3.21	8.55	0.19	0.35	55.03	45.22	48.30
8.84	10.09	0.45	0.27	50.48	35.4	43.44
22.6857	11.4781	0.6514	0.20	36.48	26.54	33.45
40.8910	12.0484	0.6340	0.17	23.67	22.89	23.49
1.4317	12.3468	0.1069	0.55	59.91	47.32	48.98
3.6257	13.3992	0.1758	0.50	49.24	42.83	44.33
10.5910	15.5976	0.3633	0.39	40.69	33.45	36.58
24.1071	17.7398	0.5803	0.28	32.5	24.31	29.25
42.6321	19.8468	0.5469	0.17	20.42	15.32	18.87

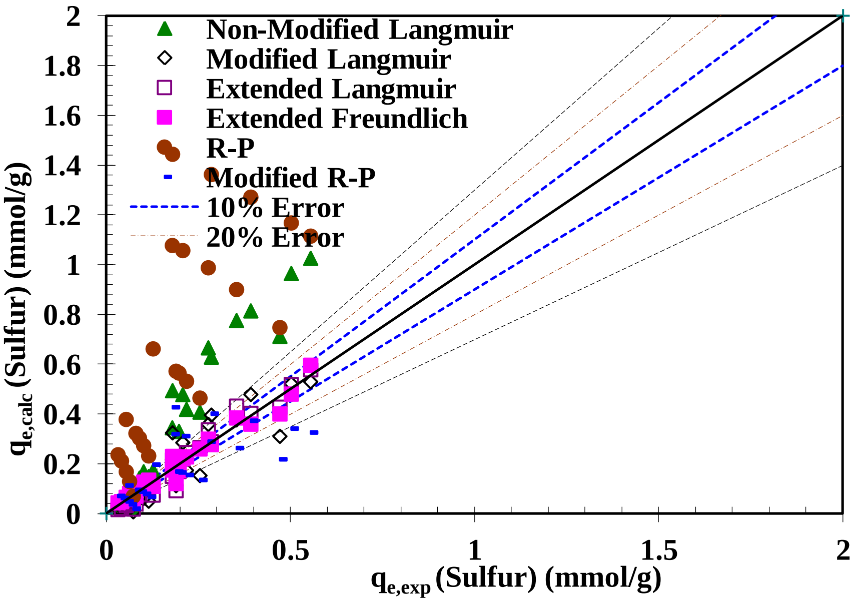
The single and binary equilibrium adsorption data indicate that adsorption capacity of Ni/AC is higher for N than S. There are interactions between the species in the solution and also potential interactions exist on the surface. Certain factors affect the adsorption capacity of adsorbent for different solute molecules like characteristics of binding sites which may include surface properties, structure, functional groups, etc., solution chemistry like pH, etc. and the properties of the adsorbate (concentration, molecular structure, redox potential, etc.

Various multi-component isotherms like non-modified, modified and extended Langmuir, R-P models, extended Freundlich, etc. have been used to fit the data obtained from simultaneous adsorption of S and N onto Ni/AC using SSE (Sum of square of errors) given by:

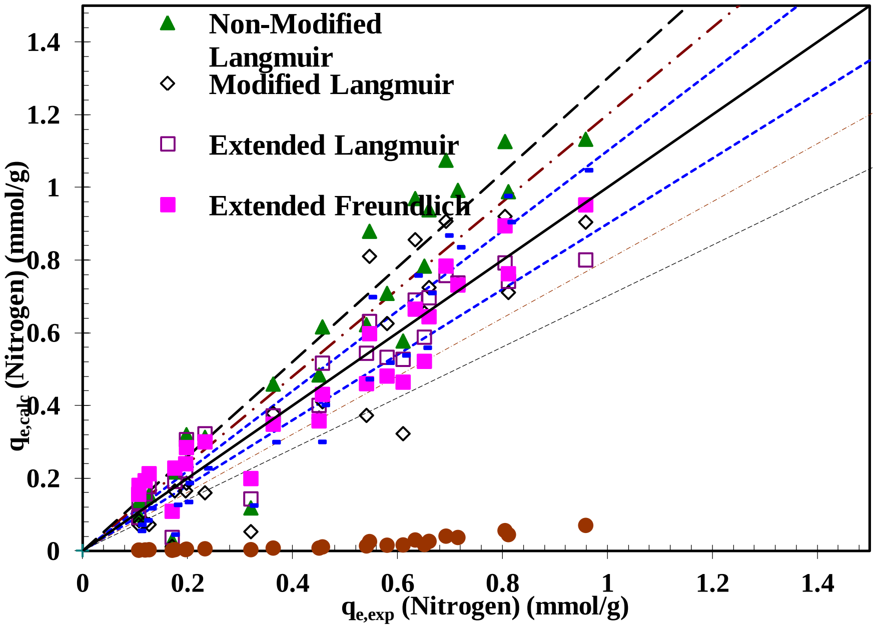
$$SSE = \sum_{i=1}^{n} ((q_{e,meas} - q_{e,calc})_N + (q_{e,meas} - q_{e,calc})_S)_i^2$$

Values of various parameters of multi-component isotherms along with SSE values between calculated and experimental q_e values for N and S data are given in Table 5.12. The parity plots (Figure 5.17) presents comparison between actual and theoretical q_e values of N and S. We can see in the plots that except for non modified Langmuir and RP model the experimental points lie around the diagonal lines for rest of the models. So the adsorption data of multicomponent system can be represented by these models.

From the table we can see that non-modified models show poor fit for adsorption data for binary system as SSE values are very large for these models. It is also found that extended Langmuir with SSE value 0.1764 has better fit as compared to modified Langmuir with SSE value 0.5476. In extended Langmuir K_i value reflects the affinity between adsorbate and adsorbent in a binary mixture which is 0.2736 for N and 0.2017 for S while overall adsorbate uptake q_{max} is 0.9004 mmmol/g. Best fit of data is given by extended Freundlich with SSE value 0.1631.



(a) Sulfur



(b) Nitrogen

Figure 5.17 Comparison of actual and theoretical equilibrium adsorption values of S and N in a binary mixture of S and N.

Table 5.12 Multi-component isotherm parameter values for the simultaneous removal of N and S by Ni/AC.

	Non- modified Langmuir model			
SSE	2.2608			
	Modified Langmuir Model	**Extended Langmuir Model**		
Adsorbate	$\eta_{L,i}$	K_i		$q_{\max}$
N	2.4320	0.2736		0.9004
S	3.4124	0.2017		
SSE	0.5476	0.1764		
	Extended Freundlich Model			
Adsorbate	X	Y		Z
N	0	0.3119		0.4717
S	0	0.7197		0.5373
SSE	0.1631			
	R-P Model			**Modified R-P Model**
Adsorbate	K_R	a_r	β	$\eta_{RP,i}$
N	0.1824	1	0.1289	0.001
S	22.9268	0.4210	87.7501	8.3008
SSE	13.8391			0.542712378

CHAPTER-6

CONCLUSIONS AND RECOMMENDATIONS

6.1. CONCLUSIONS

In the present study, nickel loaded activated carbon (Ni/AC) was synthesized and characterized by various techniques. It was further used for the adsorption of nitrogenous compound (N) (represented by quinoline) and sulfur compound (S) (represented by dibenzothiophene (DBT)). On the basis of the present study, and the results and discussion presented earlier, following conclusion can be drawn:

- Ni/AC can be used for the adsorption of liquid fuels. Calcination temperature after loading also affected the adsorption capacity of the adsorbent.
- Various characterization tests like BET, FTIR, EDX and TGA helped in understanding the mechanism of adsorption. EDX analysis confirmed the presence of S and N on the adsorbent surface. The thermal stability of activated carbon was upto 400^oC shown by TGA analysis.
- The equilibrium adsorption time was found to be 9 h for S and 6 h for N.
- The optimum adsorbent dose for both S and N was found to be 20 g/l.
- The adsorption of both S and N was found to be intra particle diffusion controlled.
- Pseudo-second-order kinetics represented the adsorption kinetics of both S and N.
- For single component system, R-P isotherm best fitted the experimental equilibrium data.
- Taguchi’s method was found to be very useful for studying the multicomponent adsorption system.
- For binary system, adsorption was found to be antagonistic in nature and that the adsorption capacity for N was found to be higher than S.
- For binary component system containing both S and N, extended Freundlich isotherm best represented the isotherm data at 30 ^oC.

6.2. RECOMMENDATIONS

On the basis of present study following recommendations can be made for future work:

- More characterization tests should be performed for better understanding of adsorption mechanism.
- Some other metals should be loaded on activated carbon and their adsorption capacities should be compared.
- Reusability of the adsorbent should be tested.

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