

Preparation, Characterization and Application of Activated Carbon for Arsenic Separation from Water



Ph. D. Thesis

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BY

ISRAT JAHAN

B. Sc (Hons), M. Sc.

Roll No. 06219

Registration No. 1709

Session: 2006-2007

**Chemical Engineering Research Laboratory
Department of Applied Chemistry and Chemical Engineering
University of Rajshahi, Rajshahi-6205
Bangladesh.
March-2013**



Declaration Certificate

The undersigned certify that all of the research works presented in this dissertation are the original works of Israt Jahan, BSc. (Hons), MSc., who carried out this research works in our laboratory. Not a part of this work has been used before by any body for any other degree.

Md. Sahedur Rahman
.....

Supervisor:

Professor Dr. Md. Sahedur Rahman

**Department of Applied Chemistry and Chemical Engineering
University of Rajshahi, Bangladesh**

Asadullah
.....

Co-Supervisor:

Professor Dr. Md. Asadullah
**Department of Applied Chemistry
and Chemical Engineering**
University of Rajshahi, Bangladesh
(On lien leave)

K Hassan
.....

Co-Supervisor:

Dr. A.T.M. Kamrul Hassan
Associate Professor
Department of Applied Chemistry and
Chemical Engineering
University of Rajshahi, Bangladesh

**Chemical Engineering Research Laboratory. Department of Applied
Chemistry and Chemical Engineering, University of Rajshahi,
Rajshahi, 6205 Bangladesh.**

DECLARATION CERTIFICATE

I do hereby declare that the Ph.D. thesis entitled, "Preparation, Characterization and Application of Activated Carbon for Arsenic Separation from Water" has been written based on my own work carried out in the Chemical Engineering Research Laboratory of the Department of Applied Chemistry and Chemical Engineering, Rajshahi University, under the supervision of Professor Dr. Md. Sahedur Rahman (supervisor), Professor Dr. Md. Asadullah (Co-supervisor) and Dr. A.T.M. Kamrul Hasan (Co-supervisor) of the same department. Not a part of this thesis has been submitted elsewhere for any degree or any award.



.....
Israt Jahan

Ph.D. Research Fellow

Session-2006-2007

Registration No. 1709

Roll no-06219

**Applied Chemistry and Chemical Engineering
University of Rajshahi
Rajshahi, 6205 Bangladesh**

Dedication



*To my beloved
Husband and
Children*

ABSTRACT

Arsenic removal from water in the form of As(III) and As(V) using activated carbon and iron loaded activated carbon has been studied. Activated carbon has been prepared from jute stick using both chemical activation and physical activation methods. In chemical activation, H_3PO_4 was used as an activating agent while in physical activation steam was used. The activated carbons produced were characterized by determining BET surface area, iodine value, methylene blue dye number, reactivity, pore volume and pore size. In addition, the studies on structural feature, surface functionality and morphology were also carried out using Raman spectroscopy, FT-IR spectroscopy and Scanning Electron Microscopy (SEM). The maximum BET surface area, iodine value and methylene blue number were found to be $1664 \text{ m}^2/\text{g}$, 1440 mg/g and 475 mg/g , respectively.

Activated carbon produced at optimum conditions was used for As(III) and As(V) separation from water in different method, such as batch process, continuous column filtration method and commercial filter method. Around 48% of As(III) separation while complete removal of As(V) was achieved using chemically activated carbon (ACC) in column filtration method. However, the main objective of this work is to remove As(III) to an acceptable range (below 0.01 ppm), which is the predominant species in the most underground water, especially in Bangladesh. To enhance the arsenic adsorption capacity, iron species was loaded onto the ACC as well as physically activated carbon (ACS).

The iron loaded activated carbon FACC exhibited superior performance in As(III) separation in column filtration method. Almost complete removal of As(III) was achieved when 9 cm of bed thickness using 1.5 g of FACC was used in a glass column. However, in order FACC to utilize in practical filtration of arsenic contaminated water an investigation in the scale of 24 L/day of water, a minimum requirement of commercial filtration, was performed. In this study a commercial house hold filter body was used after removing the ceramic candle

and layers of filter cartridge. The FACC was filled in the blank filter cartridge and used for filtration. To compare the separation capacity of FACC, ACC and FACS were also used in the commercial filtration method. The FACC showed the dominant performance and almost 99% arsenic was removed from the water.

Based on the characterization data, FACC poses much higher BET surface area, micropore surface area and micropore volume which mainly contributed in liquid phase adsorption. In addition, surface polarity due to the presence of functional groups on ACC contributed to widely distribute of iron species on the surface which in turn contributed to efficiently adsorb As(III) from water.

Finally, this study embarked an efficient way of As(III) and As(V) separation from water which can be recommended to commercially use for drinking water purification, especially in the countries where arsenic contamination in drinking water created a public health problems.

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The Authoress

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Acronyms and Abbreviation

%	◆ Percentage
μg	◆ Microgram
μm	◆ Micrometer
AAS	◆ Atomic Absorption Spectroscopy
AC	◆ Activated Carbon
ACC	◆ Chemically Activated Carbon
ACS	◆ Physically Activated Carbon
Å	◆ Angstrom (0.1nm)
B.C	◆ Before Christ
BET	◆ Brunaur-Emmett-Teller
CC	◆ Char Carbon
CRT	◆ Cathode ray tube
DTA	◆ Differential thermal analysis
FACC	◆ Iron Loaded Chemically Activated Carbon
FACS	◆ Iron Loaded Steam Activated Carbon
FH	◆ Full Height
FID	◆ Flame Ionization Detector
FTIR	◆ Fourier Transform Spectroscopy
GAC	◆ Granular Activated Carbon
IOCS	◆ Iron Oxide Coated Sand
Kcal/mole	◆ Kilocalorie Per Mole
kV	◆ Kilovolt
L/day	◆ Liter Per Day

L/min	◆ Liter Per Minute
mA	◆ Milliampere
mm	◆ Millimeter
mV	◆ Millivolt
nm	◆ Nanometer
NMR	◆ Nuclear Magnetic Resonance
NSICT	◆ National Science And Information And Communication Technology
°C	◆ Degree Centigrade
pH	◆ The logarithm of The Reciprocal of Hydrogen Ion Concentration
pm	◆ Picometer
ppb	◆ Parts Per Billion
ppm	◆ Parts per Million
RF	◆ Radio Frequency
rpm	◆ Revolutions Per Minute
SEM	◆ Scanning Electron Microscope
STP	◆ Standard Temperature And Pressure
TCD	◆ Thermal Conductance Detector
TGA	◆ Thermogravimetric Analysis
VCR	◆ Voltage Controlled Recorder
XRD	◆ X-Ray Diffraction

CHAPTER 1

Introduction

CHAPTER 1

INTRODUCTION

1.1. Background of Study

Water is the most basic thing that we need for all kind of living systems. However, sometimes this water, especially for drinking purpose, becomes harmful for human health. During the past thirty five years, millions of people in Bangladesh have lost their lives due to the contamination of drinking water with many hazardous materials including bacterial contamination. An attempt to eliminate one of the hazards, disease caused by drinking of polluted surface water, millions of shallow surface tube wells were drilled into the ground of Bangladesh. These wells have become contaminated with arsenic.

Arsenic contamination of ground water has created a big public health problem in Bangladesh. Without being aware, millions of people are drinking and using arsenic contaminated tube-well water every day. As a result, people have been suffering from various types of diseases caused by arsenic deposition in human body. To help solve the problem, it has been felt that immediate steps must be taken to identify those areas affected by arsenic contaminated water and to identify the sources of arsenic contamination and the level of contamination as a first measure.

Arsenic poisoning was first detected in Bangladesh in 1993 by the Department of Public Health Engineering (DPHE). The DPHE recently indicated that about 59 out of 64 districts have been affected by arsenic contamination. The known contamination covers almost 60 percent of the total area of the country. During 1998 under "A Rapid Action Program", 200 Villages were surveyed for studying arsenic poisoning by the Dhaka Community Hospital (DCH) and

Jadavpur University of Kolkata, India. They estimated that about 50 percent of all the tube wells in the country exceeded the safe maximum contamination level. In another report, UNDP claimed that 40 percent of all wells are contaminated by arsenic.

Arsenic (Atomic number 33) is ubiquitous and ranks 20th in natural abundance, comprising about 0.00005% of the earth's crust, 15th in the seawater, and 12th in the human body [1]. It's concentration in most rocks ranges from 0.5 to 2.5 mg/kg, though higher concentrations are found in finer grained argillaceous sediments and phosphorites [1, 2]. It is a silver-grey brittle crystalline solid with atomic weight: 74.9216. Specific gravity (metallic arsenic): 5.72. Sublimation point (metallic arsenic): 1,135 F. (613 C.). (When heated at atmospheric pressure, metallic arsenic sublimes-that is, it changes directly from a solid to a vapor. It can exist in a liquid state only at a much higher pressure.). Arsenic is mobilized by natural weathering reactions, biological activity, geochemical reactions, volcanic emissions and other anthropogenic activities. Soil erosion and leaching contribute to 612×10^8 and 2380×10^8 g/year of arsenic, respectively, in dissolved and suspended forms in the oceans [3]. Most environmental arsenic problems are the result of mobilization under natural conditions. However, mining activities, combustion of fossil fuels, use of arsenic pesticides, herbicides, and crop desiccants and use of arsenic additives to livestock feed create additional impacts.

Arsenic exists in the -3, 0, +3 and +5 oxidation states [4]. Environmental forms include arsenious acids (H_3AsO_3 , $\text{H}_3\text{AsO}_3^{2-}$), arsenic acids (H_3AsO_4 , H_3AsO_4^- , $\text{H}_3\text{AsO}_4^{2-}$), arsenites, arsenates, methylarsenic acid, dimethylarsinic acid, arsine, etc. Arsenic(III) is a hard acid and preferentially complexes with oxides and nitrogen. Conversely, arsenic(V) behaves like a soft acid, forming complexes with sulfides [5]. Inorganic forms of arsenic most often exist in water supplies. Arsenic is uniquely sensitive to mobilization (pH 6.5-8.5) under both oxidizing and reducing conditions among heavy metalloids [6]. Two forms are common

in natural waters: arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}), referred to as arsenic (III) and arsenic(V). Pentavalent (+5) or arsenate species are AsO_4^{3-} , HAsO_4^{2-} , H_2AsO_4^- while trivalent (+3) arsenites include $\text{As}(\text{OH})_3$, $\text{As}(\text{OH})_4^-$, $\text{AsO}_2\text{OH}^{2-}$ and AsO_3^{3-} . Pentavalent species predominate and are stable in oxygen rich aerobic environments. Trivalent arsenites predominate in moderately reducing anaerobic environments such as groundwater [7].

Arsenic speciation depends on pH and H_2AsO_4^- dominates at low pH (less than about pH 6.9) in oxidizing conditions. At higher pH, HAsO_4^{2-} is the dominant (H_3AsO_4^0 and AsO_4^{3-} may be presenting strong acid or base conditions, respectively). Under reducing conditions at $\text{pH} < 9.2$, the uncharged H_3AsO_4^0 predominates [8].

Arsenic occurrences in the environment, its toxicity, health hazards, and the techniques used for speciation and analysis have been studied widely in the last couple of decades [5], [9-12]. In terms of toxicity, long-term drinking water exposure causes skin, lung, bladder, and kidney cancer as well as pigmentation changes, skin thickening (hyperkeratosis), neurological disorders, muscular weakness, loss of appetite, and nausea [1], [10], [13], [14]. This differs from acute poisoning, which typically causes vomiting, oesophageal and abdominal pain, and bloody "rice water" diarrhea [13-17].

Arsenic in natural water is a worldwide problem. Arsenic pollution has been reported recently in the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, New Zealand, Japan and India [18-24]. The largest population at risk among 21 countries with known groundwater arsenic contamination is in Bangladesh, followed by West Bengal in India [25], [10], [26-28].

The WHO provisional guideline of 10 ppb (0.01 mg/L) has been adopted as the drinking water standard. However, many countries have retained the earlier WHO guideline of 50 ppb (0.05 mg/L) as their standard or as an interim target including Bangladesh and China. In 2001, US-EPA published a new 10 ppb

(0.01 mg/L) standard for arsenic in drinking water, requiring public water supplies to reduce arsenic from 50 ppb (0.05 mg/L) to 10 ppb (0.01 mg/L) [29], which has been effected from January 2006. The maximum permissible limits for drinking water in different countries are summarized in Table 1.1.

Table 1.1. Countries affected by arsenic contamination and maximum permissible limits for drinking water

Country	Maximum permissible limits (µg/L)	References
Argentina	50	[4], [30], [31], [32]
Bangladesh	50	[21], [33], [34-37]
Cambodia	50	[38]
China	50	[1], [39-42]
Chile	50	[43-47]
India	10	[20], [31], [25], [48]
Japan	-	[49]
Mexico	50	[19], [50]
Nepal	50	[51]
New Zealand	10	[52], [53]
Taiwan	10	[1], [39]
USA	10	[18], [28]
Vietnam	10	[54], [55]

Arsenic removal technologies were reviewed [56], [22], [23], [57-70]. The major arsenic removal technologies are compared in Table 1.2.

Table 1.2. Comparison of main arsenic removal technologies [135]

Major oxidation/precipitation technologies	Advantages	Disadvantages
Oxidation/precipitation: [71-75]		
Air oxidation	Relatively simple, low-cost but slow process; <i>in situ</i> arsenic removal; also oxidizes other inorganic and organic constituents in water	Mainly removes arsenic(V) and accelerate the oxidation process
Chemical oxidation	Oxidizes other impurities and kills microbes: relatively simple and rapid process; minimum residual mass	Efficient control of the pH and oxidation step is needed

Major Coagulation/coprecipitation technologies	Advantages	Disadvantages
Coagulation/electrocoagulation/coprecipitation: [76-80]		
Alum coagulation	Durable powder chemicals are available; relatively low capital cost and simple in operation; Effective over a wider range of pH	Produces toxic sludges; low removal of arsenic; pre-oxidation may be required
Iron coagulation	Common chemicals are available; more efficient than alum coagulation on weigh basis	Medium removal of As(III); sedimentation and filtration needed
Lime softening	Chemicals are available commercially	Readjustment of pH is required

Major sorption and ion-exchnage technologies	Advantages	Disadvantages
Sorption and ion-exchange techniques: [81-84]		
Activated alumina	Relatively well known and commercially available	Needs replacement after four to five regeneration
Iron coated sand	Cheap; no regeneration is required; remove both As(III) and As(V)	Not standardized; produces toxic solid waste
Ion-exchnage resin	Well-defined medium and capacity; pH independent; exclusive ion specific resin to remove arsenic	High cost medium; high-tech operation and maintenance; regeneration creates a sludge disposal problem; As(III) is difficult to remove; life of resins

Major membrane technologies	Advantages	Disadvantages
Membrane techniques: [85-89]		
Nanofiltration	Well-defined and high-removal efficiency	Very high-capital and running cost, pre-conditioning; high water rejection
Reverse osmosis	No toxic solid waste is produced	High tech operation and maintenance
Electrodialysis	Capable of removal of other contaminants	Toxic wastewater produced
Other techniques		
Foam flotation: [90], [91]		
Solvent extraction: [92]		
Bioremediation: [93]		

Most remediation methods discussed to effectively remove arsenic from water containing high initial arsenic concentrations (usually >100 mg/L) but residual arsenic concentrations exceed the 0.05 mg/L, the upper limit of the water quality standard used in most countries. Conventional and non-conventional treatment technologies for aqueous arsenic remediation were compared [94]. Many technologies described above are successful in the laboratory test; however, sometimes they are inefficient in the field test under real conditions. This is because most of the underground water contains some iron species, silica and many other non-toxic components which create problems in arsenic separation process as it has been observed in rural areas of Bangladesh and India. Real application of technologies also depends on the co-operation and

acceptance of rural people. Technology development is only possible when a partnership exists involving proper village level participation. Most of the technologies of arsenic removal suffer from one or more drawbacks, limitations and scope of application.

1.2. Problem Statement

Most of the people in the world, especially the people who live in the rural area of some countries, drink underground water which is being collected from tube-well. However, in 1993, it has been found that the underground water is contaminated with toxic arsenic species which has created a big public health problem, especially in Bangladesh. Without being aware, millions of people are drinking and using arsenic contaminated tube-well water in their daily life. As a result, people are suffering from various types of diseases caused by arsenic deposition in human body.

Long-term exposure to arsenic contaminated water causes skin, lung, bladder, and kidney cancer as well as pigmentation changes, skin thickening (hyperkeratosis), neurological disorders, muscular weakness, loss of appetite, and nausea. This differs from acute poisoning, which typically causes vomiting, oesophageal and abdominal pain, and bloody "rice water" diarrhea.

Drinking water contamination with arsenic is a worldwide problem and it has been reported recently in the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, New Zealand, Japan and India [18-24]. The largest population at risk among 21 countries with known groundwater arsenic contamination is in Bangladesh, followed by West Bengal in India [25], [10], [26-28].

In the past two decades a significant effort has been given in remediation of arsenic from drinking water. Some studies showed that arsenic can be separated from water effectively. However, the materials developed so far are effective for arsenic separation from high initial concentrations (usually >100 mg/L),

while the residual arsenic concentrations exceed the 0.01 mg/L, the upper limit of the water quality standard used in most of the countries. In addition, many technologies described in the previous section are successful in the laboratory test; however, sometimes they are inefficient in the field test under real conditions. This is because most of the underground water contains some iron species, silica and many other non-toxic components which prevent arsenic separation. It seems that a highly efficient material for arsenic separation from water with high resistivity against other impurities in water is yet to be developed.

1.3. Objectives of the Study

The main objective of the study is to develop a very effective material based on activated carbon produced from jute stick to separate arsenic completely from drinking water. The specific objectives of this study are:

- To investigate the optimum conditions for preparing activated carbon with high surface area from jute stick applying chemical activation method
- To investigate the characteristics of the prepared activated carbons and its effectiveness in arsenic separation
- To improve the effectiveness of arsenic separation of prepared activated carbon by impregnating iron on it
- To produce iron loaded activated carbon in demonstration scale and to characterize and apply for arsenic separation in a real filter.

1.4. Scope of Study

This study involves the development of iron-loaded activated carbons that can be used as an efficient adsorbent to separate heavy metal species, e.g. arsenic species from water. Activated carbon was produced from jute stick by chemical activation method using phosphoric acid. Different sizes of stainless steel reactors such as 0.3 L, 2 L and 8 L volume are used for activated carbon and

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iron-loaded activated carbon preparation in this work at different stages. Iron was loaded by impregnation, followed by the in-situ oxidation using sodium hypochlorite. Characterization of fresh and spent activated carbons has been carried out using chemical and instrumental methods. Since this study involves the preparation of advanced materials from jute stick and water purification using prepared materials, it can add some new knowledge in waste utilization and environmental protection. Upon commercialization of the product, it can solve the arsenic problems, especially in the rural area, generate wealth from waste and can create new job scope.

CHAPTER 2

LITERATURE REVIEW

CHAPTER 2

LITERATURE REVIEW

2.1 Arsenic Remediation by Adsorption

Adsorption is evolving as a front line of environmental defense. Selective adsorption utilizing biological materials, mineral oxides, activated carbons, or polymer resins, has generated increasing excitement [95], [96]. The use of carbon extends far back into history. Its origin is impossible to document. Charcoal was used for drinking water filtration by ancient Hindus in India, and carbonized wood was a medical adsorbent and purifying agent in Egypt by 1500 B.C. [97].

Modern activated carbon industrial production was established in 1900-1901 to replace bone-char in sugar refining [98]. Powdered activated carbon was first produced commercially from wood in Europe in the early 19th century and was widely used in the sugar industry. Activated carbon was first reported for water treatment in the United States in 1930 [99]. Activated carbon is a crude form of graphite with a random or amorphous highly porous structure with a broad range of pore sizes, from visible cracks and crevices to crevices of molecular dimensions [100]. Activated carbons have been prepared from coconut shells, wood char, lignin, petroleum coke, bone-char, peat, sawdust, carbon black, rice hulls, sugar, peach pits, fertilizer waste, waste rubber tire, etc. (Table 2.1). Wood (130,000 tonnes/year), coal (100,000 tonnes/year), lignite (50,000 tonnes/year), coconut shell (35,000 tonnes/year), and peat (35,000 tonnes/year) are most commonly used for the production of activated carbons [101].

Table 2.1. Feedstocks proposed for the preparation of activated carbons

Bones	Cottonseed hulls	Lampblack
Bagasse	Corn Cobs	Leather waste
Bark	Fuller's earth	Municipal waste
Beat-sugar sludges	Fertilizer waste slurry	Molasses
Blood	Fish scale	Nut shells
Coal	Fruit pits	News paper
Coffee beans	Graphite	Oil shale
Coconut shell	Human hairs	Olive stones
Coconut coir	Jute stick	Petroleum acid sludge
Cereals	Kelp and seaweed	Pulp-mill waste
Carbohydrates	Lignin	Palm tree cobs
Lignite	Refinery waste	Petroleum coke
Rubber waste	Scrap tires	Spent Fuller's earth
Rice hulls	Sunflower seeds	Tea leaves
Wood	Wheat straw	

Carbon surface chemistry has been studied widely [98], [102] [103]. This surface chemistry depends on the activation conditions and temperatures employed. Activation refines the pore structure and mesopores and micropores are formed yielding surface areas up to 2000 m²/g [104], [105]. Acidic and basic functional groups on activated carbon exist according to the Steenberg's classification [106]. The acidic groups on activated carbons adsorb metal ions [107]. Surface area sometimes may not be a primary factor for adsorption on activated carbon. High surface area does not necessarily mean high adsorption capacity [108].

The adsorption of metal ions on carbon is more complex than uptake of organic compounds because ionic charges affect removal kinetics from solution. Adsorption capacity depends on activated carbon properties, adsorbate chemical properties, temperature, pH, ionic strength, etc. Many activated

carbons are available commercially but few are selective for heavy metals. They are also expensive. Despite carbon's prolific use to treat wastewater, it remains expensive, requiring vast quantities of activated carbon. Improved and tailor-made materials are sought. Substitutes should be easily available, cheap and, above all, be readily regenerated, providing quantitative recovery.

In this review, adsorbents are broadly divided into two classes: (1) commercial and synthetic activated carbons and (2) low-cost adsorbents.

2.2 Commercial and Synthetic Activated Carbons

2.2.1 Commercial activated carbons

Allen and Whitten, 1998 have studied the production and characterization of activated carbon from many carbonaceous sources. Recently, the science and technology of charcoal production is critically reviewed [108]. Commercial activated carbons have been extensively used for As(III) and As(V) adsorption from water [109-112]. Activated carbon adsorption was investigated in arsenic and antimony removal from copper electro refining solutions [109]. A huge arsenic sorption capacity (2860 mg/g) was obtained on this coal-derived commercial carbon. Some activated carbons impregnated with metallic silver and copper were also used for arsenic remediation [113].

Eguez and Cho [110] studied adsorption of As(III) and As(V) on activated charcoal at various pH and temperature. The capacity of As(III) on carbon was constant at pH 0.16-3.5. However As(V) exhibited a maximum adsorption at pH 2.35 over the pH range of 0.86-6.33. The As(III) isosteric heat of adsorption varied from 4 to 0.75 kcal/mol and that for As(V), from 4 to 2 kcal/mol with increasing surface loading. These magnitudes suggest that physisorption occurred due to weak van der Waals forces. Activated charcoal adsorbed 2.5 wt.% As(V) and 1.2 wt.% As(III) (based on the weight of carbon) at an equilibrium concentration of 2.2×10^{-2} M of both As(III) and As(V).

Three activated carbons with different ash contents were studied for As adsorption: coconut shell carbon with 3% ash, peat-based extruded carbon with 5% ash and a coal-based carbon with 5-6% ash [111]. More As(V) was removed from water using carbon with a high ash content. Carbon pretreatment with Cu(II) improved arsenic removal capacity. The optimum pH for arsenic adsorption by Cu-pretreated carbon was 6. Arsenic formed insoluble metal arsenates with the impregnated copper. Arsenic is also simultaneously adsorbed by carbon independently. Arsenic was desorbed using strongly acidic or alkaline solutions.

Arsenic was adsorbed onto activated carbon impregnated with metallic silver and copper [112]. A combination of granular activated carbon and carbon steel wool removed arsenic from water [114]. The adsorption ability of the steel wool was due to iron-arsenic electrochemical reactions.

2.2.2 Synthetic activated carbons

Activated carbons are produced by carbonizing carbonaceous materials at around 500-600 °C, followed by activation at around 800 °C. The activation may be chemical activation using various types of chemicals such as phosphoric acid, zinc chloride, potassium hydroxide, potassium carbonate and etc. or physical activation using steam [101], [115]. The carbonization step removes volatiles while the activation step creates pores in the activated carbons. Chemical activation agent may promote cross linking forming a rigid, less volatile matrix with a smaller volume contraction at high temperature. An advantage of chemical activation is the lower temperature required for chemical activation gives higher global yields since char burn-off is not required. Post activation step removes residual catalyst, which may be recovered and reused. Some important feedstocks with activating agent and other conditions are listed in Table 2.2 [101].

Table 2.2 Some chemical activant-feedstock couples to prepare activated carbon (extended form of the table provided by Pollard et al. [101])

Feedstock	Activant	Conditions	References
Almond shell, olive stones and peach stones	-	Heating in CO ₂ at 600 °C	[115]
Coconut shell	Concentrated H ₂ SO ₄	Equal parts by weight of H ₂ SO ₄ for 24h at 150 °C	[116]
Fertilizer slurry	H ₂ O ₂ /H ₂ O, N ₂	450 °C, 1h	[117]
Palm tree cobs	H ₃ PO ₄ /H ₂ SO ₄	730 °C, 6h	[118]
Coconut shell	H ₃ PO ₄	450 °C	[119]
Petroleum coke	KOH/H ₂ O	700-850 °C, 4h	[98]
Raffination earth	H ₂ SO ₄	10% (v/v), 350°C	[120]
Algerian coal	KOH/NaOH	930°C	[121]
Almond and pecan shells	H ₃ PO ₄	Chemical activation with H ₃ PO ₄ /physical CO ₂	[123]
Eucalyptus wood chars	-	CO ₂ Activation, 400-800 °C	[124]

Continued

Feedstock	Activant	Conditions	References
Bituminous coal	ZnCl ₂	N ₂ /400-700 °C	[125]
Coal or coconut shell		Phosgene or chlorine gas at 180 °C	[126]
Petroleum coke	KOH	Dehydration at 400 °C followed by activation in 500-900 °C	[127]
Lignite	NaMoO ₄ /NaWO ₄ /NH ₄ VO ₃ /(NH ₄) ²⁻ MoO ₄ /FeCl ₃ /Fe(NO ₃) ₃	Inert atmosphere/600-800 °C	[128]
Peanut hulls	H ₂ SO ₄	150 °C, sodium bicarbonate	Rerisasamy and Namasivayam (1995)
Fly ash	-	Froth flotation, hydrophobic char was separated from hydrophilic ash with the help of methyl isobutyl ketone	[129]
Oat hulls	Steam	Fast pyrolysis at 500 °C with inter nitrogen	[130]
Solvent-extracted olive pulp and olive Stones	K ₂ CO ₃	Under vacuum and atmospheric pressure; 60 °C/min; 800 °C; activation under N ₂ at 10 °C/min	[131]

Continued

Feedstock	Activant	Conditions	References
Coconut shells and coconut shell fibers	-	Carbonized with H_2SO_4 and activated at 600 °C for 1 h	[132]

Several types of activated carbons were synthesized and used for the removal of arsenic from water/wastewater [133]. Gu et al. [134] developed iron-containing granular activated carbon adsorbents [As-GAC] for arsenic removal from drinking water. Granular activated carbon (GAC) was a support for ferric ions that were impregnated using aqueous ferrous chloride ($FeCl_2$) followed by $NaClO$ chemical oxidation. Carbons produced by lignite steam activation were most suitable among 13 tested activated carbons for iron impregnation and arsenic removal. Maximum iron loadings were 7.89 wt% for Draco 20×50 and 7.65 wt% for Draco 20×40. The BET specific surface area, pore volume, and porosity all decreased after iron impregnation. This indicated some micropores blockage. SEM/X-EDS studies showed iron (1% Fe) distributed on the As-6AC carbon surfaces. Iron extended into the granule centers at high iron loads (6% Fe). When iron content was > 7%, a ring formed at the edges of the 4.12% iron-GAC, suggesting that impregnated iron was amorphous. Arsenic was most efficiently adsorbed when the iron content was 6%. Further increases in iron decreased arsenic adsorption. The removal of arsenate occurred in a wide pH range (4.4-11), but arsenate adsorption decreased at pH >9.0. Phosphates and silicate significantly decreased arsenate removal at pH > 8.5, while sulfate, chloride, and fluoride had minimal effects. The maximum adsorption capacities of untreated GAC, GAC-Fe (0.05 M), GAC-Fe- O_2 (0.05 M), GAC-Fe- H_2O_2 (0.05 M), GAC-FeNaClO (0.05 M) were 3.78×10^1 , 2.29×10^3 , 1.92×10^3 , 3.94×10^3 , 6.57×10^3 μg As/g, respectively (Table 2.3). As(V) and As(III) were removed to below 10 $\mu g/L$ when the groundwater containing approximately 50 $\mu g/L$ of arsenic was treated.

Table 2.3. Comparative evaluation of activated carbons and various low- cost adsorbents for arsenic removal [135]

Adsorbent	Type of water	pH	Conc/ range	Surface area (m ² g ⁻¹)	Capacity (mg/g)	
					As(III)	As(V)
Iron oxide coated sand	Drinking	7.6	100 µg/L	10.6	0.041	0.043
Iron oxide coated sand (IOCS)	Natural (dose 0.5-1.20 g/100 mL); 5h		325 µg/L	5.1	-	0.018
Ferrihydrite (FH)	Natural (dose 0.02-0.09 g/100 mL); 5 h		325 µg/L	141	-	0.25
Iron oxide coated sand	Drinking (dose 20 g/L); 2 h	7.5	100-800 µg/L	-	0.028	-
Al ₂ O ₃ /Fe(OH) ₃	Drinking (63.3 g in 50 ML; 100 g in 80 ML)	8.2-8.9	0.05 mg/L	-	-	0.09
La(III) impregnated silica gel	-	-	-	-	-	8.85
Pure alumina					-	13.64

Adsorbent	Type of water	pH	Conc/ range	Surface area (m ² g ⁻¹)	Capacity (mg/g)	
					As (III)	As (V)
La(III) impregnated alumina	-	-	-	-	-	12.88
Activated alumina	-	-	-	-	-	11-24
Waste Fe(III)/Cr (III)	Aqueous solution (dose 500 mg/50 ML; 5 h)	4.0	20-100 mg/L	-	-	11.02
Activated carbon (Draco)	-	-	-	-	-	3.75
Char carbon	Aqueous solution	2-3	157-737 for As(V) and 193-992 for As(III)	36.48	89.0	34.46
Activated carbon	Aqueous solution	6.4-7.5	157-737 for As(V) and 193-992 As(III)	43.40	29.9	30.48
Bauxsol	Water (dose: 5 g/L)	4.5	0.80-32.00Mm	-	-	1.081

Adsorbent	Type of water	pH	Conc/ range	Surface area (m^2g^{-1})	Capacity (mg/g)	
					As (III)	As (V)
Bauxsol-coated sand (BCS)	De-ionized/Tap	4.5	0.45-20.34 mg/L	7.56	-	3.32
AB-coated sand (ABCS)	De-ionized/Tap	7.1	0.54-20.34 mg/L	47.29	-	1.64
Seawater-neutralized red mud (Bauxsol)	De-ionized/Tap (dose: 5 g/L)	7.3	0.08-32.00 Mm	-	-	1.081
Bead cellulose loaded with iron oxyhydroxide (BCF)	Ground water	7.0	1-100 mmol/L	-	99.6	33.2
Activated alumina	Drinking water	7.6	1 mg/L	370	0.180	-
Activated alumina (AA)	Drinking water	7.6	-	365	-	-
MnO ₂ (Mol)	Drinking water	7.9	<1 mg/L	17	-	0.172
Iron(III)-loaded Chelating resin	Aqueous Solution	9.0 for As(III); 3.5 for As(V)	-	-	62.93	55.44

Adsorbent	Type of water	pH	Conc./range	Surface area (m^2g^{-1})	Capacity (mg/g)	
					As(III)	As(V)
TiO ₂	Drinking water	7.00	-	330	59.93	37.46
TiO ₂ (Hombikat UV 1000)	Drinking water	4.0	<0.0015 M	334	22.70	22.47
TiO ₂ (Degussa P25)	Drinking water	4.0	<0.0015 M	55	3.45	4.65
HFO	Drinking water	9.0	0-60mg/L	200	28.0	7.0
Goethite	Drinking water	9.0	0-60 mg/L	39	22.0	4.0
Fe _x (OH) _y -Montm	Drinking water	9.0	0-60 mg/L	165	13.0	4.0
Ti _x H _y -Montm	Drinking water	9.0	0-60mg/L	229	13.0	3.0
FePO ₄ (amorphous)	Drinking water	7-9 for As(III); 6-6.7 for As(V)	0.5-100mg/L	53.6	21	10
FePO ₄ (crystalline)	Drinking water	7-9 for As(III); 6-6.7 for As(V)	0.5-100 mg/L	35.9	16	9
MnO ₂ -loaed resin	Drinking water	7-8.5	3-150 mg/L	-	53	22

Adsorbent	Type of water	pH	Conc./ range	Surface area (m^2g^{-1})	Capacity (mg/g)	
					As(III)	As(V)
Iron(III) oxide-loaded melted slag (IOLMS)	Wastewaters	2.5	20-300 mg/L	196	2.9-30.1	18.8-78.5
TiO ₂	Ground water	7.0	0.4-80 mg/L	251	32.4	41.0
Activated carbon (AC) produced from oat hulls	Drinking water	5.0	25-200 $\mu\text{g/L}$	522	-	3.08
Zirconium(IV)-loaded chelation resin (Zr-LDA)	Spring water	9.0 for As(III) and 4.0 for As (V)	-	7.3	49.15	88.73
Methylated biomass	Surface and ground water	6.5	0.5-2.5 Mm	6.5	-	3.75
Granular ferric hydroxide (GFH)	Surface and ground water	7.0	-	226-252	-	0.004

Adsorbent	Type of water	pH	Conc./ range	Surface area (m ² g ⁻¹)	Capacity (mg/g)	
					As(III)	As(V)
Zirconium(IV) - loaded phosphoric chelate adsorbent	NA	2.0	5 Mm	-	-	149.9
Kaolinite	Wastewater (soil liner to be used in tailings dams at a sulfidic gold ore plant)	5.5	10-1000 mg/L	8.5	-	<0.23
Untreated GAC	Drinking water	4.7	0.10- 30.0 mg/L	600-1000	-	0.038
GAC-Fe (0.05M)	Drinking water	4.7	0.10-30.0 mg/L	600-1000	-	2.96
GAC-Fe-O ₂ (0.05 M)	Drinking water	4.7	0.10-30.0 mg/L	600-1000	-	1.92
GAC-Fe- NaClO (0.05 M)	Drinking water	4.7	0.10-30.0 mg/L	-	-	2.8
Ferrihydrite			0.267- 26.7 mmol/L		266.5	111.0 2
Activated carbon	Wastewater (copper electrorefineries)	-	300 mg/L	1000	-	2860
Coconut husk caron	Industrial wastewater	12.0	50-600 mg/L	206	146.30	

Adsorbent	Type of water	pH	Conc./ range	Surface area (m ² g ⁻¹)	Capacity (mg/g)	
					As(III)	As(V)
Coconut shell carbon with 3% ash	Wastewater (processing of complex sulfide ore)	5.0	0-200 mg/L	1150- 1250	-	2.4
Peat-based Extruded carbon with 5% ash		5.0	0-200 mg/L	975	-	4.9
Coal-based carbon with 5- 6% ash		5.0	0-200 mg/L	1050- 1200	-	4.09
Biomass	-	2.0	1-10 mg/L	-	13.17	-
Nanoscale zero-valent iron (NZVI)	Ground water	7.0	1-10 mg/L	-	13.17	-
Cu/NN-MCM-48	Drinking	6.0	0-1500mg/L	635	-	37.46
Alginate bead (doped and coated with iron)	Drinking	7.0	50µg/L	-	-	0.014
Chitosan	Wastewater	4.0	400mg/L	-	-	58

Adsorbent	Type of water	pH	Conc./range	Surface area (m ² g ⁻¹)	Capacity (mg/g)	
					As(III)	As(V)
Mixed rare earth oxide	Water/wastewater	6.5	50mg/L	6.75	-	2.95
Portland cement	Drinking water	4-5	0.2mg/L	15.38	-	3.98
Iron oxide coated cement (IOCC)	Drinking water	~7	0.5-10.0 mg/L	-	-	6.43
Human hairs	Drinking water	-	90-360 µg/L	-	-	0.012
Hematite	Water/wastewater	4.2	133.49 µmol/L	14.40	-	0.20
Feldspar	Water/wastewater	4.2	133.49 µmol/L	10.25	-	0.18
Sharkey soil	Soil	5-6	5-100 mg/L	-	-	0.74
Windsor soil	Soil	5-6	5-100 mg/L	-	-	0.55

Adsorbent	Type of water	pH	Conc/range	Surface area (m^2g^{-1})	Capacity (mg/g)	
					As(III)	As(V)
Zr(IV)-loaded phosphoric acid chelating resin (RGP)	River/sea water	1.14	2.5mmol/L	29.2	-	49.0
Ferric chloride impregnated silicagel	-	-	-	-	≤ 5.24	≤ 5.24
GAC	Drinking /waste-water	7.0	1 mg/L	1.065	0.09	4.5
Fe(III) oxide-impregnated GAC	Drinking /waste-water	7.0	1 mg/L	840	4.50	4.5
Activated alumina	Drinking water/ ground water	7.0	50mg/m ³	195	-	9.20
Activated carbons from olive pulp and olive stone, carbon A	Drinking water	7.0	5-20 mg/L	1030	1.393	-
Activated carbons from olive pulp and olive stone, carbon B	Drinking water	7.0	5-20 mg/L	1850	0.855	-

Adsorbent	Type of water	pH	Conc./range	Surface area (m ² g ⁻¹)	Capacity (mg/g)	
					As(III)	As(V)
Activated carbons from olive pulp, olive stone, carbon C	Drinking water	7.0	5-20 mg/L	1610	0.738	-
Activated carbons from olive pulp, olive stone, carbon D	Drinking water	7.0	5-20 mg/L	732	0.210	-

As (V) and As(III) removal from water was studied using a char carbon (CC) derived from fly ash. Darco activated carbon [Darco S-51 (DC)] obtained from Norit Americas Inc and carbon produced by a graphite electric arc (AC). CC and AC adsorbents removed almost equal amounts of As(V) at optimum conditions. The maximum uptakes of As(V) was 34.5 mg/g (490 ppm, pH 2.2) for CC while 30.5 mg/g (159 ppm, pH 7.5) for AC. The uptake of As(III) was 89.2 mg/g (709 ppm and pH 2.2) for CC and 29.9 (992 ppm and pH 7.0) mg/g for AC. These sorbents contain different amounts of ash (28.4% for CC and 2% for AC). Since their specific surface areas are very similar, the ash contents alone did not greatly influence the adsorption of As(V).

The efficiency of As (V) adsorption by activated carbon(AC) produced from oat hulls has been investigated [130]. Adsorption capacity decreased from 30.9 to 1.57 mg As g⁻¹ when the initial pH increased from 5 to 8. A modified linear driving force model [136] coupled with the Langmuir isotherm described simultaneous rapid and slow kinetic process. The LDF model assumes that the uptake is linearly proportional to a driving force, defined as the difference between the surface concentration and the average adsorbed phase concentration. The simulation results indicate that the adsorption process is described well by the modified LDF model. Because the adsorbate is adsorbed easily on the surface (or macropore surface) of the adsorbent, rapid adsorption is resulted. In the interior (or micropore surface) of the adsorbent, the adsorbate would be adsorbed by a pore and/or surface diffusion mechanism, resulting in a slower adsorption.

As (V) removal by an iron oxide-impregnated activated carbon was modeled by Vaughan and Reed [137] using the surface complexation model (SCM) approach given by Dzombak and Morel [138] and Reed and Matsumoto [139]. As(V) removal was strongly pH dependent. A two monoprotic site triple layer model was described As(V) removal using two fitting parameters.

Activated carbon was pretreated with iron-salt solutions to improve arsenic adsorption [140]. The salt type and concentration, pH, and treatment time were examined to improve removal capacity. A 10-fold capacity increase was finally achieved compared to the untreated activated carbon. Ferrous ions were adsorbed and As removal was enhanced by arsenate complex formation. Hunag and Fu [141] examined the As(V) removal capacity of 15 brands of activated carbon over a wide pH range. The carbon type, total As(V) concentration and pH were major factors controlling As(V) removal. Treating As(V)-laden activated carbon with a strong acid or base effectively desorbed As(V) but did not restore the As(V) adsorption capacity. Modified sawdust carbon was also used to adsorb As(III) [142].

2.3 Some Low Cost Adsorbents

2.3.1 Agricultural products and by-products

Agricultural wastes or by-products, currently are being unused or used as animal feed such as rice husks and rice straw were used for arsenic removal from water. The maximum adsorption of arsenic was achieved using 1.0 g of adsorbent from 5.97×10^{-3} mol/L of arsenic solution during 5 min. The adsorption trend followed the Freundlich isotherm over the concentration range from 8.69×10^{-5} to 1.73×10^{-3} mol/L arsenic ($1/n=0.83$ and $K=4.43$ mmol/g). The uptake of arsenic increased with increasing temperature [143].

Untreated rice husk was utilized for aqueous arsenic remediation [144]. Complete removal (using rice husk columns) of both As(III) and As(V) was achieved under the following conditions: initial As concentration, 100 $\mu\text{g/L}$; rice husk amount, 6 g; average particle size, 780 and 510 μm ; flow rate, 6.7 and 1.7 mL/min; and pH, 6.5 and 6.0, respectively. Desorption (71-96%) was also achieved with 1 M of KOH.

2.3.2 Industrial by-products/wastes

2.3.2.1 Chars and coals

Lignite, peat chars [145] and bone-char [146] used in wastewater treatment have received increasing attention. They may be good substitutes for activated carbons. They are plentiful, inexpensive and locally available. Review articles have also appeared [147] on the properties, availability, and use of peat in the control of industrial wastewater pollution. Arsenic(V) removal from aqueous solution by mixture of synthetic hydroxyl apatite and baryte or bone-char was

carried out [146] in the concentration range of 4-100 mg/L. Although the hydroxyl apatite and baryte mixture had a small influence on arsenic concentrations, bone-char was found to be a very effective sorbing agent for As(V) in the pH range of 2-5.

2.3.2.2 Red mud

Red mud is a waste material formed during the production of alumina when bauxite ore is subjected to caustic leaching. A typical Bayer process plant generates a 1-2 tonnes of red mud per ton of alumina produced [148]. Red mud has been explored as an alternate adsorbent for arsenic separation [151]. An alkaline aqueous medium (pH 9.5) favored As(III) removal, whereas the acidic pH range (1.1-3.2) was effective for As(V) removal [149]. The capacities were $4.31 \mu\text{mol g}^{-1}$ at the pH of 9.5 for As(III) and $5.07 \mu\text{mol g}^{-1}$ at the pH of 3.2 for As(V). Heat and acid treatments on red mud increased its adsorptive capacity. Arsenic adsorption on acid and heat treated red mud is also pH-dependent, with an optimum range of 5.8-7.5 for As(III) and 1.8-3.5 for As(V). Adsorption followed a first-order rate expression and fit the Langmuir isotherm well. Isotherms were used to obtain the thermodynamic parameters. The As(III) adsorption was exothermic, whereas As(V) adsorption was endothermic [150]. As(V) removal by using liquid phase of red mud (LPRM) was also reported [151]. Authors suggested that it is advantageous to use a waste material of red mud liquid phase in the treatment of arsenical wastewater, possibly conjunction with red mud solids as adsorbent.

2.3.2.3 Blast furnace slag

Steel plants generate a large volume of granular blast furnace slag. It is being used as filler or in the production of slag cement. Recently, it was converted into an effective and economical scavenger and utilized for the remediation of aqueous arsenic.

Zhand and Itoh [151] synthesized an adsorbent for aqueous arsenic removal by loading iron(III) oxide onto melted municipal solid waste incinerator slag. The simultaneous generation of amorphous hydrous ferric oxide sol and a silica sol *in situ* eventually led to the formation of Fe-Si surface complexes which tightly bonded the iron oxide to the formation of Fe-Si surface. Loading of iron oxide on the slag increased the surface area of iron(III) oxide-loaded melted slag (IOLMS) by 68% compared to FeOOH, which could be attributed to the porous structure formed in IOLMS during the synthesis process. This adsorbent effectively removed both arsenate and arsenite, exhibiting removal capacities for As(V) and As(III) by 2.5 and 3 times of those of amorphous hydrous ferric oxide, respectively. About 15 g of IOLMS is sufficient to remove 200 mg As(V) from 1 L of aqueous solution to meet the metal ion concentrations allowed by regulations for industrial wastewater discharge. In contrast 65 g of IOLMS was necessary to remove As(III) from 1 L solution to meet the permissible limit.

2.3.2.4 Fe(III)/Cr(III) hydroxide waste

Chromium (VI) compounds are used as corrosion inhibitors in cooling water systems in industries. Fe(II), generated electrolytically, reduces Cr(VI) in the wastewater to Cr(III) under acidic conditions. The Fe(III)/Cr(III) ions produced in solution are precipitated as Fe(III)/Cr(III) hydroxide by the use of lime. The resultant sludge is discarded as waste. Namasivayam and Senthilkumar [152] adsorbed As(V) from water onto a Fe(III)/Cr(III) hydroxide waste generated electrolytically in the treatment of Cr(VI)-containing waste waters from fertilizer production. As(V) concentration, agitation time, adsorbent dosage, adsorbent particle size, temperature, and pH were studied. The adsorption capacity was valuated using both Langmuir and Freundlich isotherm models. As(V) adsorption followed a first-order rate expression and was independent of the initial pH (3-10). Adsorption was explained by considering ZPC of the

adsorbent material. The pH_{ZPC} of waste Fe(III)/Cr(III) hydroxide was 8.3. In the pH range 3-7, H_2AsO_4^- was predominantly adsorbed. The adsorbent acquired positive charge in this pH range and adsorption was facilitated by Coulombic interactions. In the pH range 7-10, specific interactions occurred, since dissociation of arsenic acid is expected. The transfer of a proton to the hydroxyl groups of the Fe(III)/Cr(III) hydroxide surface is also possible. A surface complexation model has also been proposed for As(V) adsorption on Fe(III)/Cr(VI) waste. Desorption of As(V) from the spent adsorbent was also achieved using NaOH solutions.

2.3.2.5 Fly ash

Coal combustion produces a huge amount of by-product, fly ash, whose disposal requires large area of land and water. Currently, its application is limited to civil engineering uses including cement and brick production and roadbeds. Bottom ash can also serve as an adsorbent [153]. Resource recovery from coal fly ash is one of the most important issues in waste management worldwide. Since the major chemical compounds contained in fly ash are aluminosilicate, intensive efforts have been recently made to utilize this material as an adsorbent.

2.3.3 Soils and constituents

2.3.3.1 Soils

Arsenate [As(V)] adsorption-desorption kinetics were reported on Olivier loam, Sharkey clay, and Windsor and followed by arsenic release using successive dilutions [154]. The As(V) retention rate was initially rapid followed by gradual or slower retention behavior with increased reaction time. A multi-reaction model (MRM) described the sorption kinetics of As(V) on Olivier

loam and Windsor sand. The model also predicted As(V) desorption kinetics for both soils. As(III) and As(V) adsorption on three acid-zone soils from California (Wasco, Fallbrook, and Wyo) was examined at varying As concentrations, pHs, and ionic strengths. Chromatographic speciation of As(III)/(V) revealed that the three soils contained low levels of background As(V). Oxidation of added As(III) to As(V) was not detected below pH 8 in soil suspensions during 16-h adsorption. However, As(III) oxidation was detected at high pHs. The soil with highest Fe levels and clay (Wyo) had the highest affinity for both As(III) and As(V). This soil displayed adsorption behavior similar to pure ferric oxide. As(V) adsorbed more strongly than As(III) under most conditions. However, a pH-dependent reversal in the relative affinity of As(III) and As(V) took place in these soils at low As surface coverage.

2.3.3.2 Sand

A variety of treated and coated sands were employed for arsenic remediation [155]. Sand coated with iron oxide had more pores and a high specific surface area. Manganese greensand (MGS), iron oxide-coated sand (IOCS-1 and IOCS-2) and an ion-exchange (Fe^{3+} form) resin columns were used for demethylarsinate removal from tap water. Batch studies of IOCS-2 demonstrated an organic arsenic adsorption capacity of 8 $\mu\text{g/g}$ IOCS-2. Higher bed volumes (585 BV) and high arsenic removal capacity ($5.7 \mu\text{g/cm}^3$) were achieved by this resin compared to the other adsorbents. Poor performance was observed with MGS and IOCS-1. Recently, Nguyen et al. [156] synthesized iron coated sponge (IOCSp) for As(III) and As(V) removal. Each gram of IOCSp adsorbed about 160 μg of arsenic within 9 h.

2.3.3.3 Clay minerals

Clay minerals are hydrous aluminum silicates, sometimes with minor amounts of iron, magnesium and other cations. Clays have structures similar to the micas and therefore, form flat hexagonal sheets. Typical clay minerals are kaolinite, illite and montmorillonite. Clay minerals and oxides are widespread and abundant in aquatic and terrestrial environments. Finely divided clay minerals and oxides exhibit large surface areas. Clay minerals and oxides adsorb the cationic, anionic, and neutral metal species. They can also take part in the cation-and anion-exchange processes. Their sorption capacities, cation-and anion-exchange properties and binding energies vary widely. Studies of arsenate and arsenite removal from water by oxides and clay minerals have appeared [157].

2.3.3.4 Zeolites

Zeolites have been received increasing attention for pollution control as standard components in wastewater treatment [158]. Both ion exchange and adsorption properties of zeolites have been used for the selective separation of cations from aqueous solution. Zeolites are crystalline, hydrated alluminosilicates of alkali and alkaline earth cations, having infinite, three-dimensional structures. They can lose and gain water reversibly and exchange constituent cations without change in structure. There are more than 30 natural zeolites known, but only seven (mordenite, clinoptilolite, chabazite, erionite, ferrierite, phillipsite, and analcime) occur in sufficient quantity and purity to be exploited.

CHAPTER 3

THEORETICAL

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THEORETICAL

3.1. Arsenic Removal Process

There are nine general categories of arsenic remediation processes. They are: (1) Oxidation, 2. Coagulation/Precipitation, 3. Sedimentation, 4. Filtration, 5. Adsorption, 6. Ion Exchange, 7. Membrane/Reverse Osmosis, 8. Biological and 9. Other. The principle, advantages and disadvantages are shortly discussed in this chapter.

3.1.1. Oxidation

Of the two predominant forms of arsenic in water, arsenate As(V) and arsenite As(III), most treatment processes are effective at removing arsenate as As(V), but not arsenite as As(III). This is because the arsenite is typically non-charged below pH 9.2. Therefore, treatment for the removal of arsenic often includes an oxidation step to convert arsenite to arsenate.

Oxidation can be simply defined as the addition of oxygen to a compound, or more generally, any reaction involving the loss of electrons from an atom. Aeration, the supplying of air, oxidizes arsenic, converting arsenite to arsenate, and the iron that co-occurs combined with arsenate to form FeAsO_4 and precipitate. Arsenic can also be oxidized by a number of other chemicals including chlorine, hypochlorite, ozone, permanganate, hydrogen peroxide and Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$). Photochemical oxidation proceeds from the reaction of radiant energy and a chemical system. Oxidation alone does not remove arsenic from solution but must be combined with an arsenic removal process.

3.1.2. Coagulation/Co-Precipitation

Coagulation encompasses all reactions, mechanisms and results in the overall process of particle growth (floc formation) and particle aggregation within water being treated, including in-situ coagulant formation, chemical particle destabilization and physical inter-particle contacts. Coagulation involves the removal of colloidal (0.001 - 100 microns) and settleable (> 100 microns) particles. However the term also commonly refers to the removal of dissolved ions (< 0.001 microns), which is actually precipitated. Chemical precipitation is the process by which dissolved ions in solution form an insoluble solid via a chemical reaction. For example, naturally occurring dissolved iron in groundwater, when exposed to oxygen, forms a precipitate. Co-precipitation occurs when an inorganic contaminant forms an insoluble complex with the coagulant. Both the valence of the inorganic contaminant and the pH of the solution are important for removal by co-precipitation.

There are 4 types of co-precipitation:

1. *Inclusion*: It is a mechanical entrapment of a portion of the solution surrounding the growing particle. Typically, this only is significant for large crystals.
2. *Adsorption*: This is an attachment of an impurity onto the surface of a particle or precipitate. This type of co-precipitation is generally not important if the particle size is large, because large particles have very small surface areas in proportion to the amount of precipitate they contain. Adsorption may be a major means of contaminant removal if the particles are small.
3. *Occlusion*: A contaminant is trapped in the interior of a particle of precipitate. This type of co-precipitation occurs by adsorption of the contaminant onto the surface of a growing particle, followed by further growth of the particle to enclose the adsorbed contaminant.

4. *Solid-solution formation:* Another type of occlusion where a particle of precipitate becomes contaminated with a different type of particle that precipitates under similar conditions and is formed from ions whose sizes are nearly equal to those of the original precipitate.

Coagulation converts soluble arsenic into insoluble reaction products, allowing separation by sedimentation and/or filtration. Factors affecting arsenic removal by coagulation/precipitation include coagulant type and dose, mixing time and speed, pH, arsenic oxidation state and concentration, presence of inorganic solutes.

Three mechanisms are potentially involved in arsenic removal:

Precipitation: The formation of insoluble compounds $\text{Al}(\text{AsO}_4)$ or $\text{Fe}(\text{AsO}_4)$

Co—precipitation: Incorporation of soluble arsenic species into the metal hydroxide floc.

Adsorption: The electrostatic binding of soluble arsenic to the external surfaces of the insoluble metal hydroxides.

Direct precipitation plays the least important role in arsenic removal; however, co-precipitation and adsorption are both active arsenic removal mechanisms [4,5].

3. 1. 3. Sedimentation

Sedimentation is the gravity separation of solids from liquid by settling. It is generally used in conjunction with coagulation/precipitation.

3.1.4. Filtration

Conventional filtration is the separation of solid particles from water by passing the solution through a medium. Particles are removed during filtration

as a result of any one or combination of mechanisms: mechanical straining, sedimentation, flocculation, adsorption and/or biological metabolism. The filter medium may be of various materials, for example, sand, anthracite coal, activated carbon, cloth, paper, that retains the solid on its surface and allows the water to pass through. Common particulates removed by filtration include silt, clay, colloidal and precipitated natural organic matter, naturally-occurring iron and manganese precipitates, precipitates from metal salt or polymer coagulation, microorganisms etc. Filters may be classified in various ways, according to the type of granular medium used, by the hydraulic system (e.g. gravity, up-flow, etc.), rate of filtration, and/or by the location of particle accumulation (e.g. cake filtration, depth filtration).

3.1.5. Adsorption

Adsorption is the accumulation of materials at an interface, the liquid/solid boundary layer. It is a mass transfer process where a substance is transferred from the liquid phase to the surface of a solid and becomes bound by chemical or physical forces. Adsorption can take place on suspended particles, as part of the process of coagulation/co-precipitation, or on fixed media. Since adsorption is a surface phenomenon, the greater the surface area of the medium, the greater its capacity to accumulate material. Each adsorbent medium has different associated properties, performances and costs. Arsenic is adsorbed onto the surface of various granular, activated, clay and cellulosic adsorbents, including:

- * oxides (e.g. hydrated ferric oxide, titanium oxide, silicium oxide);
- * iron oxide-coated or MnO_2 -coated sand;
- * bauxite, hematite, feldspar;
- * clay minerals (e.g. kaolinite, bentonite, Bijoypur clay);

- * synthetic anion exchange resins;
- * chitin and chitosan;
- * bone char;
- * cellulose materials (sawdust, newspaper pulp).

3.1.6. Ion Exchange

Ion exchange is the reversible interchange of ions between the solid and the liquid phase where there is no permanent change in the structure of the solid. Developed for large-scale applications, ion exchange is probably not appropriate for small hand-pumped wells, but could potentially be used on a village scale in Bangladesh.

Synthetic ion exchange resins are based on a cross-linked polymer matrix, typically composed of polystyrene cross-linked with vinylbenzene. Charged functional groups are attached to the matrix through covalent bonding and fall into four groups (Clifford, 1999) [63] as follows:

- Strongly acidic
- Weakly acidic
- Strongly basic
- Weakly basic

Various strong base anion exchange resins are commercially available that can effectively remove arsenic from water, producing effluents with less than 1 $\mu\text{g/L}$ arsenic. Arsenic, being uncharged, is not removed, unless an oxidation step to convert arsenite to arsenate is included in the process.

Conventional sulfate-selective resins are particularly suited for arsenate removal. Nitrate-selective resins also remove arsenic, but arsenic breakthrough occurs earlier. Ion exchangers are typically down-flow, packed bed columns

with ion exchange resin beads pre-saturated with an exchangeable ion. Source water is passed through the packed bed until the appearance of the unwanted contaminant in the effluent. At this stage, the ion exchange media is reactivated with a regenerant solution and rinsed with water in preparation for another treatment cycle. Both the redox potential and pH are important factors with regard to arsenic removal by ion exchange.

3.1.7. Membrane/Reverse Osmosis

Membrane separation uses semi-permeable membranes that are selectively permeable to water and certain solutes to separate impurities from water. Membranes are able to remove many different kinds of dissolved solids, including arsenic, from water. However, they are usually expensive and therefore, are typically considered in applications such as desalination, brackish water conversion and for removal of specific ions, such as arsenic, that are difficult to remove by other means. There are many different membrane alternatives including microfiltration, reverse osmosis, electrodialysis, ultrafiltration and nanofiltration. Membrane process treatment performance is dependent on the quality of the feed water and the desired quality of the product water. Generally, the more contaminated the feed water and the higher the desired product water quality, the greater the likelihood of membrane fouling caused by particulate matter, scaling and biofouling.

3.1.8. Biological

Biological treatment transforms, stabilizes and/or removes arsenic by means of microorganisms. Microorganisms, primarily certain specific bacteria, accomplish this by oxidation/reduction, mineralization, detoxification or

methylation. Critical factors include energy and carbon source; aerobic, anoxic or anaerobic conditions; temperature, pH.

3.1.9. Other

It includes Dug Wells, Deeper Tube Wells, Ponds, Solar Distillation etc. Solar distillation uses the sun's energy to evaporate water, which then recondenses. The process of evaporation and recondensation separates all chemicals, including arsenic, from water. In Bangladesh, where solar energy is plentiful, this approach may be especially suited for application in crisis areas, and, if cost-effective approaches can be developed, in rural areas generally.

3. 2 Theory of the Present Work

Adsorption process for arsenic removal from water was applied in this work using high surface area activated carbon modified with iron oxide. Therefore, the theoretical aspects relating to the adsorption should be studied in details. Gas phase and liquid phase adsorption are the main characteristics of activated carbons. When two immiscible and chemically non-reactive phases are brought into contact, it is a common observation that the concentration of one phase is greater at the interface. This is due to the fact that the atoms, ions, molecules at the interior of a solid, liquid or a gas are subjected to equal forces of attraction in all directions, whereas those at the surface experience unbalanced forces, the inward pull being greater than the outward forces. As a result in most cases, there is a tendency of any surface to decrease its free energy by accumulation of atoms, ions or molecules at the interface without involving a formal chemical bond. Such accumulation has been termed adsorption. It is probable that adsorption occurs on all surfaces but the effects are not evident unless the adsorbing material, i.e., adsorbent is porous and has a very large surface area

for a given mass. But it is not axiomatic that accumulation at the interface will occur when two immiscible phases are brought into contact.

Thus, inspite of logical prediction that all surfaces are potentially capable of decreasing its free energy, it is pragmatic to assume that there must be some specificity in the nature of the surface in order that adsorption may take place. It may also be noted from obvious thermodynamic reasons that adsorption normally takes place with decrease in entropy, because by confining an adsorbet molecule to a thin surface layer, certain degrees of freedom are lost. Using equation

$$\Delta E = \Delta H - T \Delta S$$

for adsorption, it obviously shows that ΔH is also negative, that is, adsorption in general exothermic. No case of endothermic adsorption is definitely known, although De Boer [159] has suggested that in one or two cases where a transient chemisorption takes place to very limited extent, an endothermic process may be involved.

The main work of saturating a surface is usually accomplished by adsorption of a single layer of molecules and in such a case the phenomenon is termed unimolecular or monomolecular adsorption. However, adsorption involving the formation of several layers is by no means infrequent, and these are called multimolecular adsorption.

Although there may be wide and continuous variations of the degree of unsaturation of surfaces, experiences have taught that there are only two kinds of adsorption. The surfaces of many substances are inert in the sense that the valence requirement of their atoms may be thought to be satisfied by bonding with adjacent atoms. With this type of surface, adsorption tends to take place simply through forces of physical attraction, similar to those causing deviation of real gases from ideal laws, the liquefaction of gases and so on. This kind of adsorption is called physical or van der Waals' adsorption.

On the other hand, many surfaces are much more unsaturated and the valence requirement of their surface atoms may be thought not to be fully satisfied by bonding with nearby atoms. In adsorption, such a surface will tend to form chemical bonds with a nearby phase and this process is called chemisorptions.

From an intimate point of view the difference between chemical and physical adsorption lies in how the combining species electronically interact with each other, in the latter case such interaction is far less discrete and menacingly inconceivable while in chemical adsorption the phenomenon can be considerably explained and the part played by active groups present in the adsorption can sometimes be reasonably predicted. Since our knowledge about the intricacies of either processes is countless uncertainties and also that both the processes lead to what is called docking of the adsorbate to the adsorbent surfaces with far less affinity than what a traditional chemical bond effects; it will be prudent to accept that no simple criterion proves to be so sharp as to enable decision to be made about the specificity of the processes occurring. Nevertheless, the following points of distinction have been observed through analysis, scrutiny and interpretation of the experimental results obtained during the last 50 years.

1. Chemical bonds being stronger than physical forces of attraction and the heats of chemisorptions should be larger than that of the heats of physical adsorption. The heat of the chemisorptions is of the order of chemical reaction and the heat of the physical adsorption is equivalent to heat of liquefaction.
2. Physical adsorption takes place near or below the boiling point of adsorbate while chemisorptions can usually take place at still high temperatures.
3. On obvious grounds, chemisorptions requires activation energy to commence; physical adsorption on the other hand requires a negligible

amount of activation energy. But many surfaces are so unsaturated that they undergo rapid chemisorptions even at low temperature.

4. Chemisorptions ceases when the adsorbate can no longer make direct contact with the surface and is, therefore, a single layer process. With physical adsorption no such limitation applies, and under suitable conditions of temperature and pressure, physically adsorbed layers of many molecules thick may be obtained. This aspect of difference between the processes has a special significance in the present work.
5. Physical adsorption is non-specific and reversible, whereas chemisorptions is an irreversible process.
6. In physical adsorption the amount of adsorbate increases gradually with increasing concentration or pressure and complete saturation is not obtained until the concentration or pressure is relatively high. In this case, amount of adsorbate take up increases with decrease of temperature, other conditions remaining same. On the other hand chemisorptions increases with the increase of concentration or pressure and soon reaches to a saturation value at a given temperature beyond which further increase of pressure does not alter the amount of adsorption.

3.2.1. Localized and Non-Localized Adsorption

A surface may be represented diagrammatically as a plane, the potential energy of which fluctuates from point to point. When these fluctuations are appreciable through the represented adsorption sites, and adsorption is, therefore, said to be localized. If fluctuations are so small as effective to vanish, there are no-adsorption sites and adsorption is said to be non-localized.

Chemisorptions are always localized and in localized adsorption, two extreme conditions may be distinguished. If the energy fluctuation is the same between any pair of sites and all sites have the same energy, the surface is said to be uniform or homogeneous. If the fluctuation is irregular and the sites have different energies, the surface is said to be non-uniform or heterogeneous. Homogeneous and heterogeneous surfaces have very different properties of adsorption.

In non-localized adsorption there are no energy barrier opposing movements of a particle from point to point on the surface but in localized adsorption, there is a barrier. Therefore, with non-localized layers, the kinetic thermal energy of the adsorbed particles is sufficient to ensure that they will be mobile and move over the surface, but localized layers may be usually immobile.

As a conclusion about the nature of the forces that cause the adsorption, a smooth idealized surface is always considered. In most calculation for the adsorption energy, the same assumption is maintained. But it is observed that the majority of surfaces are not idealized. Surfaces developed with many corners, ribs, edges, cavities and lattice disturbances increase the adsorption capacity. Since no solid surface can be ideally smooth, the residual field at the surface responsible for adsorption will not be uniform. An atom on a flat surface is attached to similar atoms over a solid angle of 180° , but the atom at the apex of a peak, or at the edge or corner of a crystal, will have a much smaller fraction of its electrostatic attraction shared by others, and so its residual field will be large.

Brunauer et.al [160] has suggested that such unsaturated atoms constitute the active centers which are associated with high adsorption capacity. Very often adsorption occurs between two surfaces which are only a very small distance apart and in many cases the adsorbed molecules have to widen this distance to

create the surface at which they will be adsorbed. This is closely related to the well-known swelling phenomenon.

Adsorption of gases and vapours on solid and adsorption of dye and electrolyte from solution have been known for a long time. Both experimental and theoretical investigations of Langmuir, Sigmondy, Freundlich and F. Paneth and others furnished us with considerable knowledge of the adsorption phenomena.

In the case of adsorption from solution on solid surfaces, it is an experimental result that the extent of adsorption depends upon the specific nature of the adsorbing solid and the molecules to be adsorbed and also depend upon the concentration and temperature. For a given weight of substance with a given surface area, the amount of solute adsorbed from solution depends upon concentration of the solution. The higher the concentration, the greater the amount adsorbed. The amount of solute adsorbed at equilibrium is a function of final temperature and concentration as follows:

$$W = f(CT)$$

Where, W = Weight of adsorbate adsorbed per gram of adsorbent.

C = Equilibrium concentration of the solution.

T = Absolute temperature.

When the concentration of the solution is varied and the temperature kept constant, plot of the amount adsorbed against the concentration is called the “adsorption isotherm”.

$$W = f(C) \text{ when } T \text{ is constant.}$$

When the concentration is constant and the temperature is varied, the plot is the “adsorption isobar”.

$$W = f(T) \text{ when } C \text{ is constant.}$$

The plot of the variation of equilibrium concentration with respect to temperature is the “adsorption isoster”.

$C = f(T)$ when W is constant.

The variation of adsorption with concentration can often be represented over a limited range of concentration, at constant temperature by the empirical equation.

$$\frac{x}{m} = KC^{1/n} \dots\dots\dots (3.1)$$

Where k and n are temperature dependent constants

Where ‘ x ’ is the mass of substance adsorbed by ‘ m ’ gram of adsorbent when the concentration is C .

‘ K ’ and ‘ m ’ are constant for the given system and temperature.

This relationship is known as the “classical adsorption isotherm” or Freundlich Adsorption isotherm. Equation (3.1) is very simple convenient and can be regarded as approximately applicable for a small range of concentration. At high concentration, it has been found that the Freundlich equation does not hold good.

Langmuir in 1916 proposed a theory which depends upon the assumption that the surface of solid consists of elementary spaces or points of residual valance. The adsorptive forces are concentrated at these points and adsorption consists in the fixing of the absorbed atoms in the elementary spaces for a certain time. He assumed that these spaces or points of residual valance can hold only one atom or molecule, therefore, the adsorbed layer can be only one molecule thick. Thus, the force between the atoms of surface of the adsorbent and the atoms of the adsorbed substance decreases rapidly with the distance between the atoms. He further assumed that all the elementary spaces were identical in their affinity for adsorbate molecule and that the presence of one molecule on one

space did not affect the properties of the neighboring spaces. For adsorption of gases on solids Langmuir equation, the final form of which is

$$\frac{x}{m} = \frac{k_1 k_2 p}{1 + K_1 p} \text{-----}(3.2)$$

Where k_1 and k_2 are constants for a given system and p is the gas pressure. This equation may be written in the form

$$\frac{p}{x/m} = \frac{p}{k_2} + \frac{1}{k_1 k_2} \text{-----}(3.3)$$

Equation (3.3) is known as Langmuir adsorption isotherm. This equation is applicable for solid-gas system-provided the adsorbents are nonporous. At moderate concentration, Langmuir adsorption isotherm also holds good for adsorption from solution. Hence replacing the pressure term by equilibrium concentration the equation (3.3) becomes

$$\frac{C}{W} = \frac{C}{K_2} + \frac{1}{K_1 K_2} \text{-----}(3.4)$$

Where, $W = x/m$

Equation (3.4) represents a straight-line, the slope of which is equal to $\frac{1}{k_2}$. If the concentration of the solution increase to such an extent that the adsorbate forms a complete unimolecular layer, at that point the slope of the straight line will be $\frac{1}{W_m}$, where W_m is the weight of the adsorbate required to form a complete unimolecular layer. At that condition K_2 can be replaced by W_m and the equation (4) reduced to

$$\frac{C}{K} = \frac{C}{W_m} + \frac{1}{K_1 W_m} \text{-----}(3.5)$$

The equation of Langmuir has been verified by experiments on adsorption from both gas-phase and solution. When the concentration is higher, the possibility of multimolecular layer formation has been suggested notably by Brunauer, Emmett and Teller [160] their predictions have also been shown to be correct.

3.2.2. Types of Adsorption [161]

During the first three decades of this century innumerable investigations were made on adsorption of gases under different circumstances with various systems. A careful analysis of the results of these investigations has led to the inescapable conclusion that there are two different types of adsorption; one is the chemical adsorption or chemisorptions and the other one is the physical adsorption or van der Waal's adsorption. The observed characteristics of any adsorption process usually allow it to be placed in one or the other category.

All gases have a tendency to be held to the surface by physical forces and thus exhibit van der Waal's adsorption, but when valence forces also come into play in adhering the molecules to the surface, chemisorptions takes place. In both types there is a decrease in the extent of adsorption with rise in temperature, hence the processes are exothermic.

In van der Waals adsorption, the heat of adsorption is relatively small, about 5 Kcal/mole which are of the same order as heats of vaporization. On the other hand in chemisorptions, larger amounts of heat of adsorption are evolved, about 20 to 100 Kcal/mole, as usually found in chemical reaction. The physical adsorption is more pronounced at temperature below the boiling point of the adsorbate whereas the chemisorptions occurs usually at high temperature. The physical adsorption equilibrium is established rapidly and is generally reversible but in chemisorptions the attachment is much stronger, the equilibrium is attained relatively slowly and is irreversible in the sense that if subsequently pressure is reduced desorption may not occur.

In physical adsorption multilayer are formed whereas in chemisorptions most commonly a unimolecular layer occurs governed by Langmuir isotherm. The extent of van der Waals adsorption is more a function of the adsorbate than the adsorbent but the amount of adsorption in chemisorptions is characteristic of both adsorbate and adsorbent.

Many instances of adsorption are neither one type nor the other, but a combination of the two. A typical isotherm for a chemical adsorption is often found as in Fig. 3.1(a), the extent of adsorption increases with pressure and ultimately reaches a limiting value. In some instances of simple monolayer physical adsorption attended with small heat-change at low pressure and moderate temperature, also similar isotherm-curves are found.

But in adsorption involving multilayer formation at low temperature, at least for other types of isotherm curves are found experimentally.

These are shown in Fig. 3.1(b-e).

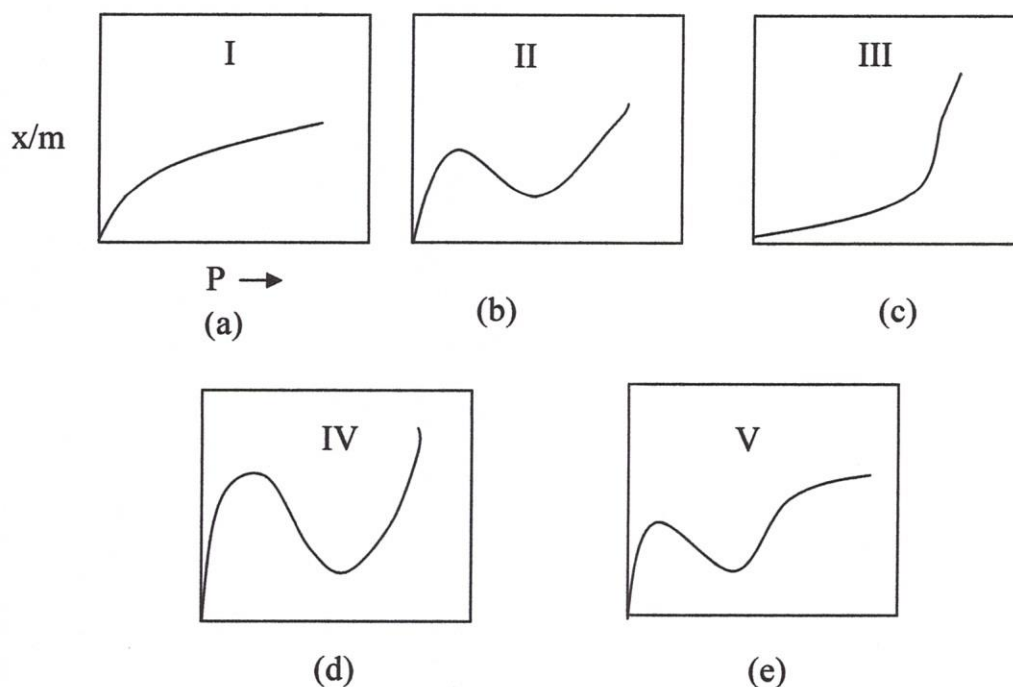


Figure 3.1. Various types of adsorption isotherms

Adsorption isotherm of the types II and III (Fig. 3.1) are explained as that when $E_L > E_1$ the resulting curve is of the type III.

For understanding types IV and V isotherms, it is necessary to assume that not only multilayer adsorption occurs but also that the pores and capillaries of the adsorbent are filled by condensation at a pressure much lower than the saturation pressure P_0 , type IV is obtained when $E_1 > E_L$ and type V when $E_L > E_1$.

3.2.3. Adsorption from Solution [162]

Solid surfaces can also adsorb solutes from the solution. An application of adsorption from solution is the use of activated charcoal for decolourizing sugar solution. Activated charcoal can adsorb colouring impurities on its surface. Other examples of this type of adsorption are the adsorption of ammonia from ammonium hydroxide, phenolphthalein from solutions of acids or bases and acetic acid from its solution in water, etc. by activated charcoal.

It has been observed that carbon adsorbs non-electrolytes more readily from a solution than electrolytes and inorganic solids. This behavior of adsorbents to attract certain substances in preference to other substance leads to a phenomenon of negative adsorption i. e. concentration of the solute becomes more after treatment with the adsorbent.

Adsorption from solution in most of the cases leads to the formation of layer single molecule in thickness on the surface of the solid as was observed in the chemisorption of gas on a solid.

This type of adsorption is also affected by temperature and concentration. The extent of adsorption decreases with increase of temperature and increases with increase of concentration. In order to represent the variation of extent of adsorption with concentration, Freundlich suggested an empirical equation similar to equation (3.6). This equation is,

$$\frac{x}{m} = KC^{1/n} \dots\dots\dots (3.6)$$

Where 'x' and 'm' are the masses of the substance adsorbed and of adsorbent, respectively. C is the equilibrium concentration of the adsorbed substance in the solution, K and n are empirical constants. Taking logarithms of equation (3.6), we get,

$$\text{Log} \frac{x}{m} = \log K + \frac{1}{n} \log C \dots\dots\dots (3.7)$$

Equation (3.7) implies that a plot log x/m against log C should be a straight line with slope 1/n and intercept K.

3.2.4. Objectives of Adsorption Studies

The importance of adsorption studies can hardly be over emphasized. Extensive work has been carried out on adsorption from solution as gas solid system. The adsorption in gas solid systems is generally more amenable because of the absence of any other entity except adsorbate and adsorbent. But adsorption from solutions may become complicated due to presence of solvent which may also be adsorbed and sometimes compete with the adsorbate. The extent of competition may vary from system to system.

Adsorption phenomena plays an important role in chemical, analytical and technical sides. Catalysis (heterogeneous), gas-solid, solid-liquid, gas-liquid reactions, corrosion etc. are included in the chemical process. The extent of reaction, the power of catalyst may be indicated by the adsorption study. The prevention of corrosion and its study may be made easier with the help of adsorption study.

In the analytical side purification, separation, identification of gases and liquids using chromatographic technique, measurement of surface area, characterization of solid surfaces and its activity measurements are included.

The technical side includes the processes such as lubrication, adhesion and stabilization of colloids.

Besides, many metal oxides are used as catalyst for oxidation-reduction reaction and many other reactions for accelerating or retarding a particular reaction. Such oxides used in the industry as catalyst or any other agent should be well investigated about their surface area, adsorption tendency, what types of adsorbent they are etc.

The above mentioned processes are all involved surface phenomena. The surface phenomena and adsorption are correlated with each other. Hence the adsorption is important particularly to the chemists.

3. 3. Adsorbent and Adsorbate [163]

It is generally believed that gases are adsorbed on the surface of all solids but the effects become noticeable only when the surface area of the adsorbent for a given mass is quite large. For this purpose, therefore, the adsorbent must be sufficiently porous and in a finely divided state. Charcoal, silica gel, platinum black, nickel powder, etc. are very effective as adsorbent for they have large exposed surfaces to take up appreciable quantities of different gases. The adsorbents are sometimes specially treated to raise their adsorbing quantities. Charcoal prepared from bone or coconut shells are heated to about 400°C-1000°C in vacuum or in chlorine. Such treatment distils away the hydrocarbon impurities from charcoal rendering its surface free and clean where adsorption would readily occur.

A gas is adsorbed in different amounts on different adsorbents. Hydrogen is strongly adsorbed on nickel surface but not so on alumina's surface under identical conditions. On the other hand, the amounts of various gases adsorbed on a given surface are different. This implies that the extent of adsorption also depends upon the adsorbate. This is illustrated in the table (3.1) here.

Table 3.1: Volumes (X) of gases by 1g of charcoal at 15°C less than 1 atmosphere

Gas	Volume adsorbed (X C.C.)	B. pt. (°K)	Cr. temperature (°K)
O ₂	8.2	90.2	154
N ₂	8.0	77.3	126
H ₂	4.7	20.3	33
CH ₄	16.5	111.7	190
CO ₂	48.0	-	304
HCl	72.0	188.0	324
NH ₃	181.0	239.7	406
Cl ₂	235.0	238.5	417

Evidently, there is a parallelism between the extent of adsorption of a gas on a surface and the boiling point or critical temperature of the adsorbate. Easily liquefiable gases, consequently having large cohesive forces, are more readily adsorbed. It should, however, be realized that it does not mean that in the adsorbed state the adsorbate is in liquid phase.

The amounts of gases adsorbed are either measured gravimetrically from the increase in weight of the adsorbent or volumetrically from the variation in pressure.

3.3.1. Measurement of Physical Properties of Adsorbent

By measuring the physical properties of the adsorbent due to adsorption, information about the nature of adsorption can be obtained. Thus, change in electron concentration in the solid, consequent upon adsorption may be ascertained from electrical conductivity, magnetic susceptibility and work function measurements. Such changes take place only as a result of chemisorptions.

Solids having unpaired electron change magnetic properties because of chemisorptions. So one can calculate the change in number of unpaired electrons by measuring the magnetic properties.

3.3.2. Surface Area of Adsorbents [163]

The determination of the surface area of finely divided solids is of paramount importance in the field of industrial catalysis and in the study of colloids. The procedure depends upon finding out the volume of a gas required to form a unimolecular adsorbed layer on the solid. For this purpose the B.E.T isotherm is now a days extensively employed. The B.E.T equation:

$$\frac{P}{V(P^0 - P)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} \cdot \frac{P}{P^0} \dots\dots\dots (3.8)$$

The plot of $P/V (P^0 - P)$ against P/P^0 is linear. The slope = $(C-1)/V_m \cdot C$ and the intercept = $1/V_m \cdot C$. Hence, the volume of gas to form a unimolecular layer,

$$V_m = \frac{1}{\text{Slope} + \text{intercept}}$$

Thus V_m is known and V_m is expressed under S. T. P.

The number of molecules in $V_m C$. = No. $V_m/22414$. If A (cm^2) be the cross section of each adsorbed gas molecule and if m g of solid adsorbent be present, then the surface area (s) per gram of the solid is

$$S = \frac{\text{No. } V_m \cdot A}{22414 \times m} \quad (\text{cm}^2)$$

The gas usually employed for this measurement is nitrogen. The value of A is obtained from the density of liquid nitrogen at its boiling point (-195°C), for nitrogen. A is equal to $16.2 \text{ \AA}^2$. The value of S is hence known. Some of the experimental results are appended below.

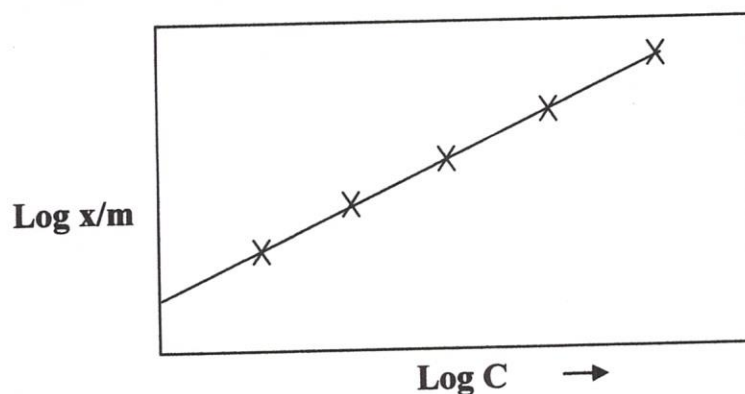
Table 3.2: Surface areas of adsorbents determined from BET isotherm

Adsorbent	Adsorbate used	Area per molecule $\text{\AA}^2$	Vol. adsorbed to produce a monolayer	Surface area per gm of adsorbent (Sq. cm)
Ni	Kr	14.6	-	9×10^4
Ni	n-butane	24.5	-	8.5×10^4
Cu (fused)	N_2	16.2	0.09	0.39×10^4
Fe- Al_{203}	N_2	16.2	2.86	12.4×10^4
Silica-gel	N_2	16.2	116.2	500×10^4

3. 4 Application of Adsorption

Adsorption finds extensive applications both in the laboratory and in the industry. Some of the important applications are:

- (I) Adsorption of gases on solids is employed for creating a high vacuum between the walls of Dewier containers designed for storing liquid air or liquid hydrogen. This is achieved by placing activated charcoal between the walls which has already been exhausted to the maximum extent using a vacuum pump. The activated charcoal will adsorb any gas which may appear due to glass imperfection or diffusion through the glass.

**Fig 3.2 :** Adsorption of acetic acid by char coal

- (II) Adsorption of gases on solids is also utilized in gas masks which contain an adsorbent or a series of adsorbents. These adsorbents purify the air for breathing by adsorbing all the poisonous gases from the atmosphere. In the same manner, suitable adsorbents can also be employed in the industry for recovering the solvent vapours from air or particular solvents from the mixture of other gases.
- (III) Char coal finds an extensive application in the sugar industry. It is used as a decoloriser for the purification of sugar liquors. It can also be used for removing coloring matter from various other types of solutions.
- (IV) Adsorption is employed for the recovery and concentration of vitamins and other biological substances.
- (V) Adsorption finds extensive applications in chromatography which is based on selective adsorption of a number of constituents present together in a solution or gas.
- (VI) Adsorption also plays an important role in catalysis.

CHAPTER 4

EXPERIMENTAL

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EXPERIMENTAL

4.1. Introduction

Various types of materials, chemicals and equipment were used for the preparation and characterization of activated carbons and iron loaded activated carbons and they were used for arsenic separation from water. Experimental part is divided into four sections: (1) preparation of activated carbons from jute stick, (2) iron loading on activated carbons, (3) characterization of activated carbons and iron loaded activated carbons and (4) separation of arsenic from water using activated carbons and iron loaded activated carbons. Description of equipment and materials used for the work and methodology applied in the whole work are described in details in the following sections.

4.2. Materials

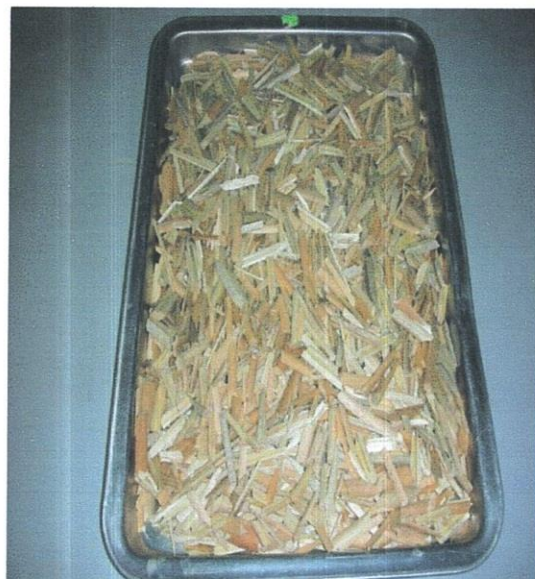
4.2.1. Feed Stock Collection and Preparation

The feedstock considered in this study is “jute stick”, which is agricultural residue and abundantly available in Bangladesh. The raw “jute (*Corchorus capsularis*) sticks” were collected from a local farmer. After collecting jute sticks, they were processed by washing, drying to around 10% moisture content and grinding with a crushing machine to around 1.0 – 2.0 mm in size. The most important concern in feedstock processing is the moisture content. In chemical activation of feedstock, the moisture content must be reduced to

less than 10% to ensure the adequate soaking of activating agent solution. Figure 4.1 shows the jute sticks as collected and grinded jute sticks. For chemical activation process, the particles of jute stick were soaked in the activating agent solution.



(a)



(b)



(c)

Figure 4.1 (a)Jute sticks, as collected,(b) before grinding (c) after grinding.

4.2.2. Chemicals and their Sources

The following chemicals were used in this work.

Name of Chemicals	Producers	Purity
Ethanol	E.Merck, India	99.0%
Methanol	E.Merck, India	99.9%
Acetone	E.Merck, India	99.9%
Iodine	Loba, India	99.5%
Sodium thiosulphate	Loba, India	99.5%
Potassium Iodide	Loba, India	99.9%
Hydrochloric acid	Loba, India	99.9%
Phosphoric acid	Loba, India	99.9%
Arsenic trioxide	Aldrich	99.0%
Sodium dithiodimethyl carbamate	Aldrich	99.9%
Pyridine	Aldrich	99.9%
Zinc dust	Aldrich	99.0%
Stanous chloride	Aldrich	99.5%

4.3. Equipment

4.3.1. List of Experimental Equipment and Instruments

The following equipment and instruments were used for experiments in this research.

Name of Equipment	Maker, Model, Origin
Grinding machine	Retsch – SM100
Oven	Gallenkamp Regd, Model – OV-445, England
Standard testing sieve	W.S. Taler Incorporated, A.S.T.ME-II, Mentor OH 10 44060, USA
Reactor for carbonization and activation	Bangladesh, Malaysia
Pipeline system	Bangladesh, Malaysia
Thermal gas mass flow controller	Cole-Parmer, U.S.A.
pH meter	Model-HI 8624, Cole-Parmer, U.S.A.
Temperature controller	Model – KKK03, China
Muffle furnace	Lindburg Blue M, Model – CBFS 518C, U.S.A.
Electronic Balance	Shimadzu, Model – AY220, Japan
Activation reactor	Bangladesh, Malaysia
Reactor heating system	Bangladesh, Malaysia
Micro-level water supply pump	Ismatec, Model – CP 78017-10, Switzerland

4.3.2. List of Analytical Instruments

The following analytical instruments were used in this research.

Name of Instruments	Model and Origin
Elemental Analyzer	Costech - ECS 4010
CHNSO BET Instrument	Autosorb- iQ/MP-XR
TG-DTA	Shimadzu, Model – DTA 60A, Japan
SEM	JEOL JSM 840
FT-IR	Perkin-Elmer Spectrum GX FT-IR spectrometer
Raman	Bruker RFS100 FT-Raman
X-RD	TD-3500 XRD
Incubator Shaker	Model Brunswick Scientific 12400
UV-Visible Spectrophotometer	Model SECOMAM Uvi Line 9400
Atomic Absorption Spectrometer	Thermo Scientific iCE 3300
Gas chromatograph	(Model-14 B,TCD and FID
Inductively coupled plasma atomic emission spectrometer (ICP-AES)	Thermo Scientific iCAP 6000

4.4. Description of Equipment and Instruments

4.4.1. Grinding Machine Retsch – SM100

After collecting jute stick, it was dried and ground using a grinding machine Retsch – SM100 as shown in Figure 4.2. This machine is a specially designed powerful crusher for different materials such as wood, plastic, rubber, corncob and etc. It has excellent wearing ability and impact-resistance for time and labor saving and large busting capacity and easy feeding system. The shaft rest for the cutter head is constructed of round hollow with special angle to keep cooling for long hour's usage. Cutter head angle cutting

design allows aggressive cutting rates and high speed shredding of waste. It has movable screen for changing the size of chips and easy clean-up as well as energy efficient and quiet running industrial motor.



Figure 4.2. Grinding Machine Retsch – SM100

4.4.2. Standard Testing Sieve (Mentor OH10 44060)

In this work, after grinding the jute stick, it was sieved using different mesh sizes of standard testing sieve. Figure 4.3 shows the standard testing sieve loaded on a shaker. Analytical sieves (Screens) are defined by 4 criteria as follows:

1. Nominal sieve opening for wire cloth also called mesh size
2. Diameter of sieve
3. Height of frame
4. Material for frame and cloth.

Nominal Sieve Opening

This means the ASTM E-11 or ISO 3310-1 standards.

- ☐ ASTM E-11 standard (American Society for Testing Materials)
- ☐ This is the standard most widely used in North America.
- ☐ The opening is defined by a number, number 635 (20 μm) to number 3-1/2 (5.6 mm)), or in inches (1/4 in. (6.3 mm) to 5 in. (125 mm)).
- ☐ ISO 3310-1 standard (International Standards Organization)
- ☐ This is the standard used in Canada in the field of construction materials.
- ☐ The opening is defined in micrometers (20 μm to 37,500 μm).

Diameter

Sieves that conform to current ASTM E-11 standards, have a diameter of 8", 12" and 3". The 6", 10" and 18" diameters are also available. Sieves that conform to ISO 3310-1 standards are offered with a 200 mm diameter, and more rarely 400 mm.

Height

Analytical Sieves are generally available in 3 heights (see table below):

- FH=Full Height
- HH=Half Height
- IH=Intermediate Height

Material

Sieves are generally available in three material combinations:

- ☐ Brass Frame and Brass screen (cloth)
- ☐ Brass Frame and Stainless Steel screen/cloth
- ☐ Stainless Steel Frame and SS screen.



Figure 4.3. Standard testing sieve loaded on a shaker for jute stick screening.

4.4.3. Elemental Analyzer

This elemental analyzer uses the technique of combustion/gas chromatography to analyze samples in an accurate, precise, easy-to-use way. It is ideal for the analysis of total nitrogen, carbon, hydrogen, sulfur, or oxygen in soil, sediments, plant material, pharmaceuticals, organic chemicals, oil additives, fuels and many other organic and inorganic samples. In this work, this instrument was used for ultimate analysis to determine carbon, hydrogen, oxygen, sulfur and nitrogen content determination. The picture of the instrument is shown in Figure 4.4.



Figure 4.4. Costech - ECS 4010 CHNSO elemental analyzer

4.4.4. Oven (Model – OV-445)

As shown in Figure 4.5, this oven can be operated within the temperature range of 0 - 260 °C. Temperature is accurately and reliably controlled by a compensate thermostat. An indicator lamp lights when the oven reaches at set temperature. In addition a safety thermostat is fitted which may be set to any desired interval above the oven operating temperature. In the event of incorrect setting or failure of compensate the safety thermostat takes oven control and a warning lamp indicates the fault condition. This oven was used for feedstock drying under controlled temperature at 105°C for overnight to ensure less than 10% moisture content in jute stick after soaking in activating agent solution.



Figure 4.5. Oven (Model – OV445) used for drying feedstock and product sample

4.4.5. Muffle Furnace (Model – CBFS 518C)

The stable temperature CBFS series of Muffle furnace is a family of ultra lightweight, economical, laboratory box furnaces as shown in Figure 4.6. The low thermal mass Moldatherm insulation/heating element provides fast duty cycles, energy conservation, and efficient programming. The Muffle furnace was used for calcination of iron-loaded activated carbons. After loading iron salts such as ferrous sulfate on activated carbons by impregnation, the solid mass was calcined at 500°C for 1 h in order to decompose iron salt to iron oxide.



Figure 4.6. Muffle furnace for calcination and ash content determination.

4.4.6. Electronic Balance (Model – AY220)

The Shimadzu AY series electronic balances are high performance, multiple function balances. The AY series balances are equipped with various application weighing functions, and unit conversion functions. These functions allow for a great variety of applications when used in conjunction with the peripheral units. This was used for all type weighing of samples. Figure 4.7 exhibits the picture of electronic balance used in this work.



Figure 4.7. Electronic balance used for taking accurate weight.

4.4.7. pH Meter (Model – HI 8424)

As shown in Figure 4.8, HI 8424 is a portable microprocessor-based pH/mV/temperature meter. It features a user-friendly membrane keyboard, low battery detection, automatic calibration and error codes to guide the user in calibration and troubleshooting.

The pH calibration procedure automatically recognizes three memorized buffer values: pH 4.01, 7.01 and 10.01. This instrument can also be used for ISE and ORP measurements with automatic range switching when readings exceed +399.9 mV. Temperature measurements can be displayed in $^{\circ}\text{C}$ or $^{\circ}\text{F}$, selected by the user through a slide switch in the battery compartment. To save and prolong battery life, the meter is also provided with an auto-off feature, which can be disabled through a slide switch in the battery compartment.

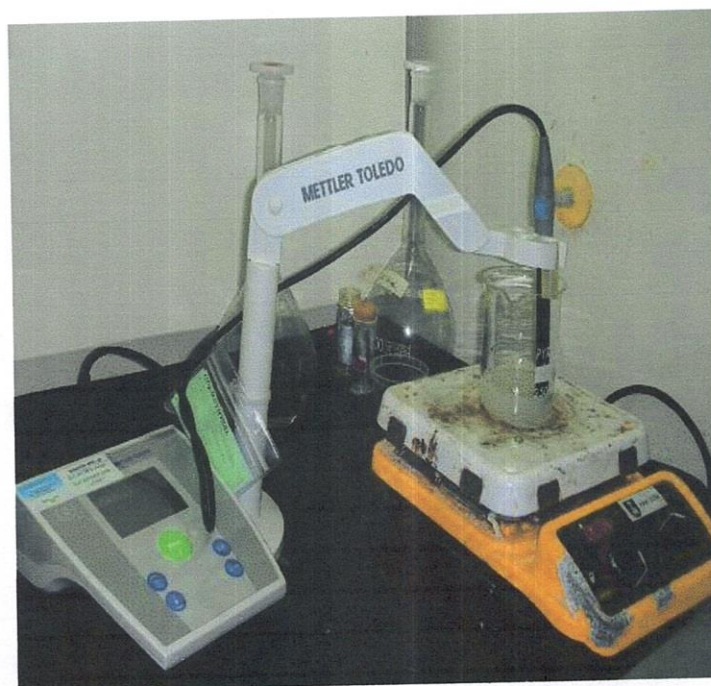


Figure 4. 8. pH meter (Model – HI 8424)

4.4.8. TG-DTA (Model – DTA 60A)

Thermogravimetry-Differential Thermal Analysis instrument of Model DTA 60A as exhibited in Figure 4.9 can be operated under different environments such as air, nitrogen, oxygen and hydrogen. Aluminum and platinum bins for sample holding are provided for low and high temperature operation. High vacuum pump is provided for replacing air from the oven of the machine. This machine simultaneously plots the weight loss curve and differential temperature curve. This can indicate either the decomposition of materials is exothermic or endothermic. From the weight loss curve, the moisture content, volatile matter content, fixed carbon content and ash content in the sample can be determined.

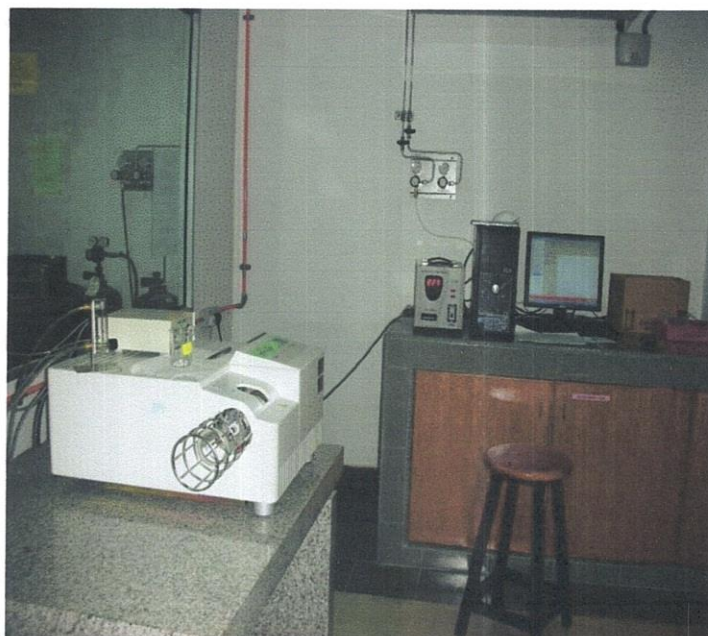


Figure 4.9. TG-DTA (Model – DTA 60A) used for the determination of volatile carbon, fixed carbon measurement and ash content measurement in raw biomass as well as in activated carbon samples.

4.4.9. BET Instrument (Autosorb- iQ/MP-XR)

The Brunaur-Emmett-Teller (BET) instrument of Model- Autosorb- iQ/MP-XR is very sensitive and accurate to automatically plot the data acquired from nitrogen adsorption on the solid surface of the experimental sample under liquid nitrogen temperature condition. The instrument is exhibited in Figure 4.10. This machine directly shows the BET curve from where it automatically calculates the total surface area of the experimental sample. This machine can also measure the pore volume.

It has two physisorption analysis ports for surface area analysis and pore size measurements, both of which can be equipped for low pressure micropore analysis including optional 0.1 torr transducer.

Metal-to-metal (VCR) fittings employed in the measurement manifold(s) for extremely low leak rate, a dedicated P_0 (saturation pressure) transducer, and a long life dewar (90+ hours, even with two samples) are all standard

features. 12 mm, 9 mm and 6 mm sample cells (with or without bulbs) offer the most sample-type flexibility.

One port is available as a chemisorption station, complete with high temperature furnace with fan-assisted cooling. The chemi- version is also offered with optional flow-based measurement capabilities (TPX, pulse titration). The chemi-station retains full physisorption capability.

A vapor dosing option is available for both physi-and chemi-units and features a 50°C thermostated manifold chamber. The two built-in degas stations (turbo pumped vacuum is standard on the MP and C models) feature computer-controlled ramp/hold/test protocols, a dedicated cold-trap, and optionally a second (dedicated) vacuum system. No need to degas on the analysis stations thus preventing contamination of the analysis section.

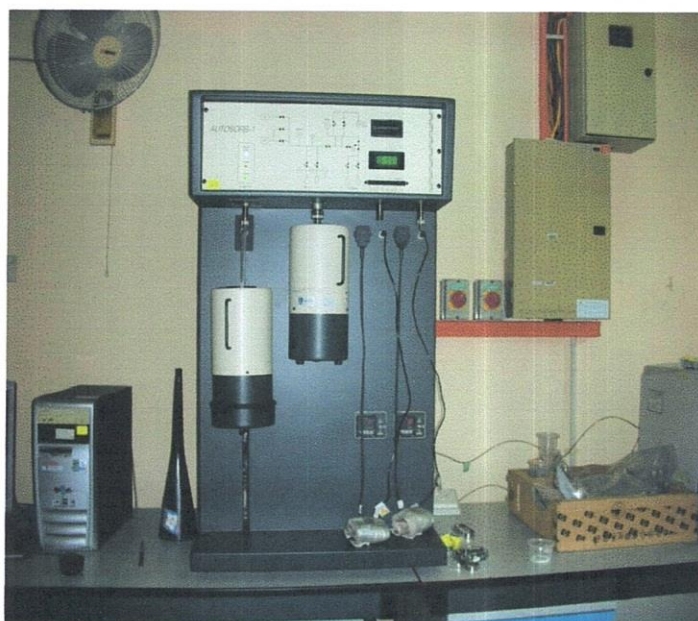


Figure 4.10. BET Instrument (Autosorb- iQ/MP-XR) used for the determination of surface area, pore volume and pore size of the activated carbon samples.

4.4.10. Gas Chromatograph (Model – 14B, TCD and FID)

Gas Chromatograph 14B is equipped with capillary and packed column as shown in Figure 4.11. It is also equipped with flame ionization detector (FID) and thermal conductance detector (TCD).



Figure 4.11. Gas Chromatograph (Model – 14B, TCD and FID) used for the determination of gas composition during activation of charcoal by physical activation method.

Capillary column is connected with FID and packed column is connected with TCD. Any organic compounds which are volatile at around 200°C can be qualitatively and quantitatively analyzed by FID-GC. TCD-GC can analyze the burnable gases such as hydrogen. The carrier gas for FID is nitrogen and for TCD is helium.

4.4.11. JEOL JSM-840 Scanning Electron Microscope

As with other scanning electron microscopy, the JSM-840 as shown in Figure 4.12 examines structure by bombarding the specimen with a scanning beam of

electrons and then collecting slow moving secondary electrons that the specimen generates. These are collected, amplified, and displayed on a cathode ray tube (CRT, typically a slower version of the picture tube of a television set) although now, most are driven by PCs and these computer-generated images are displayed on LCDs. The electron beam is scanned using a raster pattern so that an image of the surface of the specimen is formed. Specimen preparation typically includes drying the sample and making it conductive to electricity, if it is not already. Photographs are taken at a very slow rate of scan in order to boost the signal and capture greater resolution.

The SEM is typically used to examine the *external* structure of objects that are as varied as biological specimens, rocks, metals, ceramics and almost anything that can be observed in a dissecting light microscope. The JEOL JSM- 840 is used for conventional samples of normal sizes using the airlock. These specimens are usually mounted on multiple "stubs" (up to 4 specimen stubs fit) and each are observed individually. An alternative for large specimens is to vent the column and use the specimen drawer, which allows silicon disks and other objects to be viewed, but takes longer to pump as the whole specimen viewing area is brought to room pressure.

JEOLJSM-840 SEM Characteristics

- accelerating voltages: 1,000 volts to 40,000 volts
(1,000 volt increments)
- useful magnification: X 10 to X 300,000
- 30 Angstrom resolution (LaB₆ source at 40KV)
- solid state backscattered electron detector

- Kevex X-ray analyzer with light element capabilities and IXRF software and digital imaging capability
- Equipped for x-ray feature analysis, mapping and quantitative analysis
- Nability e-beam lithography package



Figure 4.12. Scanning Electron Microscope (SEM) used for morphological study of activated carbons.

4.4.12. FT-IR Spectroscope (Model Perkin-Elmer Spectrum GX FT-IR spectrometer)

Fourier transform spectroscopy is a measurement technique whereby spectra are collected based on measurements of the coherence of a radiative source, using time-domain or space-domain measurements of the electromagnetic radiation or other type of radiation. It can be applied to a variety of types of spectroscopy including optical spectroscopy, infrared spectroscopy (FTIR, FT-NIRS), nuclear magnetic resonance (NMR) and magnetic resonance

spectroscopic imaging (MRSI), mass spectrometry and electron spin resonance spectroscopy. There are several methods for measuring the temporal coherence of the light, including the continuous wave *Michelson* or *Fourier transform* spectrometer and the pulsed Fourier transform spectrograph (which is more sensitive and has a much shorter sampling time than conventional spectroscopic techniques, but is only applicable in a laboratory environment). Figure 4.13 exhibits a Perkin-Elmer Spectrum GXFT-IR spectrometer.



Figure 4.13. Perkin-Elmer Spectrum GX FT-IR spectrometer.

The term *Fourier transform spectroscopy* reflects the fact that in all these techniques, a Fourier transform is required to turn the raw data into the actual spectrum, and in many of the cases in optics involving interferometers, is based on the Wiener–Khinchin theorem.

Light passes through a monochromator, an instrument that blocks all of the light *except* the light at a certain wavelength (the un-blocked wavelength is set by a knob on the monochromator). Then the intensity of this remaining (single-wavelength) light is measured. The measured intensity directly

indicates how much light is emitted at that wavelength. By varying the monochromator's wavelength setting, the full spectrum can be measured. This simple scheme in fact describes how *some* spectrometers work.

Fourier transform spectroscopy is a less intuitive way to get the same information. Rather than allowing only one wavelength at a time to pass through to the detector, this technique lets through a beam containing many different wavelengths of light at once, and measures the total beam intensity. Next, the beam is modified to contain a different combination of wavelengths, giving a second data point. This process is repeated many times. Afterwards, a computer takes all this data and works backwards to infer how much light there is at each wavelength.

To be more specific, between the light source and the detector, there is a certain configuration of mirrors that allows some wavelengths to pass through but blocks others (due to wave interference). The beam is modified for each new data point by moving one of the mirrors; this changes the set of wavelengths that can pass through.

The method of Fourier transform spectroscopy can also be used for absorption spectroscopy. The primary example is "FTIR Spectroscopy", a common technique in chemistry.

In general, the goal of absorption spectroscopy is to measure how well a sample absorbs or transmits light at each different wavelength. Although absorption spectroscopy and emission spectroscopy are different in principle, they are closely related in practice; any technique for emission spectroscopy can also be used for absorption spectroscopy. First, the emission spectrum of a broadband lamp is measured (this is called the "background spectrum"). Second, the emission spectrum of the same lamp *shining through the sample* is measured (this is called the "sample spectrum"). The sample will absorb some of the light, causing the spectra to be different. The ratio of the "sample spectrum" to the "background spectrum" is directly

related to the sample's absorption spectrum.

Accordingly, the technique of "Fourier transform spectroscopy" can be used both for measuring emission spectra (for example, the emission spectrum of a star), and absorption spectra (for example, the absorption spectrum of a liquid).

4.4.13. Bruker RFS100 FT-Raman

This spectrometer as shown in Figure 4.14 can employ 90 and 180° sampling geometries. It uses a 1.5 W Nd:YAG air-cooled laser delivering an excitation wavelength of 1064 nm. The detector is a liquid nitrogen cooled germanium detector, allowing a spectral range 3500 to 50 (stokes) and -100 to -2000 cm^{-1} (anti-stokes). Liquid samples are presented in mirrored quartz cuvettes and solid samples can be presented as powders through to large pieces. A microscope is fibre optically couple to the spectrometer allow analysis of samples at a microscope scale.

Raman spectroscopy is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, photons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system. Infrared spectroscopy yields similar, but complementary, information.

The following Figure shows the energy level diagram showing the states involved in Raman signal. The line thickness is roughly proportional to the signal strength from the different transitions.

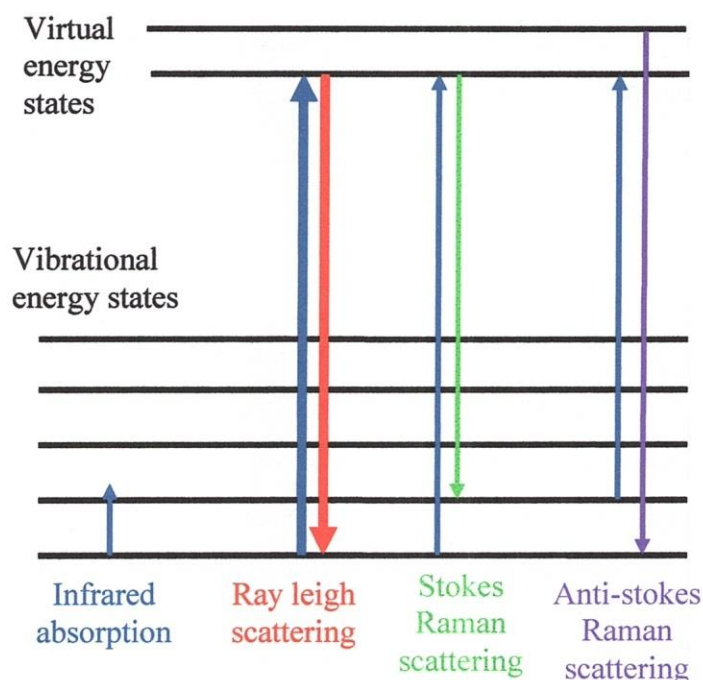


Diagram-1: Energy level diagram

Typically, a sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and sent through a monochromator. Wavelengths close to the laser line due to elastic Rayleigh scattering are filtered out while the rest of the collected light is dispersed onto a detector. Spontaneous Raman scattering is typically very weak, and as a result the main difficulty of Raman spectroscopy is separating the weak inelastically scattered light from the intense Rayleigh scattered laser light. Historically, Raman spectrometers used holographic gratings and multiple dispersion stages to achieve a high degree of laser rejection. In the past, photomultipliers were the detectors of choice for dispersive Raman setups, which resulted in long acquisition times. However, modern instrumentation almost universally employs notch or edge filters for laser rejection and spectrographs (either axial transmissive (AT), Czerny-Turner (CT) monochromator, or FT (Fourier transform spectroscopy based), and CCD detectors.

There are a number of advanced types of Raman spectroscopy, including surface-enhanced Raman, resonance Raman, tip-enhanced Raman, polarised Raman, stimulated Raman (analogous to stimulated emission), transmission Raman, spatially offset Raman, and hyper Raman.

The Raman effect occurs when light impinges upon a molecule and interacts with the electron cloud and the bonds of that molecule. For the spontaneous Raman effect, which is a form of light scattering, a photon excites the molecule from the ground state to a virtual energy state. When the molecule relaxes it emits a photon and it returns to a different rotational or vibrational state. The difference in energy between the original state and this new state leads to a shift in the emitted photon's frequency away from the excitation wavelength. The Raman effect, which is a light scattering phenomenon, should not be confused with absorption (as with fluorescence) where the molecule is excited to a discrete (not virtual) energy level.

If the final vibrational state of the molecule is more energetic than the initial state, then the emitted photon will be shifted to a lower frequency in order for the total energy of the system to remain balanced. This shift in frequency is designated as a Stokes shift. If the final vibrational state is less energetic than the initial state, then the emitted photon will be shifted to a higher frequency, and this is designated as an Anti-Stokes shift. Raman scattering is an example of inelastic scattering because of the energy transfer between the photons and the molecules during their interaction.

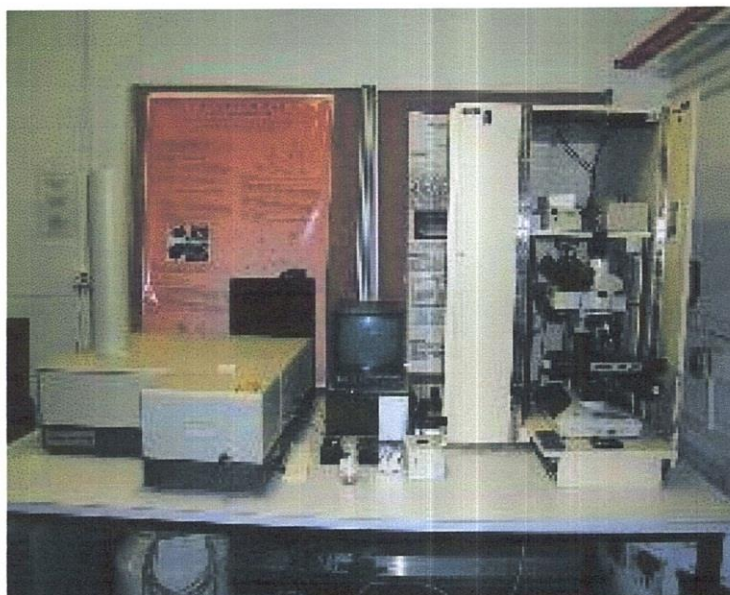


Figure 4.14. FT-Raman Spectrometer.

A change in the molecular polarization potential or amount of deformation of the electron cloud with respect to the vibrational coordinate is required for a molecule to exhibit a Raman effect. The amount of the polarizability change will determine the Raman scattering intensity. The pattern of shifted frequencies is determined by the rotational and vibrational states of the sample. This dependence on the polarizability differs from Infrared spectroscopy where the interaction between the molecule and light is determined by the dipole moment; this contrasting feature allows to analyze transitions that might not be IR active via Raman spectroscopy, as exemplified by the rule of mutual exclusion in centrosymmetric molecules.

4.4.14. TD-3500 XRD

In theory, when X-ray radiation passes through matter, the radiation interacts with the electrons in the atoms, resulting in scattering of the radiation. If the

atoms are organized in planes (i.e., the matter is crystalline) and the distances between the atoms are of the same magnitude as the wavelength of the X-rays, constructive and destructive interference will occur. This results in diffraction where X-rays are emitted at characteristic angles based on the spaces between the atoms organized in crystalline structures called planes.

The following figure is a First Look at Bragg's Law (with incident rays too close to 45 deg for derivation)

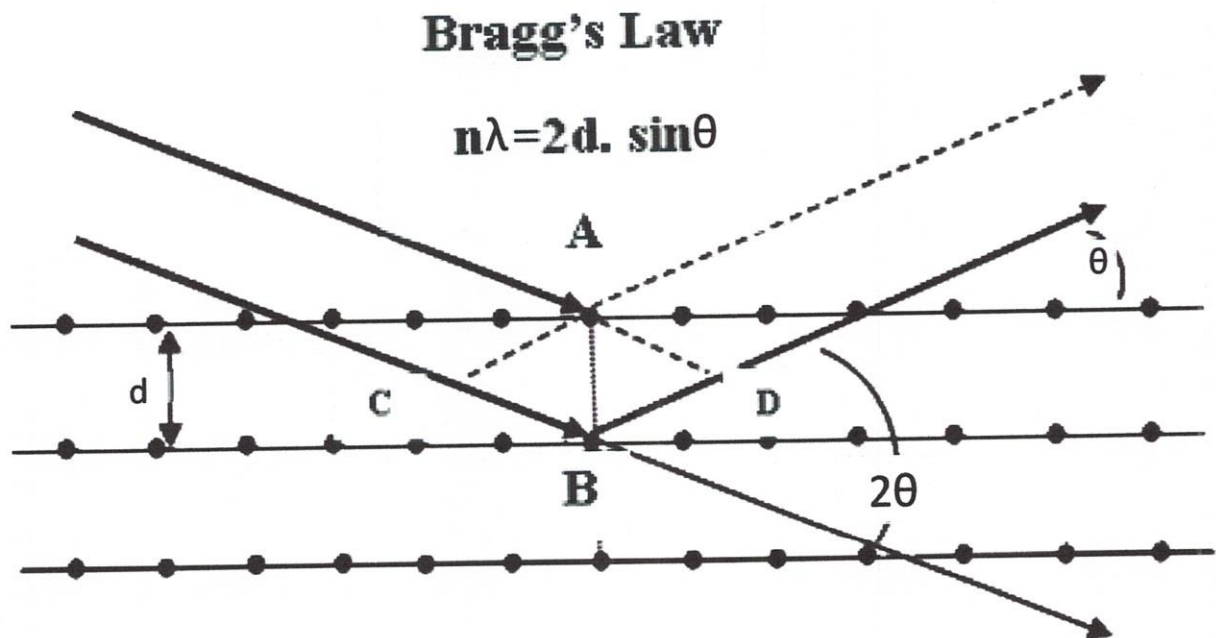


Figure 4.15 shows a XRD-spectrometer with the following specifications.

- SA-HF3 X-Ray Generator 3 KW
- X-Ray Tube: 2.2KW, Cu, Long-Fine Focus
- AFC8-Partial-c, 4- Circle

Goniometer:

❖ Axial angle ranges:

- ω -axis: $\pm 90^\circ$
- 2θ -axis: 0° to 120°
- χ -axis: -5° to 60°
- ϕ : 0° to 360°

Collimators:

- ✚ 0.02mm, 0.05mm, 0.1mm, 0.2mm (Square)
- ✚ 0.3mm, 0.5mm, 0.8mm (Circle)
- ✚ 50 ~ 800 microns pin-hole collimators and 20 micron mono capillary collimator which provides analysis in micro area
- ✚ CCD video (color) microscope: Magnification: 70x
- ✚ Saturn 70 Digital CCD camera system
- ✚ Monochromator optical system with flat graphite monochromator with rock, tilt and translation adjustments

Applications

- Phase analysis of powders and multi crystal matters
- Orientation of single crystal ingots or wafer
- Lattice parameter measurement
- Surface residual stress

X-Ray Diffraction Analysis (XRD) investigates crystalline material structure, including atomic arrangement, crystallite size, and imperfections. Intertek XRD analysis and expertise is available for a very wide range of sample types and applications.

XRD analysis provides:

- ❖ Analysis of Solids, Powders and Liquids

- ❖ Reflection, Transmission or Capillary Geometry In-Situ High. Temperature and Reactive Environment
- ❖ Orientation and Texture Data
- ❖ Grazing Incidence
- ❖ Reflectometry
- ❖ Kratky Small Angle X-ray Scattering (SAXS) XRD analysis applications:
- ❖ Nano-Materials: Phase Composition, Crystallite size and shape, Lattice Distortions and Faulting, Composition Variations, Orientation, In-Situ Structure Development
- ❖ Catalyst evaluation
- ❖ Reservoir core analysis
- ❖ Fuel quality testing
- ❖ New materials research and development
- ❖ Polymers and Composites: Crystalline form, Crystallinity, Crystalline Perfection, Orientation
- ❖ Pharmaceuticals and Organics: Polymorphs, Crystallinity, Orientation



Figure 4.15. TD 3500 XRD

4.4.15. Incubator Shaker (Model Brunswick Scientific 12400)

Incubator shaker (Fig-4.16), as the name suggests, is incubator that can be set to shake at variable speeds. They are most often used in studies of cell biology.

Function

Incubator shakers incubate cell cultures by providing stable temperature conditions under which the cells can grow. Inside the incubator shaker is a tray that moves in a circular motion, onto which the cell cultures are placed. This orbital agitation is used to affect the growth of the cell cultures. The same stable condition is needed for adsorption of solid from liquid by adsorbent and used this machine for methylene blue and iodine adsorption by activated carbon.

Time Frame

This incubator shaker is equipped with timer, so that it can automatically stop after completing a course of adsorption.

Purpose

The agitation provided by the incubator shaker affects the movement of solid in the liquid and brought into contact with liquid under a stable concentration.



Figure 4.16. Incubator shaker.

4.4.16. UV-Visible Spectrophotometer (Model SECOMAM Uvi Line 9400)

The UviLine 9400 concept represents the first spectrophotometer series featuring Advanced Digital Signal Processing technology. ADSP ensures reliable data acquisition, a superb sensitivity level to allow linear measurements even at high OD values, and a very low instrument noise. UviLine in combination with the easy to use Windows compatible LabPower, UV VISION or UV VISION Pharma software packages supports the entire range of daily routine applications.

Benefits:

100% symmetric true double beam technology for high data precision and stability.

- Rotating mirror (chopper) system to achieve reliable data even in concentrated samples.

Specification:

- Range 190-1100 nm
- 100% symmetric double beam optics
- Fixed 1.8 nm bandwidth
- Pharmacopeia compliant
- High quality Zeiss optics

Gross weight : 52Kg (with
palette) Dimensions : 120 x
80 x 53

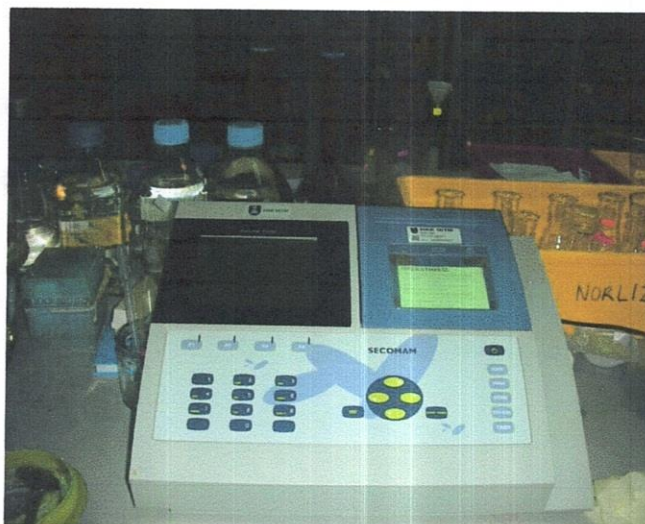


Figure 4.17. UV-Visible Spectrophotometer

4.4.17. Atomic Absorption Spectroscopy (AAS, Model iCE 3300)

The iCE 3300 AA Spectrometer makes even the most complicated analyses simple. The picture is shown in Figure 4.18. Superior double beam optics provide unrivalled performance, while the innovative hardware and software design ensures that running samples, developing methods and maintaining the instrument is easy.

Atomic absorption spectroscopy (AAS) is a spectroanalytical procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state. In analytical chemistry the technique is used for determining the concentration of a particular element (the analyte) in a sample to be analyzed. AAS can be used to determine over 70 different elements in solution or directly in solid samples. Atomic absorption spectrometry was first used as an analytical technique, and the underlying principles were established in the second half of the 19th century by Robert Wilhelm Bunsen and Gustav Robert Kirchhoff, both professors at the University of Heidelberg, Germany. The modern form of AAS was largely developed during the 1950s by a team of Australian chemists. They were led by Sir Alan Walsh at the CSIRO (Commonwealth Scientific and Industrial Research Organization), Division of Chemical Physics, in Melbourne, Australia.

AAS Principles

The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It requires standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and relies therefore on the Beer-Lambert Law. In short, the electrons of the atoms in the atomizer can be promoted to higher orbitals (excited state) for a short period of time (nanoseconds) by absorbing a defined quantity of energy (radiation of a given wavelength). This amount of energy, i.e., wavelength, is specific to a particular electron transition in a particular element. In general, each wavelength corresponds to only one element, and the width of an absorption line is only of the order of a few picometers (pm), which gives the technique its elemental selectivity. The radiation flux without a sample and with a sample in the atomizer is measured using a detector, and the ratio between the two values (the absorbance) is converted to analyte concentration or mass using the Beer-Lambert Law

Instrumentation

In order to analyze a sample for its atomic constituents, it has to be atomized. The atomizers most commonly used nowadays are flames and electrothermal (graphite tube) atomizers. The atoms should then be irradiated by optical radiation, and the radiation source could be an element-specific line radiation source or a continuum radiation source. The radiation then passes through a monochromator in order to separate the element-specific radiation from any other radiation emitted by the radiation source, which is finally measured by a detector.



Figure 4.18. Atomic absorption spectrophotometer AAS, Model iCE 3300.

4.4.18. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP- AES, Thermo Scientific iCAP 6000)

ICP-AES also referred to as inductively coupled plasma optical emission spectrometry (ICP-OES), is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

Mechanism

The ICP-AES is composed of two parts: the ICP and the optical spectrometer. The ICP torch consists of 3 concentric quartz glass tubes. The output or "work" coil of the radio frequency (RF) generator surrounds part of this quartz torch. Argon gas is typically used to create the plasma.

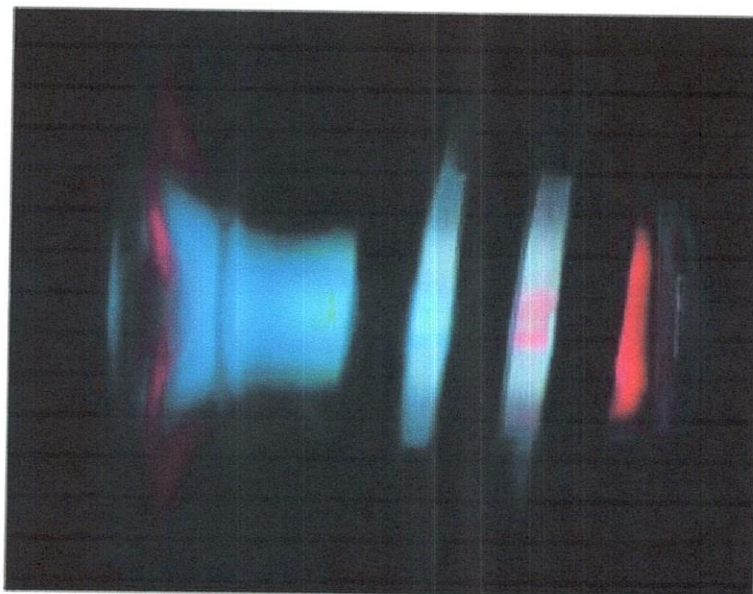


Figure 4.19. ICP Plasma "torch".

When the torch is turned on, an intense electromagnetic field is created within the coil by the high power radio frequency signal flowing in the coil. This RF signal is created by the RF generator which is, effectively, a high power radio transmitter driving the "work coil" the same way a typical radio transmitter drives a transmitting antenna. The argon gas flowing through the torch is ignited with a Tesla unit that creates a brief discharge arc through the argon flow to initiate the ionization process. Once the plasma is "ignited", the Tesla unit is turned off.

The argon gas is ionized in the intense electromagnetic field and flows in a particular rotationally symmetrical pattern towards the magnetic field of the RF coil. A stable, high temperature plasma of about 7000 K is then generated as the result of the inelastic collisions created between the neutral argon atoms and the charged particles.

A peristaltic pump delivers an aqueous or organic sample into a nebulizer where it is changed into mist and introduced directly inside the plasma flame. The sample immediately collides with the electrons and charged ions in the plasma and is itself broken down into charged ions.

The various molecules break up into their respective atoms which then lose electrons and recombine repeatedly in the plasma, giving off radiation at the characteristic wavelengths of the elements involved.

In some designs, a shear gas, typically nitrogen or dry compressed air is used to 'cut' the plasma at a specific spot. One or two transfer lenses are then used to focus the emitted light on a diffraction grating where it is separated into its component wavelengths in the optical spectrometer. In other designs, the plasma impinges directly upon an optical interface which consists of an orifice from which a constant flow of argon emerges, deflecting the plasma and providing cooling while allowing the emitted light from the plasma to enter the optical chamber. Still other designs use optical fibers to convey some of the light to separate optical chambers.

Within the optical chamber(s), after the light is separated into its different wavelengths (colors), the light intensity is measured with a photomultiplier tube or tubes physically positioned to "view" the specific

Wavelength(s) for each element line involved, or, in more modern units, the separated colors fall upon an array of semiconductor photodetectors such as charge coupled devices (CCDs). In units using these detector arrays, the intensities of all wavelengths (within the system's range) can be measured simultaneously, allowing the instrument to analyze for every element to which the unit is sensitive all at once. Thus, samples can be analyzed very quickly.

The intensity of each line is then compared to previously measured intensities of known concentrations of the elements, and their concentrations are then computed by interpolation along the calibration lines.

In addition, special software generally corrects for interferences caused by the presence of different elements within a given sample matrix. The ICP- AES, Thermoscientific iCAP 6000 is shown in Figure 4.20.

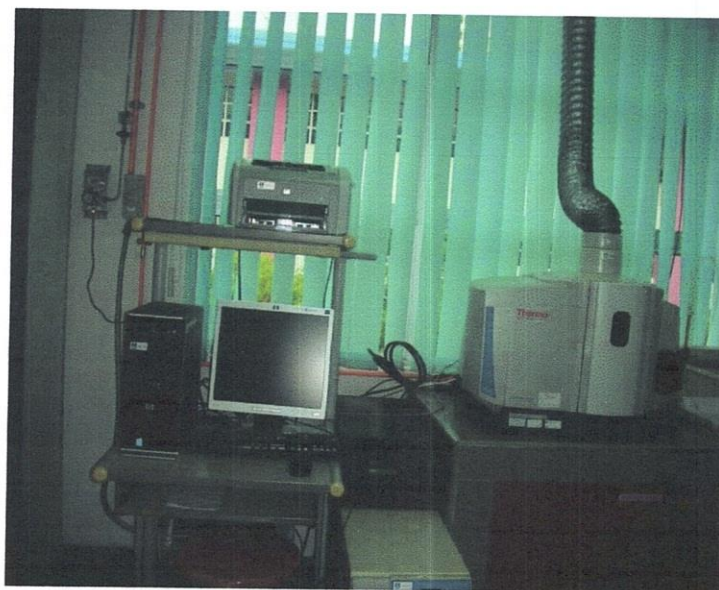


Figure 4.20. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP- AES, Thermo Scientific iCAP 6000)

4.5. Experimental Method

Activated carbon was prepared from jute stick by chemical activation method using phosphoric acid (H_3PO_4) as an activating agent. Initially, the jute stick was prepared as described in the previous section and then it was soaked in phosphoric acid solution for about 20 h. The ratio of jute stick to phosphoric acid plays an important role in pore development in the activated carbon, and thus it has been investigated. The wet jute stick was placed in a stainless steel made carbonization reactor to carbonize followed by activation in an activation reactor.

4.5.1. Characterization of Jute Stick

The jute stick was characterized by measuring the particle size, density, moisture content, heating value and by ultimate and proximate analyses as shown in Tables 5.1 and 5.2 in the next chapter. The ultimate analysis of jute stick was carried out by Japan Institute of Energy and the results are shown in Table 5.2. Proximate analysis is based on the thermogravimetric

analysis (TGA) profile as shown in Figure 5.1. The TGA analysis of jute stick was carried out under N_2 atmosphere. About 5 mg of jute stick powder was taken on the TGA analysis platinum bin. The bin was put on the pan of TGA. The TGA chamber was evacuated by a high vacuum pump. Then the chamber was filled with nitrogen gas. The TGA machine was started so as to increase the temperature at the rate of $15\text{ }^{\circ}\text{C}$ until 1 h.

4.5.2. Carbonization of Jute Stick in a Small Reactor

The carbonization of phosphoric acid impregnated jute stick has been carried out in a laboratory scale batch feeding reactor. The reactor diagram is shown in Figure 4.21. The reactor is made of stainless steel with a height of 25 cm and an internal diameter of 5 cm. It has gas inlet and outlet tube connection to flow nitrogen gas. The gas inlet pipe is inserted into the reactor and extended up to the bottom of the reactor. The opening of the inlet pipe is set just 1 cm above the bottom of the reactor. However, to ensure the proper ventilation of the inlet gas, the opening of the gas outlet pipe is just below the top of the reactor. A thermo well is inserted into the reactor in which a thermocouple is inserted for monitoring the inside temperature of the reactor. The other part of the thermocouple is connected to the temperature controller from which the reactor temperature is controlled properly.

After loading the required amount of phosphoric acid impregnated jute stick granules, the reactor was closed and sealed with stainless steel flange. To ensure the complete sealing of the reactor, high temperature tolerable metallic gaskets were used and tighten with 8 screws by means of an Allen key. Nitrogen gas flow of 200 mL/min was usually used for making inert environment inside the reactor and transporting out the volatile carbonization products.

The carbonization was carried out at $200\text{ }^{\circ}\text{C}$ for 30 minutes. The reactor was

placed in an oven and heated up to the desired temperature. The carbonization of acid treated jute stick is entirely different than that of conventional carbonization of biomass. The conventional carbonization is usually carried out at around 400°C for charcoal production. During conventional carbonization, the organic volatiles entirely evolved, leaving behind the solid charcoal. However, during acid treated jute stick carbonization, most of the phosphoric acid from outer surface of jute stick along with water is evolved. The vapor was condensed and collected for further use by making up the concentration of phosphoric acid.

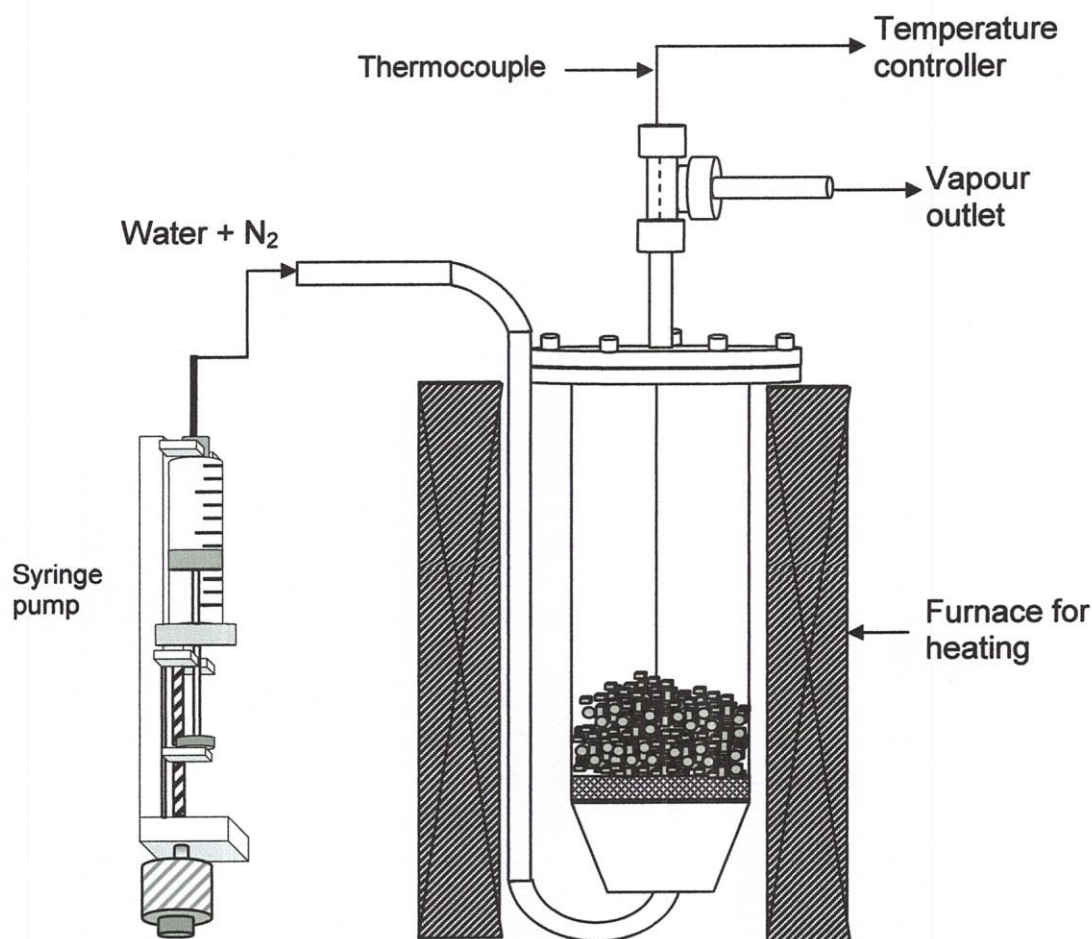


Figure 4.21. Conceptual design of a carbonization and activation reactor system for activated carbon preparation.

4.5.3. Production of Activated Carbon

The carbonized product was activated at different temperatures by flowing nitrogen gas. A certain amount of carbonized product was placed in the activation reactor as shown in Figure 4.22. The reactor was placed in the tube furnace where the desired temperature (400 °C-600 °C) was maintained. The temperature was controlled by a temperature controller through two thermocouples. The nitrogen gas was continued to flow through the char bed at the rate of 200 mL/min. At the activation temperature, the rest of the phosphoric acid, water and organic volatiles are evolved. The pore generation in chemical activation of biomass is usually taken place by dehydration of the functional groups in biomass.

After cooling down the reactor to room temperature, it was opened and the solid mass was collected. It was washed with hot water several times to remove residual acid. Finally, 0.05 molar sodium hydroxide solution was used to completely neutralize the final product. pH paper was used to check the acidity of the water after washing activated carbon.

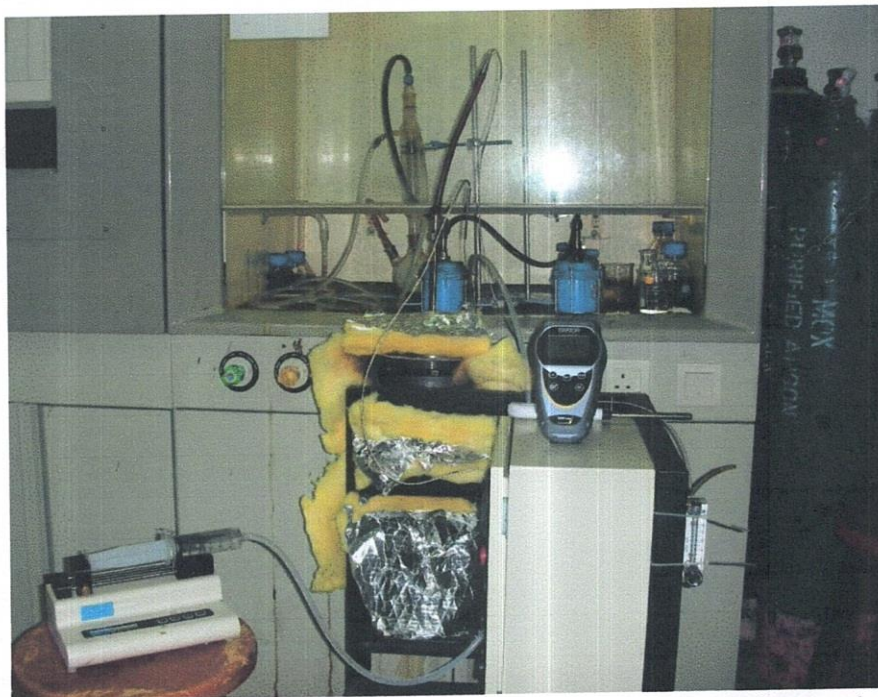


Figure 4.22. Activated carbon preparation reactor (1 liter volume).

4.5.4. Activated Carbon Production in a Large Reactor

This part of the work has been carried out in the Faculty of Chemical Engineering, Universiti Teknologi Mara, Shah Alam, Malaysia. Jute stick has been brought from Bangladesh. A stainless steel reactor of 11 cm diameter and 80 cm length was used for activation of jute stick. The picture of the reactor is shown in Figure 4.23. Around 1 kg of phosphoric acid soaked jute stick was loaded into the reactor. The reactor was closed air tightly and placed in a vertical tube furnace. The nitrogen gas flow was controlled using a Thermal Mass Flow Controller and pass into the reactor through a 8 mm diameter stainless steel tube mounted at the center of the reactor. A thermocouple was inserted into the reactor to control the temperature of the reactor.

The carbonization and activation of jute stick were carried out in the same reactor. Initially the temperature was maintained at around 200 °C for 30 min, while the phosphoric acid and water vapour was evolved. The vapour was passed through a condenser where it was condensed and collected for reuse. After completing carbonization at 200 °C, the temperature was increased to the optimum activation temperature 500 °C where it was continued around 1 h. At the activation temperature, mostly the dehydration and decarboxylation reactions are proceeded.



Figure 4.23. Ten liter volume activation reactor.

The reactor was cooled down when the activation time was over. It took around 3 h to cool down to room temperature. The reactor was opened and the product was collected. As described in the previous section, the activated carbon was washed with hot water several times to remove residual acid. Finally, it was neutralized using 0.05 molar sodium hydroxide solution. Then the product was kept in an oven at 105 °C over night to dry it up. The dried sample was kept in a desiccator for characterization and for further application.

4.5.5. Preparation of Activated Carbon by Physical Activation Method

In this method, first the jute sticks were washed with distilled water to remove external dirt and dried at 105 °C over night. The dried feedstock was then loaded in a stainless steel reactor. The reactor with all accessories is

shown in Figure 4.23. The reactor dimension is 12 cm diameter and 15 cm height which is connected to nitrogen gas and steam supply lines. After closing the reactor air tightly, it was placed in a vertical tube furnace. Then the reactor was heated slowly up to temperature of 500 °C and kept for 30 minutes at final temperature. In this stage, the devolatilization of biomass occurred. The organic vapour and producer gas were burnt at the exit of the outlet tube to avoid any air contamination in the laboratory. In order to avoid any condensation of organic vapour in the reactor and to make the reaction system inert environment, nitrogen gas was passed at the rate of 200 mL/min into the reactor. When the flame at the exit of the outlet tube retarded, the carbonization of jute stick was considered completed.

After completion of the carbonization of jute stick, the temperature of the reactor was increased to around 800 °C while the steam was started to pass through the char bed in the reactor. For steam generation, water was supplied with a highly precised and controlled syringe pump. The pump was connected to an inlet tube of the reactor at the bottom. About 40 cm of the inlet tube was extended inside the furnace before connecting to the reactor. The inlet tube and the syringe were connected by a Teflon tube. During operation, water was flashed vaporized when it was exposed into the hot zone of the tube and the steam was then passed into the reactor. The super heated steam at 800 °C spontaneously reacts with charcoal in the reactor, which is termed as gasification reacton, producing carbon monoxide while it creates pores on the charcoal surface. The pore generation starts on the surface and progressively penetrates into the inner part of the charcoal. The time of the gasification reaction for optimum porosity was investigated. After the desired length of time of reaction, the steam supply was stopped while the nitrogen gas supply was continued. When the reactor temperature reached to the room temperature, it was opened and activated carbon was collected and stored in a desiccator.

4.5.6. Loading of Iron on Activated Carbon

Iron precursor was loaded on the activated carbon surface by impregnation method. Figure 4.24 represents the flow sheet diagram of iron loading on activated carbon. In this method, 10% iron sulfate solution was prepared in a beaker. Then a desired amount of activated carbon was added into the solution. The mixture was shaken for 5 h at room temperature. During this period, iron sulfate salt was adsorbed on the activated carbon surface. A desired amount of 5% NaOCl solution was then added into the mixture and stirred for another 2 h. Sodium hypochloride oxidized the ferrous ion to ferric ion, which can be strongly adsorbed on the activated carbon surface. Then the mixture was dried at 70-80 °C and calcined at 500 °C for 1 hour. The nitrogen gas was continued to flow through the activated carbon bed at the rate of 200 mL/min during calcination. The metal particles usually agglomerate while calcination takes place at high temperature; however, in this case since the ferric ion was strongly adsorbed on the surface, the agglomeration was not significant, and thus the metal dispersion was quite high.

Calcination under nitrogen is a highly reducing atmosphere and under this condition the iron salt can be reduced to metallic form, and thus the activated carbon surface become highly reactive. It can vigorously react with oxygen when it exposes to air and can cause explosion. Therefore, a care had been taken to collect and stored into an airtight condition. Before using, it was open in an controlled air condition at low temperature to avoid any vigorous Oxidation.

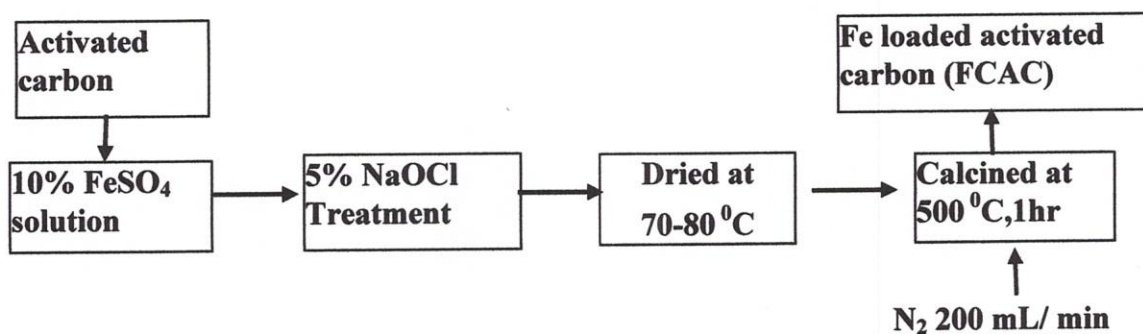


Figure 4.24. Flowsheet diagram for iron loading on activated carbon surface.

4.6. Activated Carbon Characterization

The activated carbons and iron loaded activated carbons were characterized by measuring the iodine number, methylene blue dye number, BET surface area as well as by using FT-IR spectroscopy, Raman spectroscopy, XRD, and Scanning Electron Microscopy (SEM).

4.6.1. Determination of Iodine Value

For iodine value determination, several reagent solutions were needed such as potassium dichromate solution, sodium thiosulfate solution, iodine solution and starch solution.

4.6.1.1. Preparation of potassium dichromate solution (0.1N):

Potassium dichromate is a primary standard substance and often used for sodium thiosulfate solution standardization. It is an oxidizing agent and its oxidation number is 6. The equivalent weight of potassium dichromate is calculated by dividing molecular weight 294 with 6 and it is 49.

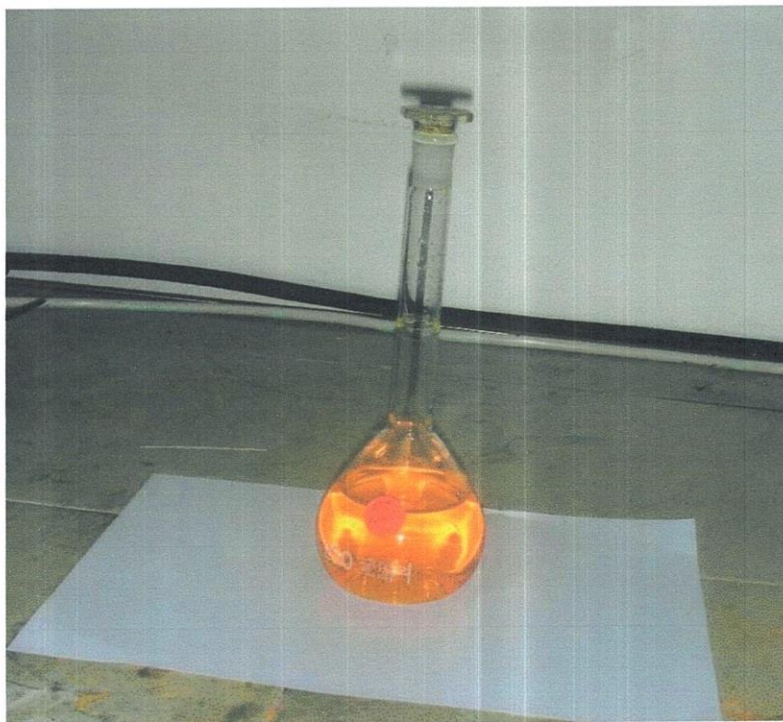


Figure 4.25 0.1N potassium dichromate solution.

To prepare a standard solution, a desired weight of it was calculated based on the equivalent weight. For 0.1N and 250 mL potassium dichromate solution, exactly 1.225 g of solid potassium dichromate was dissolved in a 250 mL volumetric flask by distilled water. Then water was added up to the mark. The flask was shaken for complete dissolution of solid potassium dichromate. Figure 4.25 shows a 250 mL volumetric flask, containing potassium dichromate solution.

4.6.1.2. Preparation of iodine solution:

20 g of iodate -free potassium iodide was taken in 30-40 mL of water in a 1-liter flask with a glass stopper. 12.7 g of analytical grade iodine was weighed out on a watch glass by a two decimal balance, and transferred it by means of a small dry funnel into the concentrated potassium iodide solution.

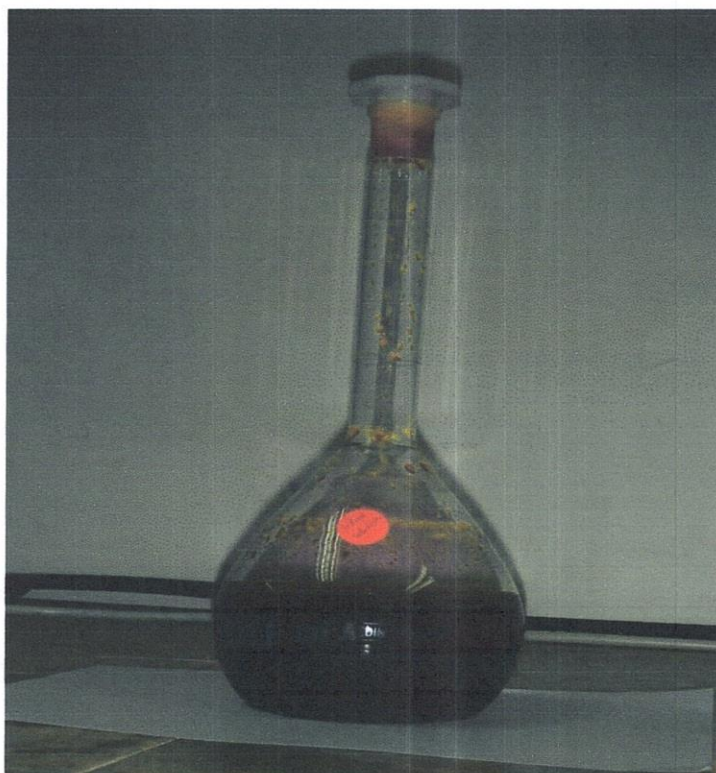


Figure 4.26. 0.1N iodine solution.

The flask was closed and shaken well until all of the iodine was dissolved. Then allowed the flask to acquire the room temperature, and make up to the mark with distilled water. This solution was used as a stock solution for iodine adsorption studies of activated carbons and iron loaded activated carbons. The Figure 4.26 shows the stock solution of iodine and it was usually kept in the dark place.

4.6.1.3. Preparation of sodium thiosulfate solution (0.1N):

About 12.5 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ was weighed and dissolved in distilled water in a 500 mL volumetric flask and was made up to the mark with distilled water. To use this solution for a few days, 3 drops of chloroform was added. Figure 4.27 shows the sodium thiosulfate solution and it was used for several days as a stock solution for iodine estimation.

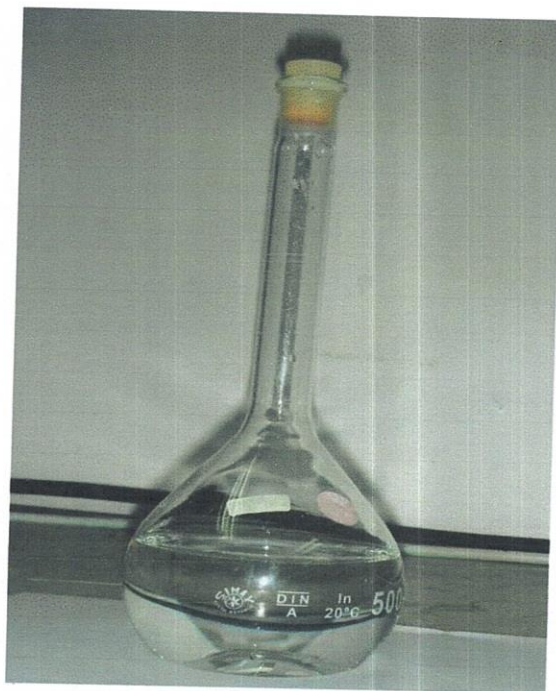


Figure 4.27 0.1N sodium thiosulfate solution.

4.6.1.4. Preparation of starch solution:

About 2 g of soluble starch was pasted with a little amount of distilled water and the paste was poured with constant stirring into 200 mL of distilled water and the mixture was then boiled for one minute and cooled. About 2 g of potassium iodide was added into the solution.

4.6.1.5. Determination of the strength of the sodium thiosulfate solution:

Sodium thiosulfate is a secondary primary standard substance and often used for iodometric and iodimetric titration. The strength of the solution varies when it stored for several days. Therefore, its strength needs to be determined before using for iodine estimation. To determine the strength, 10 mL of standard decinormal potassium dichromate solution was taken in a conical flask and was diluted with 50 mL distilled water. About 1-2 g of solid potassium iodide, 0.5 g of sodium bicarbonate and 2 mL of concentrated hydrochloric acid were added respectively. The mouth of the flask was

covered with a piece of paper and was allowed to stand in the dark for five minutes.

The liberated iodine was titrated with sodium thiosulfate solution contained in a burette by usual iodometric method. During titration, the wall of the conical flask was rinsed with distilled water several times in order to wash down the iodine. A few drops of starch solution were added into the titration mixture almost at the end of the titration when the solution colour became fade. The titration procedure is shown in Figure 4.28.

The sodium thiosulfate solution strength was determined using the following equation.

$$S_1V = S_2V_t$$

$$S_2 = S_1V_1/V_t$$

where

S_1	=	concentration of standard solution of potassium dichromate (0.1 N)
V	=	volume of potassium dichromate solution (10 mL)
S_2	=	concentration of sodium thiosulfate solution ?
V_t	=	volume of sodium thiosulfate solution needed for the titration
V_f	=	final burette reading for sodium thiosulfate solution
V_i	=	initial burette reading for sodium thiosulfate solution
V_u	=	unused sodium thiosulfate solution

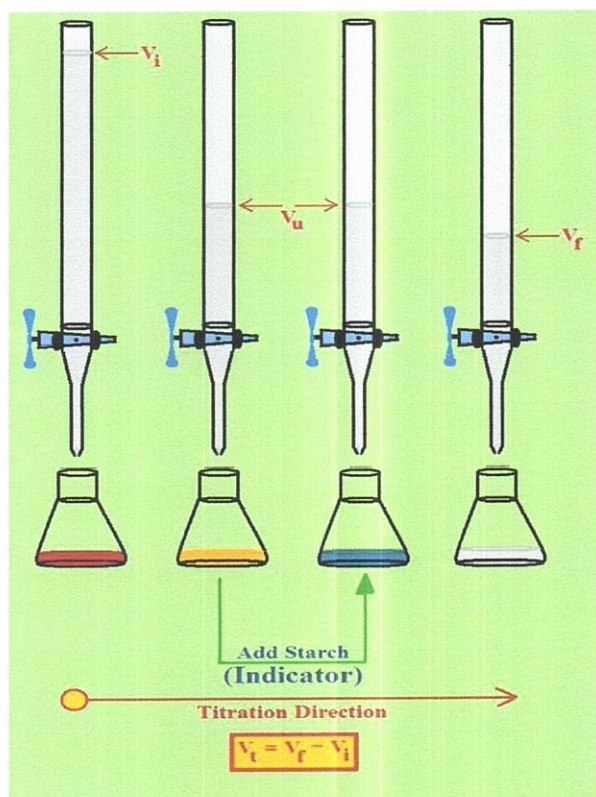


Figure 4.28. Pictorial flowchart for iodometric titration.

4.6.1.6. Determination of iodine value of activated carbon:

In this experiment, 0.1 g of activated carbon was taken in a 250 mL conical flask. For each of the sample, 20 mL of the iodine solution was added into the flask. The flask was then put onto the incubator shaker and shaken for about 2 h for equilibrium adsorption of iodine. During this time iodine was adsorbed on the surface of the activated carbon. At the same time, 10 conical flasks were shaken for 10 different samples. The solid mass was then filtered out and rest of the iodine in solution was titrated using 0.1 N sodium thiosulfate solution. All of the operation was performed under the dim light, so as to prevent the iodine decomposition by bright light. The iodine value was calculated by milligram of iodine adsorbed by one gram of activated carbon.

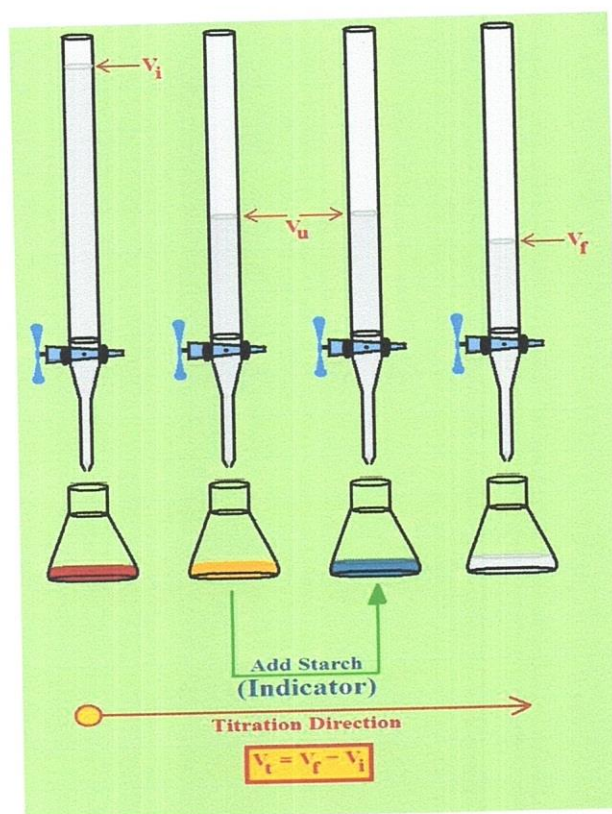


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To calculate the iodine value using the method described, the values we need are the volumes of $\text{Na}_2\text{S}_2\text{O}_3$ used in the titration of both the samples and the blank and plug them into the following formula:

$$\text{Iodine value} = \frac{(\text{mL } 0.1\text{N } \text{Na}_2\text{S}_2\text{O}_3 \text{ Blank} - \text{mL } 0.1\text{N } \text{Na}_2\text{S}_2\text{O}_3 \text{ Test})(12.7)}{(1000)(0.1)}$$

where "mL 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ Blank" = the volume of sodium thiosulfate required to titrate the blank solution, "mL 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ Test" = the volume of sodium thiosulfate required to titrate the test solution that contained activated carbon, "12.7" is the amount of grams of iodine contained in one liter of 0.1 N iodine, and, "0.1" is the amount of activated carbon taken in grams.

4.6.2. Determination of Methylene Blue Dye Number

Activated carbon is a widely used adsorbing material for dye adsorption from waste water. Methylene Blue dye is a representative compound for textile dyes and often used for activated carbon characterization. It is considered as a standard dye for adsorption studies. In this experiment Methylene Blue dye number is defined as milligram of dye adsorbed per gram of activated carbon. For the dye number determination, it was weighed using an analytical balance described in the previous section for stock solution preparation.

4.6.2.1. Preparation of stock solution of Methylene Blue (MB)

A 0.2M stock solution of MB was prepared as follows: 15.95 g of Methylene Blue was weighed accordingly by using an analytical balance. It was

weighed on a white plain paper to prevent the minor error. Then it was dissolved in a 250 mL volumetric flask by using distilled water until the calibrated mark as shown in Figure 4.29. The calculation given below is showing how a 0.2M of MB solution was prepared by weighing accurately

15.95 g of MB in powder form.

Molecular weight of MB = 319 g/mol

Required concentration : 0.2 M $\xrightarrow{\times 5}$ Standard concentration : 1M
Required Volume : 250 mL $\xrightarrow{\times 4}$ Standard volume : 1L

Amount needed to prepare the stock solution : $\frac{319\text{g}}{(5 \times 4)} = 15.95 \text{ g of MB}$

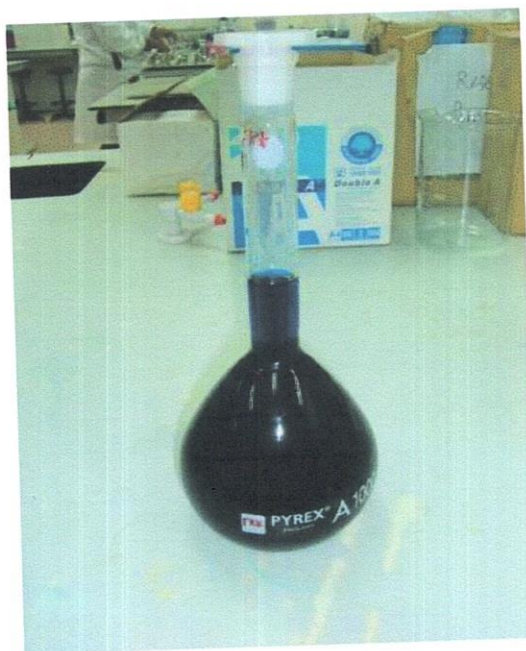


Figure 4.29. Standard solution of Methylene Blue dye.

4.6.2.2. Calibration Curve Preparation

In order to prepare the calibration curve, 0.50×10^{-3} M solution was prepared from 0.2 M standard solution. Then, from 0.50×10^{-3} M solution, the solutions of 3.20×10^{-4} M, 2.80×10^{-4} M, 6.41×10^{-5} M, 5.20×10^{-5} M, 2.56×10^{-5} M, 1.28×10^{-5} M and 5.12×10^{-6} M were prepared. The solution picture is shown in Figure 4.30. This method was done repeatedly. All the dilutions were calculated using equation below. Then, the calibration curve was plotted as Figure 4.31.

$$S_1 V_1 = S_2 V_2$$

S_1 = concentration of standard solution (mg/L)

V_1 = volume need to be diluted (calculated, mL)

S_2 = concentration needed (mg/L)

V_2 = volume needed (50 mL)



Figure 4.30. Solution for preparing calibration curve.

For calibration curve, six concentrations were analyzed at wavelength of 540 nm to get their maximum absorbance readings. The profile of the absorbance readings versus dye concentrations has been plotted in Figure 4.31.

The slope 4146.9 in the calibration curve was used for the determination of the concentration of experimental samples. For the experimental samples, they were diluted to many times to make the concentration in the measurable range by the spectrophotometer. After determining the concentration using the slope it was multiplied by the dilution factor in order to get the real concentration of the experimental sample and from where the amount of dye adsorbed was determined.

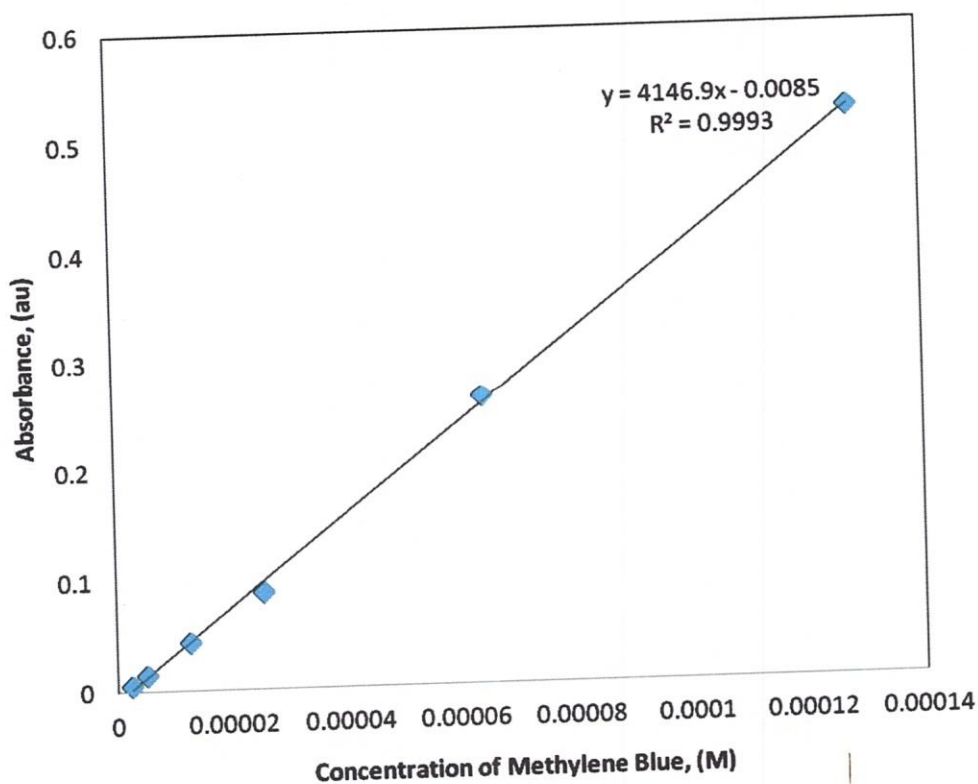


Figure 4.31. Calibration curve for Methylene Blue dye.

4.6.2.3. Methylene Blue (MB) adsorption study

About 20 mL of dye solution was added into a 250 mL conical flask and then 0.1 g of activated carbon was added into the flask. The flask was then shaken for about 4 hour in a incubator shaker at a constant 70 rpm with standard room temperature and was put it aside for a while without disturbing it in order to let the activated carbon to be settled down.

After that, the MB was then filtered by filter paper to separate the activated carbon from MB. The concentration of MB before and after adsorption was measured by using UV-visible spectrophotometer as shown in Figure 4.17 in the previous section. This procedure has been repeated using the activated carbon samples prepared using different preparation conditions.

The concentration of the MB solutions used for adsorption study was much higher than that of the measurable range of the spectrophotometer, and thus it was diluted into the measurable range. The concentration of the solution was measured by dividing absorbance with slope of the calibration curve.

4.6.3. BET Surface Area Measurement

The BET surface areas, pore size and pore volume of chemically activated carbons (ACC), physically activated carbons (ACS), char and iron loaded activated carbons were determined by nitrogen adsorption method at -196°C using a Autosorb- iQ/MP-XR surface area measurement machine. About 0.1 g of sample was taken into a glass sample tube for BET instrument. The tube was inserted into the tube holder of the machine and degassed for overnight. After degassing, the sample holder was replaced at the analytical port where it was hanged in a liquid nitrogen pot. The nitrogen adsorption was carried out automatically under different equilibrium pressure. The surface area, pore size and pore volume data were automatically recorded in computer. The process was repeated six times and finally the adsorption data was

automatically plotted to show the final and average surface area, pore size and pore volume of the solid samples.

4.6.4. FT-IR Spectroscopy

In order to know the surface functional groups, the FT-IR spectra of jute sticks, ACC, ACS and charcoal were recorded between 4000 and 400 cm^{-1} using a Perkin-Elmer Spectrum GX FT-IR spectrometer. Fifty scans were recorded at 4 cm^{-1} spectral resolution. The samples were ground and diluted to 0.5 wt% with spectroscopic grade KBr. A thin film was prepared from the resulting mixture using Perkin-Elmer manual hydraulic press.

4.6.5. FT-Raman Spectroscopy

The structural features of activated carbons and char have been evaluated with a Bruker RFS100 FT-Raman spectrometer equipped with an excitation laser of 1064 nm following the procedure developed elsewhere (Li et al., 2006a; Keown et al., 2007). Briefly, to record a Raman spectrum, the sample was prepared as the samples of FT-IR with the same concentration of the samples in KBr. A back scattering configuration with an InGaAs detector was used to collect the spectra. The diameter of the incidental laser spot was about 1 μm , much larger than the micro-crystallites in the samples. Therefore, the Raman microprobe provided averaged information of a large number of randomly distributed micro-crystallinities. The spectra in the range between 800 and 1800 cm^{-1} were curved-fitted with the GRAMS/32 AI software (Version 6.0) using 10 Gaussian bands and a detailed discussion of Raman band assignments may be found elsewhere (Li et al., 2006a; Keown et al., 2007).

4.6.6. Scanning Electron Microscopy

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity.

A scanning electron microscope (SEM) (Model JEOL 840) equipped with an energy dispersive X-ray microanalysis was used to determine the surface textural characteristics of the samples. As with other scanning electron microscopy, the JSM-840 examines structure by bombarding the specimen with a scanning beam of electrons and then collecting slow moving secondary electrons that the specimen generates.

For SEM analysis the samples are sized appropriately to fit in the specimen chamber and are mounted rigidly on a specimen holder called a specimen stub. For conventional imaging in the SEM, specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Metal objects require little special preparation for SEM except for cleaning and mounting on a specimen stub. Nonconductive specimens tend to charge when scanned by the electron beam, and especially in secondary electron imaging mode, this causes scanning faults and other image artifacts. The activated carbons are usually non-conductive and, therefore, they were coated with an ultrathin coating of gold by low-vacuum sputter coating.

4.6.7. XRD Analysis

X-ray diffraction (XRD) patterns of iron loaded activated carbons were acquired with a TD-3500 XRD diffractometer with Cu K α radiation (25 mA and 40 kV) at a scan rate of 2° min^{-1} and a step size of 0.02° .

4.7. Separation of Arsenic from Water

4.7.1. Laboratory Investigation for Removal of Arsenic from Water using Activated Carbons and Iron Loaded Activated Carbons

4.7.1.1. Preparation of stock solution

About 4.5 gm of caustic soda (NaOH) was taken in a 500 ml beaker and dissolved in 50 mL distilled water. Then 1.32 gm of As_2O_3 (powder form) is added in the flask and the mixture was stirred with a glass rod for a few minutes. This mixture is heated up to boiling temperature for dissolving As_2O_3 . The hot solution is allowed to cool and transferred to a 1000 mL volumetric flask and diluted by adding distilled water up to the mark. This solution is called stock solution. The concentration of the solution was 1000 ppm.

Specification of As_2O_3 used: Arsenic content is not less than 99.8% (As_2O_3).

4.7.1.2. Preparation of standard samples (model mixtures)

Model samples of definite arsenic concentration e.g. 0.25, 0.20, 0.15, 0.10 and 0.05 ppm are now prepared by taking accurately 62.5, 50, 37.5, 25 and 15 mL of 1 ppm solution, respectively, in separate 250 mL volumetric flasks. Approximately 1 drop of concentrated sulfuric acid (H_2SO_4) into each flask was added and diluted the content with distilled water up to the mark.

4.7.1.3. Column filtration method for arsenic removal

A column filter is shown in Figure 4.32. Desired amount of Fe-loaded activated carbon was loaded in a 1.2 cm diameter glass column. The activated carbon was packed with quartz wool or cotton. The standard As (III) solution

was percolated from the top of the column. The fresh water sample was collected from the bottom of the column in a conical flask. The arsenic concentration was measured by AAS method

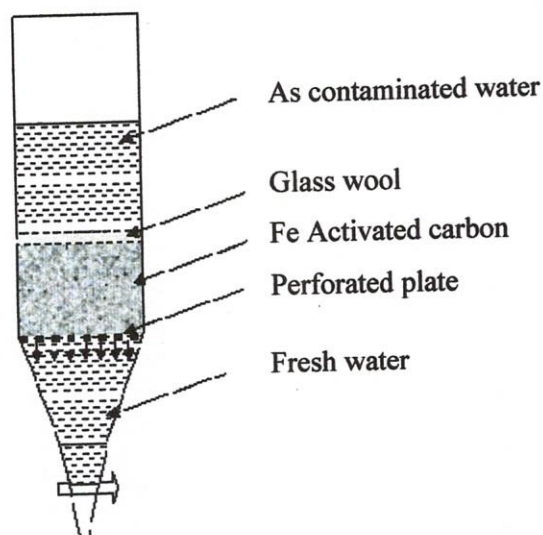


Figure 4.32. Column filter packed with Fe-activated carbon

4.7.1.4. Arsenic removal using Fe-loaded activated carbon in a commercial filter

Iron loaded activated carbon exhibited potential efficiency to adsorb As(III) and As(V) in the column filtration method. Arsenic concentration reduced to below WHO imposed upper limit (0.01 ppm). However, to investigate the efficiency of adsorption under practical scale of filtration, i.e., 24 L of water in a day, the iron-loaded activated carbon was used in a commercial filter as shown in Figure 4.33. For this investigation, a commercial household filter was purchased from the local market. The ceramic candle and the materials of filter cartridge were removed. In addition, the cartridge was cut into half of the total length. Then the upper half of the cartridge was filled with iron-loaded activated carbon. The cartridge was replaced to complete the filtration system. The model solutions of arsenic with concentration of 0.10 and 0.15 ppm were passed through the cartridge with a rate of 33 mL/min. The fresh water from the bottom of the filter was collected and analyzed with a

Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Thermo Scientific iCAP 6000)



Figure 4.33. Commercial household water filter

4.7.2. Determination of Arsenic Concentration in Water

4.7.2.1. Determination of arsenic in water by Atomic Absorption Spectrophotometer (AAS)

Principle

If a sample containing metal element, heated on high temperature, then a vapor is formed containing the atom of the same element. Gaseous metal atom absorb energy in the form of radiation of particular wave length and amount of absorbed radiation/energy is proportional to the concentration of the metal atom in the solution. Computerized Thermo Scientific Model iCE 3300 Atomic Absorption Spectrophotometer (AAS) Coupled with Hydride Vapour Generator, HVG-1 was used for this estimation.

Reagents of AAS

Sl.	Name of the reagent
1	5M HCl
2	0.5 wt/v NaBH ₄ in 0.5%
3	Potassium iodide
4	Ascorbic acid

Conditions for hydride generation

- ▣ Reagent flow 2.5 mL/min
- ▣ Sample flow rate=3.5 mL/min
- ▣ Carrier gas (Ar) flow rate =8 L/min

Optics Parameters

- ▣ Element: As
- ▣ Socket #: 1
- ▣ Lamp Current Low (mA): 12
- ▣ Wavelength (nm): 193.7
- ▣ Slit Width (nm): 0.5
- ▣ Lamp Mode: BGC-D2

Atomizer Gas Flow Rate Setup

- ▣ Fuel Gas Flow Rate (L/min): 2.0
- ▣ Flame Type: Air-C₂H₂

☐ Burner Height(mm): 16

☐ Burner Angle: 0

Measurement Parameters

☐ Order: 1st Zero Intercept: Yes Conc. Unit: ppb

☐ Repetition Sequence: SM-SM-.....

☐ Pre-Spray Time (sec): 3

☐ Integration Time (sec): 5

☐ Response Time (sec): 1

4.1. Data for constructing calibration curve for AAS

Concentration (ppm)	Absorbance
0.100	0.2570
0.150	0.3638
0.200	0.5041
0.250	0.6476

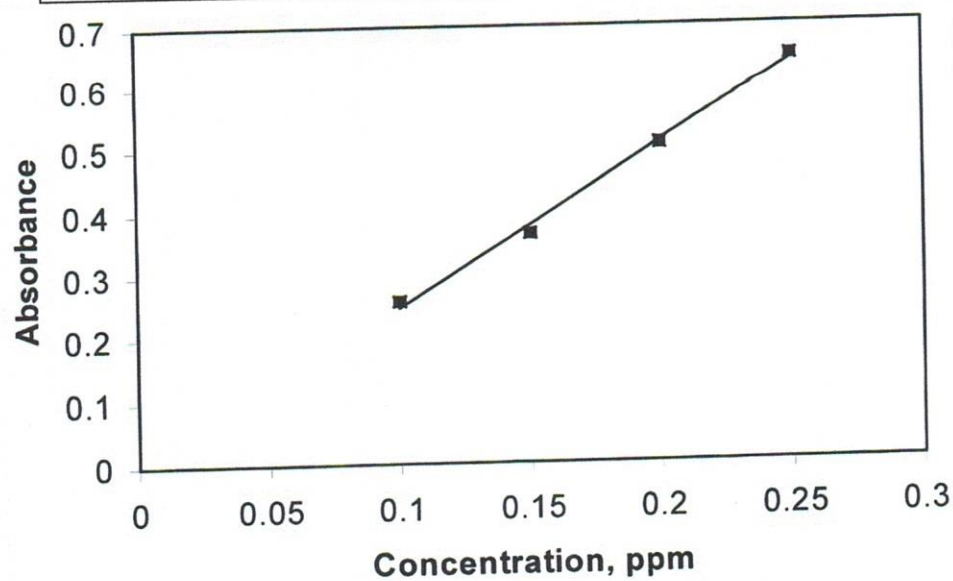


Figure 4.34. Calibration curve for AAS.

To construct a calibration curve, 0.1 ppm, 0.15 ppm, 0.2 ppm and 0.25 ppm standard samples are prepared carefully. Then these samples were passed through the computer controlled Atomic Absorption Spectrophotometer (AAS) which coupled with Hydride Vapour Generator (HVG) and thus the Calibration Curve (Absorbance vs. Concentration) is made automatically as Figure 4.34.

4.7.2.2. Determination of arsenic in water by Inductively Coupled Plasma Atomic Emission Spectrometer:

Principle

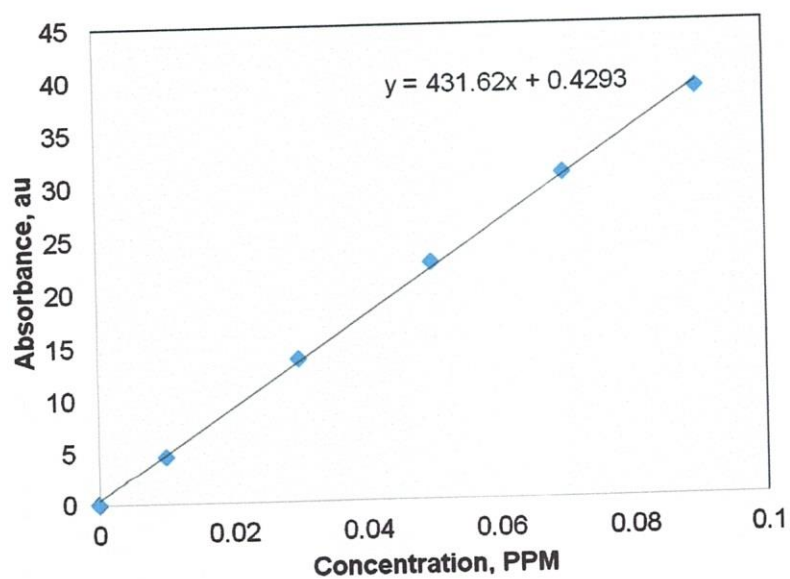
ICP-AES is an analytical technique used for the detection of trace metals almost similar as Atomic Absorption Spectrometer. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

Preparation of calibration curve

For the preparation of a calibration curve, a standard solution of 1000 ppm was used. The standard solution was further diluted to 1 ppm by taking 1 mL solution into 1000 mL volumetric flask. Finally the solutions of 0.01 ppm, 0.03 ppm, 0.05 ppm, 0.07 ppm, 0.09 ppm and 0.1 ppm were prepared by taking 1 mL, 3 mL, 5 mL, 7 mL, 9 mL and 10 mL solution in 100 mL volumetric flask. Then the absorption was taken by ICP-AES which is automatically plotted against concentration to construct the calibration curve. The data are tabulated in Table 4.2.

Table 4.2. Data for constructing calibration curve for ICP

Concentration (ppm)	Absorbance
0.01	4.64
0.03	13.70
0.05	22.61
0.07	30.83
0.09	88.7

**Figure 4.35.** Calibration curve for ICP-AES.

CHAPTER 5

RESULTS AND DISCUSSION

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5.1. Introduction

Activated carbon (AC) had been proven to be an effective adsorbent for the removal of wide varieties of organic and inorganic pollutants from aqueous media or from gaseous environment as widely described in the introduction and literature survey. It is a widely used adsorbent in the treatment of drinking water and waste water due to its exceptionally high surface area, which ranges from 500 to 2000 m²/g. Additionally, it has well-developed internal micropore structure as well as the presence of a wide spectrum of surface functional groups [163]. Many reports described the uses of AC for metal ion separation as mentioned in the literature survey. In this work, we have produced AC from jute stick and it has been used for arsenic separation. However, the capacity of arsenic separation by AC does not meet the WHO regulated upper limit concentration (0.01 mg/L). The maximum arsenic separation capacity was found to be 50% [164].

The commercial activated carbon was found less effective to separate arsenic from water. Thus, it is evident that the arsenic removal using freshly prepared char or activated carbon is not efficient. Literature shows that the iron species can easily combine the arsenic species to form complex. Therefore, iron was loaded on the activated carbon prepared by chemical activation (ACC) as well as physical activation method (ACS). Iron was loaded on ACC which was termed as FACC, while it was loaded on ACS before activation and termed as

FACS. The ACC, FACC as well as FACS were used in this work for arsenic separation from water.

5.2. Characteristic Study of Jute Stick

Before using jute stick for the production of activated carbon, it was characterized to determine its moisture content, particle size, density, volatile and fixed carbon contents and elemental composition. The proximate analysis and other characteristic results are summarized in Table 5. 1 and the ultimate analysis data is summarized in Table 5. 2.

5.2.1. Moisture Content

Activated carbon production from jute sticks needs moisture content as low as possible. Under the weather in Bangladesh, biomass like jute stick exists naturally in dried condition. However, the moisture content in jute sticks varies in different season. In dry condition, the moisture content was determined and the result is included in Table 5.1. The moisture content was determined using both of the oven dried method and thermo gravimetric analysis (TGA) method. The TGA profile is shown in Figure 5. 1 and this sample was collected in dry season. The figure shows that the jute stick contains only about 3 wt% of moisture. The oven dry method was performed in both of the seasons and it can be seen from the results in Table 5.1 that the moisture content of jute stick was maximum of 12% in the rainy season. For carbonization of jute stick to produce char for activated carbon, around 10 wt% of moisture content in the feedstock was preferred.

In carbonization, the energy required to heat dry biomass to its carbonization temperature has been estimated to be about 2 MJ/kg [109]. So, if a carbonization reactor throughput is limited by heat transfer to the biomass,

energy input that could otherwise carbonize about double of jute stick. In our experiment, when the reactor was heated up in order to carbonize jute stick, the temperature was quite constant at around 100 °C for quite a long time. This means that the heat supplied to the reactor from the furnace was taken away by the steam as a latent heat of vaporization. The temperature was further started to rise when the moisture was completely driven off. This finding is a clear indication of effective heat transfer limitation by the moisture content and suggests reducing moisture content as low as possible by natural drying of jute stick even after soaking the activating agent in the case of chemical activation of jute stick.

5.2.2. Particle Size

The particle size plays an important role for heat transfer during carbonization and activation process. The thickness of the particle has an important role in the surface area per unit weight and subsequently the heating rate of the jute stick in a particular heat flux environment. For particular particle size of activated carbon the jute stick size was considered to be 1.0 to 2.0 mm.

5.2.3. Density

The density of any solid material is usually defined as its weight/volume. However, for biomass its density is sensitive to moisture content, and since biomass varies widely in moisture content as well as in material composition it is more difficult to define its density. The fundamental measure for biomass is basic density. The density of jute stick is the weight of oven-dry jute stick contained in a unit volume of green jute stick (50% moisture content) in g/cc. It was found that the density of jute stick is about 0.11 g/cc. It is useful to know the available carbon content in a given volume of biomass when planning a

biomass to activated carbon project as it affects the size of the plant, the storage area needed and the transportation arrangements. The lower carbon density of most biomasses compared with that of coal is a limitation that increases their delivery energy cost. Comparing the density of jute stick with cedar wood of Japan, it has been found that the density of jute stick measured in this work is 0.11 g/cc, which is higher than that of the density of cedar wood (0.07 g/cc) [110].

5.2.4. Calorific Value

The calorific value depends on the carbon and hydrogen content in any biomass. It varies only to a small degree with the biomass resource type. For example, when calorific value measured on a dry and ash-free basis for hard wood whole-tree biomass it is 19.6 MJ/kg and for soft wood whole-tree biomass it is 19.4 MJ/kg and, if the bark is removed, it is 20.9 MJ/kg. Owing to the variation in moisture contents, comparisons with other fuels are best made in terms of net energy values. The heat value of jute stick found is included in Table 5.1. This value is 19.7 MJ/kg with around 10% moisture content. This value is comparatively higher than that of other woody biomass and rice straw [111]. The heat value is directly proportional to the carbon content in the biomass which is inevitably important for activated carbon production. Comparing with bituminous coal, the heat value of bituminous coal with 5% moisture content is higher (28.2 MJ/kg) than that of jute stick with 10% moisture content (19.7 MJ/kg). However, it is quite comparable with any hard wood [110].

5.2.5. Proximate Analysis

Proximate analysis of biomass always measures the amount of volatile and fixed carbon fractions. The proximate analysis is based on the thermo gravimetric analysis (TGA) as shown in Figure 5.1. The thermo gravimetric analysis of jute stick was carried out under N_2 atmosphere. From the result of proximate analysis in Table 5. 1 and Figure 5. 1, it can be seen that the volatile fraction of jute stick until around 400 °C is 76 – 78 wt%, the fixed carbon is 21.4 – 23.4 wt% and the rest 0.62 wt% is ash content in jute stick. Most of the volatile materials usually derived from the cellulose and hemicellulose present in the jute stick. However, the devolatilization of acid soaked jute stick is unlikely different. In this case the most of the organic molecules re-polymerize and form solid carbons and thus the fixed carbon fraction is much higher than that of conventional carbonization. The fixed carbon is difficult to vaporize at pyrolysis temperatures at around 500 °C. From the TGA profile it can be seen that the fixed carbon does not evaporate even at around 1000 °C.

Table 5.1. Proximate analysis and other characteristic data of jute stick

Moisture content (wt%)	3-12
Particle size (mm)	1.0 – 2.0
Density (dry powder) (g/cc)	0.11
Heat value (HHV) (MJ/kg)	19.7
Proximate analysis	
Volatile fraction (wt%)	76 – 78
Fixed carbon (wt%)	21.4 – 23.4
Ash content (wt%)	0.62

The fixed carbon is actually converted to char in the carbonization process. The result suggests that the higher the fixed carbon formation during carbonization the higher is the char formation and ultimately the higher is the yield of activated carbon. The jute stick seems to be a suitable raw material for the low temperature carbonization as well as activation. In addition, since jute stick contains very small amount of ash comparing with other agricultural biomass such as rice straw (22.6% ash) [111] and other poisonous component such as sulfur, it has potential to convert activated carbons by easy carbonization and activation processes.

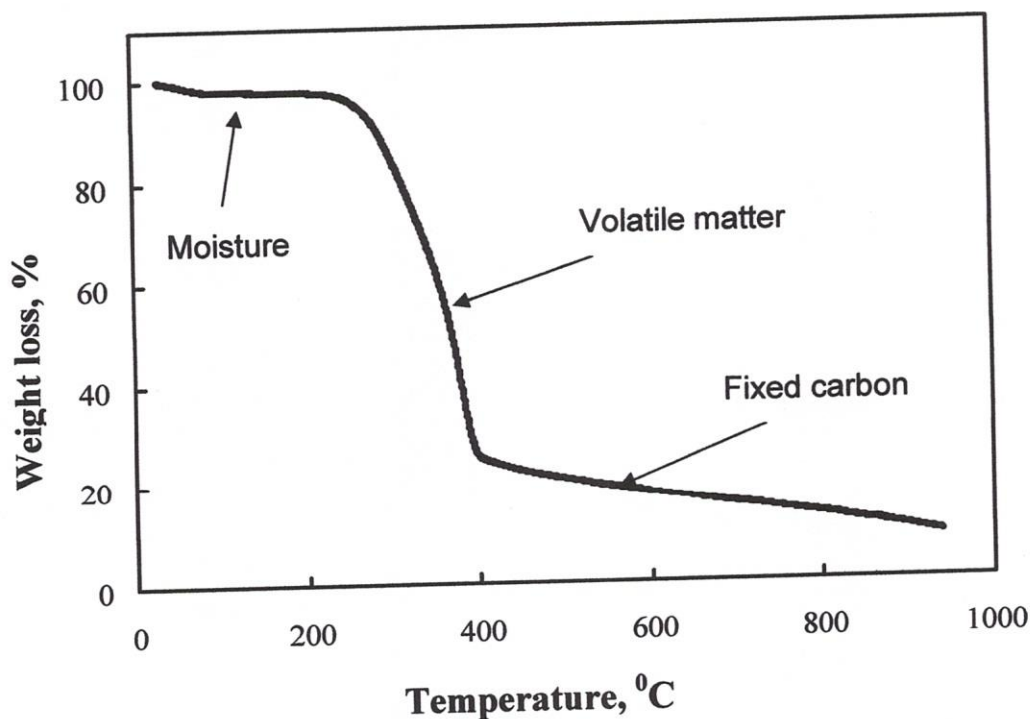


Figure 5.1. Thermogravimetric analysis of jute stick under the flow of nitrogen with temperature increasing rate of 15 °C/min.

5.2.6. Ultimate Analysis

The ultimate analysis of jute stick was performed and the results are summarized in Table 5.2. Ultimate analysis provides the chemical composition of the biomass in elemental terms, and is used to determine combustion air requirements, flue losses and likely emission levels. From this analysis, it has been found that the jute stick contains 49.79 wt% C, 6.02 wt% H, 41.37 wt% O, 0.19 wt% N, 0.05 wt% Cl and 0.05 wt% S. Carbon content in jute stick is higher than bagasse and much higher than rice straw [111]. The carbon content in jute stick ultimately goes to char and finally in activated carbon. The sulfur and other elements such as N and Cl content in jute stick are much lower than any types of coal [112].

Table 5.2. Ultimate elemental analysis (dry basis) of jute stick

Element	Weight%
C	49.79
H	6.02
O	41.37
N	0.19
Cl	0.05
S	0.05

5.3. Activated Carbon Production from Jute Stick

Activated carbon was produced in this work from chemical activation of jute stick using H_3PO_4 as an activating agent as well as by physical activation method. In the chemical activation method, H_3PO_4 solution was first

impregnated in jute stick and the solid mass was heated to 200 °C for at least 30 min. At this temperature H_3PO_4 reacted with the functional groups of chemical components in jute stick as a dehydrating and decarboxylating agent, and thus released H_2O and CO_2 , leaving behind a char like solid mass. Some of the H_3PO_4 also evaporated and condensed together with water in a condenser, which was reused.

The char produced by carbonization was placed into the activation reactor and the reactor was heated to a desired activation temperature ranging from 400 °C to 700°C for different duration of activation. At this temperature the activating agent soaked into the inner core of biomass reacted with the functional groups, producing small gaseous molecules, which upon evacuation created micropore structures. In the micropore structure, some of the H_3PO_4 was trapped which upon washing after taking out from the reactor with hot water was removed. After drying of the final product, it was weighed to determine the activation burn-off or mass loss due to activation. The following equation was used for calculating the activation burn-off of jute stick.

$$\text{Activation burn-off (\%)} = \{\text{mass loss (g)}/\text{original mass of jute stick (g)}\} \times 100.$$

The porosity and pore structure of activated carbons are directly related to the activation burn-off, which in turn further related to the activation temperature and duration of activation. To obtain high surface area and highly porous activated carbon the activation conditions are optimized and discussed in the following sections.

5.3.1. Effect of Temperature on the Activation Burn-off and Yields of Activated Carbon

The mass decreased during activation due to release of volatile compounds such as H_2O , NO_x , SO_x and some of CO and CO_2 is called activation burn-off and this was varied with varying activation temperatures. The activation burn-off and yields of activated carbons at different temperatures are summarized in Table 5.3. In activation, the primary products H_2O , CO and CO_2 subsequently reacted with char, so as to produce more gases which released from the solid mass [165]. This reaction usually takes place on the outer surface as well as in the inner surface, so as to increase the number of micropores as well as the size of the pores. The reactivity of carbon and other elements in the activation reaction is completely temperature dependent. Thus, different yields of activated carbons at different temperatures were obtained.

Table 5.3. Activation of jute stick char at different temperatures Amount of jute stick, 10g; nitrogen gas flow rate, 200 mL/min and time of activation, 1 h

Activation temperature (°C)	Activation burn-off (wt%)	Yield of activated carbon (wt%)
400	33.0	67.0
450	39.0	61.0
500	49.0	51.0
550	49.0	51.0
600	50.0	50.0
700	51.0	49.0

It can be seen from the results in Table 5.3 and Figure 5.2 that the activation burn-off is linearly increased until 500 °C and above this temperature the activation burn-off slowly increased with increasing temperature. During the activation of carbonized char, the dehydrating agent, H_3PO_4 helps remove in some extent of extraneous materials, but its primary function is the removal of water at elevated temperatures (around 500 °C). The hydrogen and oxygen are selectively removed and a large proportion of the original carbon skeleton is retained. This is the cause of linear relationship of the activation burn-off with temperature.

The Figure 5.2 also shows the yield of activated carbons. As it can be seen in the figure, the yield is inversely proportional to the activation burn-off. As temperature increased, the yield of activated carbon decreased due to increasing activation burn-off. The elevated temperature usually accelerates the activation burn-off reaction, and thus the yield of activated carbon decreased with increasing temperature.

The yield of activated carbon decreased significantly up to 500 °C and above this temperature the decreasing trend is very slow. This means that the reaction between functional groups and H_3PO_4 has almost been completed and the porous carbon skeleton rearranged by proceeding the re-polymerization reaction to form highly ordered and rigid activated carbon. The carbon compounds in ordered structure are highly unreactive even at higher temperature and this may be one of the reasons of slow activation burn-off. In addition, some activation burn-off may take place by secondary reforming reaction of carbons with steam generated by the primary dehydration reaction. However, this reaction is also very limited by the insufficient steam and lower temperature. The usual temperature of steam reforming reaction of carbon is above 700 °C.

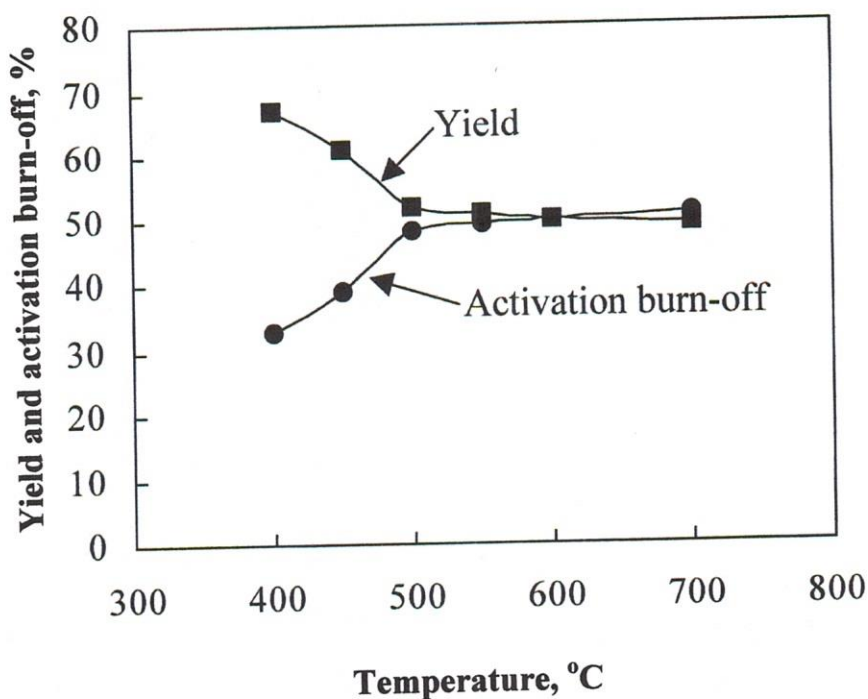


Figure 5.2. Effect of temperature on the activation burn-off and yield of activated carbon.

Figure 5.3 exhibits the TG-DTA curve of jute stick char under air atmosphere. The char samples were heated in an oven prior to the TGA tests to remove moisture. It can be seen that the char released unbound moisture at around 100 °C (**curve a**). The combustion was started at around 350 °C and completed within 400 °C. Since combustion of char is exothermic, the heat was evolved and thus the DTA curve (**curve b**) sharply increased.

About 75 wt% carbon materials in the char were combusted within the temperature range of 350 – 400 °C. The rest 25 wt% fixed carbon was combusted slowly above 400 °C and completed at 480 °C. DTA line also shows decreasing trend of releasing heat because of slow combustion of fixed carbon. During the activation of char, this fixed carbon corresponded to the activated carbon.

In the chemical activation, when the phosphoric acid impregnated jute stick was heated to 200 °C, a significant amount of cellulose, hemicellulose and lignin was re-polymerized by condensation reaction. The re-polymerized fraction of carbon materials are highly ordered and rigid compared to the molecules in indigenous biomass. This implies that during the treatment of jute sticks by H_3PO_4 , a significant fraction of carbon converted to fixed carbons, which in turn converted to activated carbons. Since the activation burn-off of fixed carbon is limited under nitrogen atmosphere the yield of activated carbon did not alter significantly above 500 °C as in Figure 5.2.

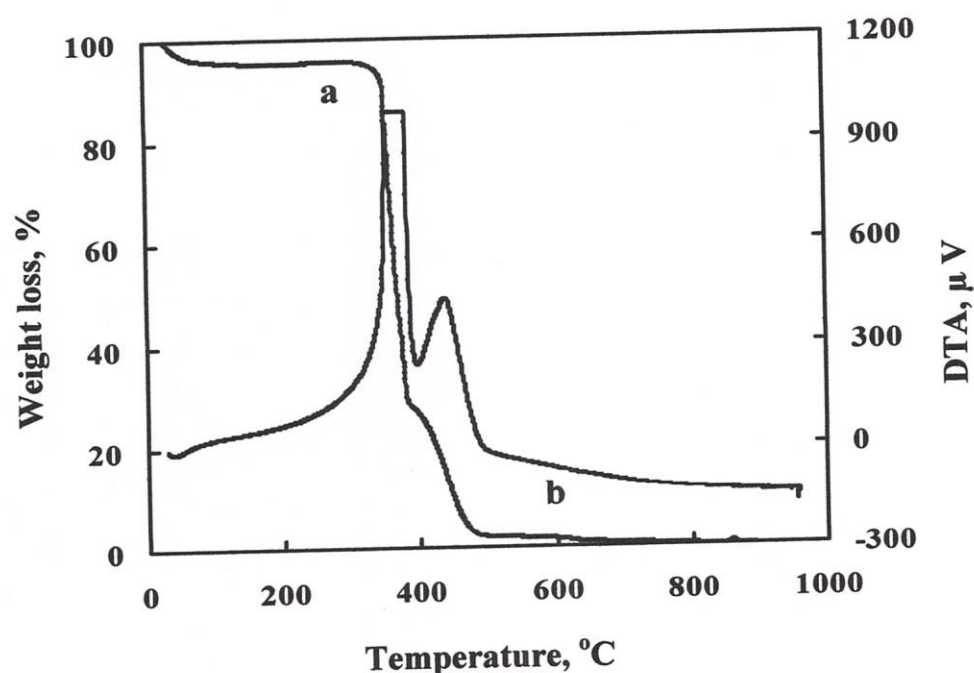


Figure 5.3. TG-DTA Thermogram of jute stick char under air atmosphere: (a) Weight loss curve and (b) DTA curve.

Interestingly, as shown in Figure 5.3 almost all of the materials in the jute stick char were burnt-off within the temperature of 700 °C, which indicated that the char contained negligible amount of ash. The ash usually blocks the pores of

activated carbon, and thus lower the ash content in the feedstock better is the performance of activated carbon in a specific application.

5.3.2. Effect of Activation Time on the Activation Burn-off and Yields of Activated Carbon

Duration of activation plays an important role in the yields as well as properties of activated carbon. From Table 5.4 it can be seen that the activation burn-off greatly varied with activation time. Since activation burn-off is not a vigorous process it needs a course of time to attain the optimum value. As shown in Figure 5.4, the activation burn-off is linearly increased with increasing time even until 120 min while the yield is decreased proportionally. However, the properties of the activated carbons such as BET surface area and pore volumes do not depend on the maximum activation burn-off. Thus, the optimization of the activation time and activation burn-off is necessary in view to develop the maximum surface area of the activated carbons.

Well defined pore structure and sufficient pore volume can be developed with optimum activation burn-off. Higher activation burn-off usually causes the destruction of the pore walls, so as to decrease the number of pores, and thus the surface area of the activated carbons decreased. The optimum activation time would be decided based on the properties such as surface area, iodine value and methylene blue number of activated carbon as described in the latter section. Especially, the surface area is a determining factor of the quality of activated carbons and it depends on the generation of microporosity.

Table 5.4. Effect of activation time on activation burn-off and yield of activated carbon, Activation temperature, 500 °C, Nitrogen gas flow rate, 200 mL/min , Amount of jute stick, 10 g

Activation time (min)	Activation burn-off (wt%)	Yield of activated carbon (ACC)
20	41	59
40	45	55
60	49	51
80	49	51
100	51	49
120	54	46

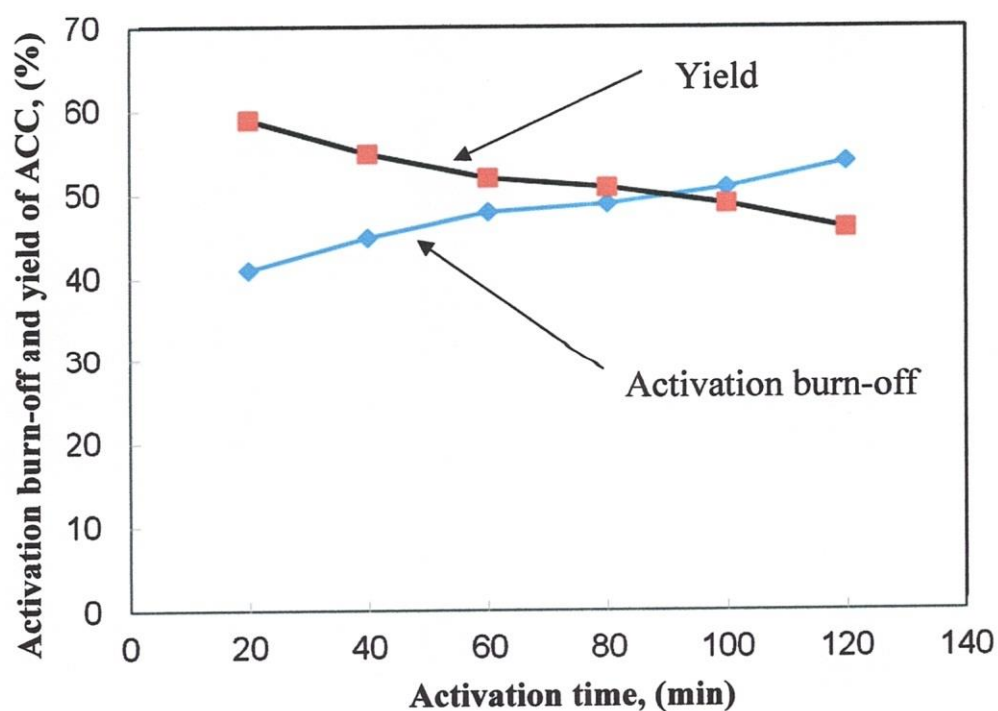


Figure 5.4. Effect of time on the activation burn-off and yield of activated carbon.

5.3.3. Effect of Impregnation Ratio of H_3PO_4 to Jute Stick on the Activation Burn-off and Yields of Activated Carbon

The impregnation ratio has been found to be one of the important parameter in preparation of activated carbon using chemical activation [166]. In order to study the effect of impregnation ratio on the yield, activation burn-off and characteristics of activated carbons, carbonization time 1 h and carbonization temperature 500 °C were used. The activation burn-off and yield of activated carbon are tabulated in Table 5.5 and the trend of them is shown in Figure 5.5. The activation burn-off of the process decreased with increasing of impregnation ratio as seen in Figure 5.5.

Table 5.5. Effect of impregnation ratio on activation burn-off and yield of activated carbon, Activation temperature, 500 °C, Nitrogen gas flow rate, 100 mL/min, Amount of jute stick, 10 g , Activation time, 1 h

Jute sick :Phosphoric acid	Activation burn-off (wt%)	Yield of activated carbon (wt%)
1 :0.0	65	35
1 :0.5	54	46
1 :1.0	49	51
1 :1.5	44	56
1 :2.0	46	54
1 :2.5	42	58

Phosphoric acid promoted the re-polymerization reaction in jute stick during processing by evolving water and also some carbon dioxide. The re-polymerization of the components in jute stick resulted in increasing of ordered structure in final product. This suggests that the devolatilization of volatile

matters from jute stick decreased, which corresponds to the decreasing of activation burn-off and in other word increasing of activated carbon yield.

5.4. Characterization of Activated Carbon

The jute stick derived activated carbon was characterized using different instrumental methods such as BET surface area measurement, pore volume measurement, IR spectroscopy, Raman spectroscopy, TGA and SEM as well as chemical characterization methods such as iodine value determination and methylene blue dye adsorption. Based on the characteristics the optimum preparation method of activated carbon is proposed.

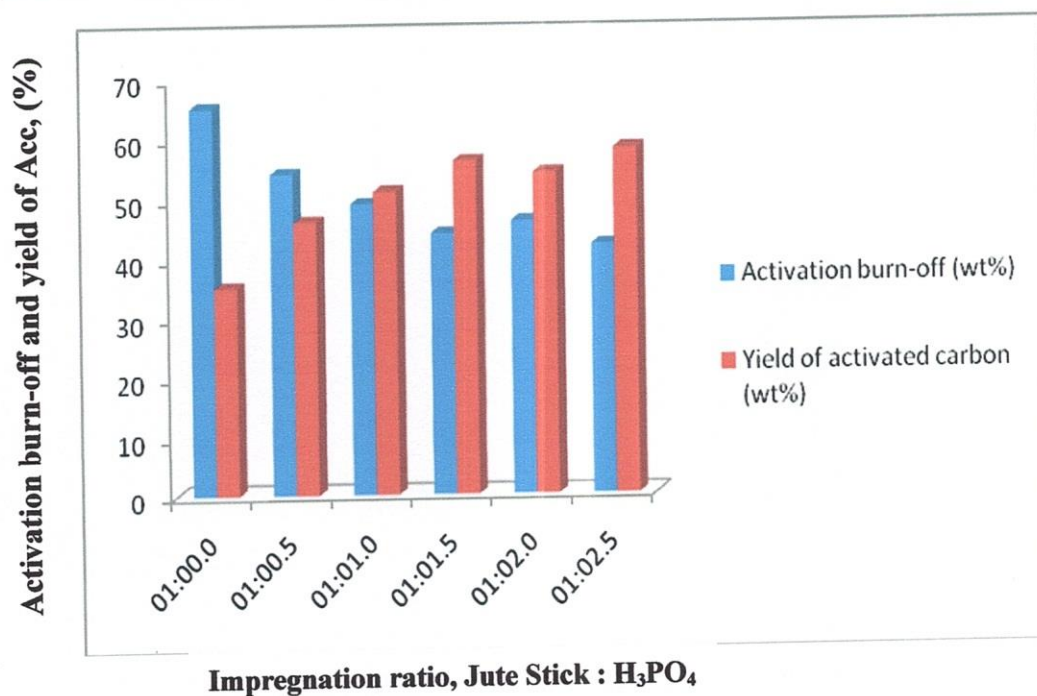


Figure 5.5. Effect of impregnation ratio on the activation burn-off and yield of activated carbon.

5.4.1. Effect of Temperature on the BET Surface Area and Iodine Value

The variation of activation temperature significantly varied the characteristics of activated carbon. The characterization results of activated carbon obtained from jute stick are shown in Table 5.6.

The BET surface area increased with increasing temperature until 500°C and soon after this temperature, the BET surface area decreased as shown in Table 5.6 and Figure 5.6. The same trend was also observed in the case of iodine number vs temperature plot as shown in Figure 5.7. The maximum surface area of activated carbon was obtained to be 1664 m²/g. The maximal sorption capacity, which defined the fitness of activated carbon depends not only on the surface area but also on the pore size and pore volume. Low activation temperature results in incomplete activation burn-off, resulting in a higher yield of activated carbon but low surface area. This result reflects to the incomplete activation burn-off and many of the potential sites are occupied by the degraded organic molecules.

Table 5.6. Effect of temperature on the activation burn-off, BET surface area and iodine number, Amount of jute stick = 5g, N₂ gas flow rate =150-200 mL/min, Time of activation = 1 h

Activation temperature (°C)	Activation burn-off (wt%)	BET surface area (m ² /g)	Iodine number (mg/g)
400	41	1295	1230
450	48	1509	1315
500	49	1664	1440
550	60	1566	1170
600	74	1240	1090

The higher activation temperature resulted in lower surface area which suggested that the high temperature activation may cause high pore size due to

the over activation burn-off by the destruction of the pore wall. It is obvious that the destruction of the pore wall inevitably reduces the total surface area as reflected in Figure 5.6. The sudden fall of the surface area over 500 °C is a clear evidence of the pore wall destruction. The details of the pore size and pore volume along with surface area will be discussed in the subsequent sections. However, this study helps decide the optimum temperature for activation of H_3PO_4 impregnated char from jute stick and it is suggested that 500 °C temperature may be the optimum activation temperature in order to get the maximum surface area. This result is also supported by the iodine value and methylene blue dye adsorption results.

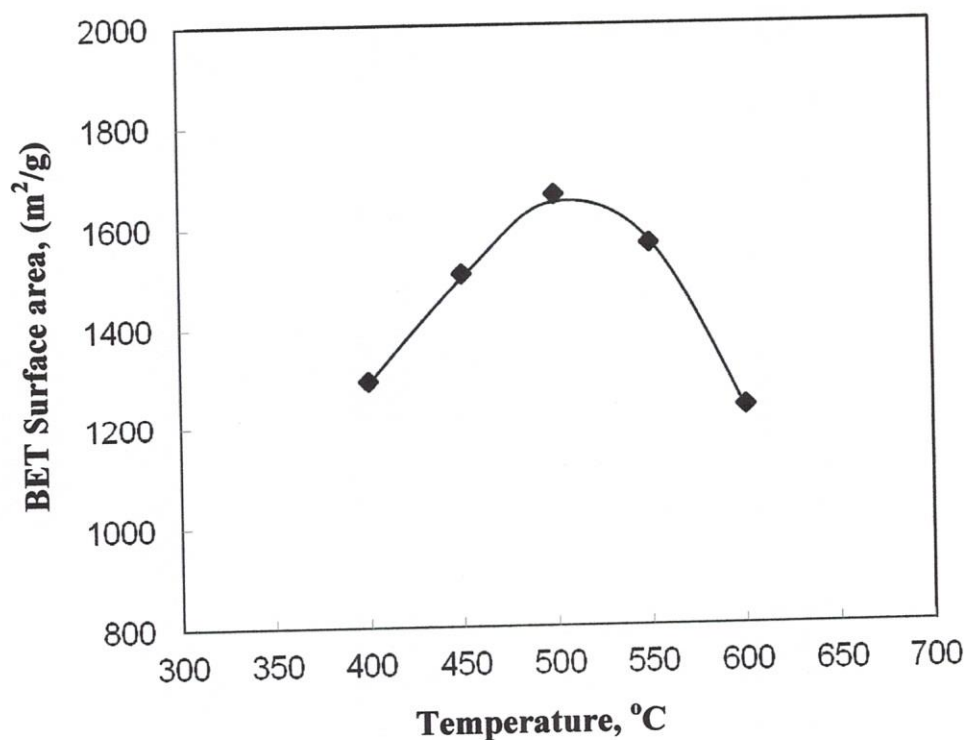


Figure 5.6. Effect of temperature on the BET surface area of activated carbon.

The iodine value, defined as the mg of iodine adsorbed on one gram of activated carbon, which initially increased with temperature as can be seen

from Figure 5.7. The maximum value (1440 mg/g) was attained at 500 °C. Low activation temperature results in incomplete activation burn-off, resulting in a higher yield but low surface area as well as iodine value. The higher activation temperature resulted in lower surface area and iodine sorption capacity. High temperature activation may cause high pore size due to the high activation burn-off; however, it may cause the destructive effect to pores, resulting in decrease of surface area and iodine number.

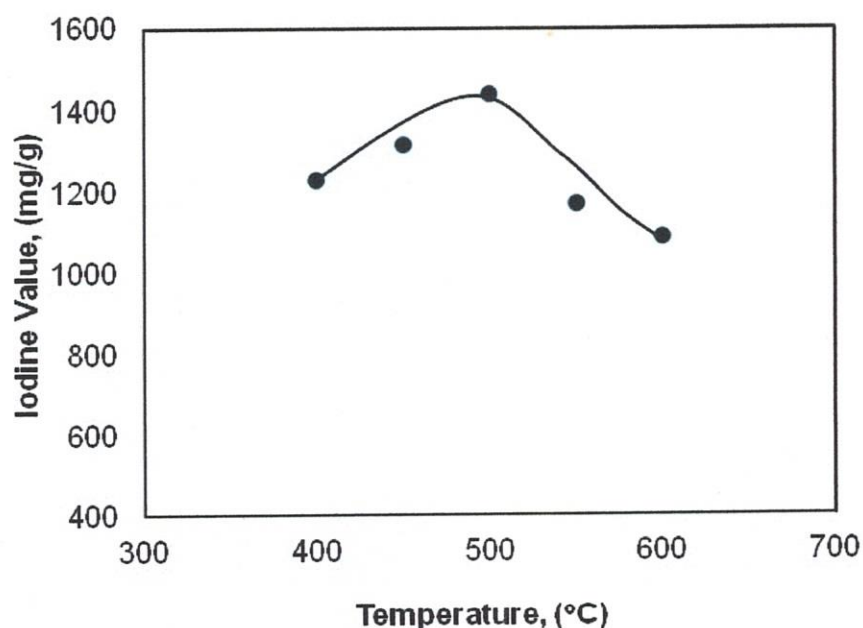


Figure 5.7. Effect of temperature on iodine value of activated carbon.

Figure 5.8 shows the effect of activation burn-off on the BET surface area and iodine number. There are no linear relationships between activation burn-off and BET surface area and iodine number. They reached to maximum values at an activation burn-off of 54 wt% and then declined at higher activation burn-off. This is because the higher activation temperature is generally attributed to the increase in pore size leading to collapse of the small pores. This result is

quite consistent with many reported results [12, 114]. The present data shows that the main trends in the variation of surface area and sorption ability with degree of activation burn-off are similar, but maximal capacities of Iodine sorption are different. Activated carbons with optimal surface area ($1664 \text{ m}^2/\text{g}$) can be obtained at 54 wt% activation burn-off at 500°C .

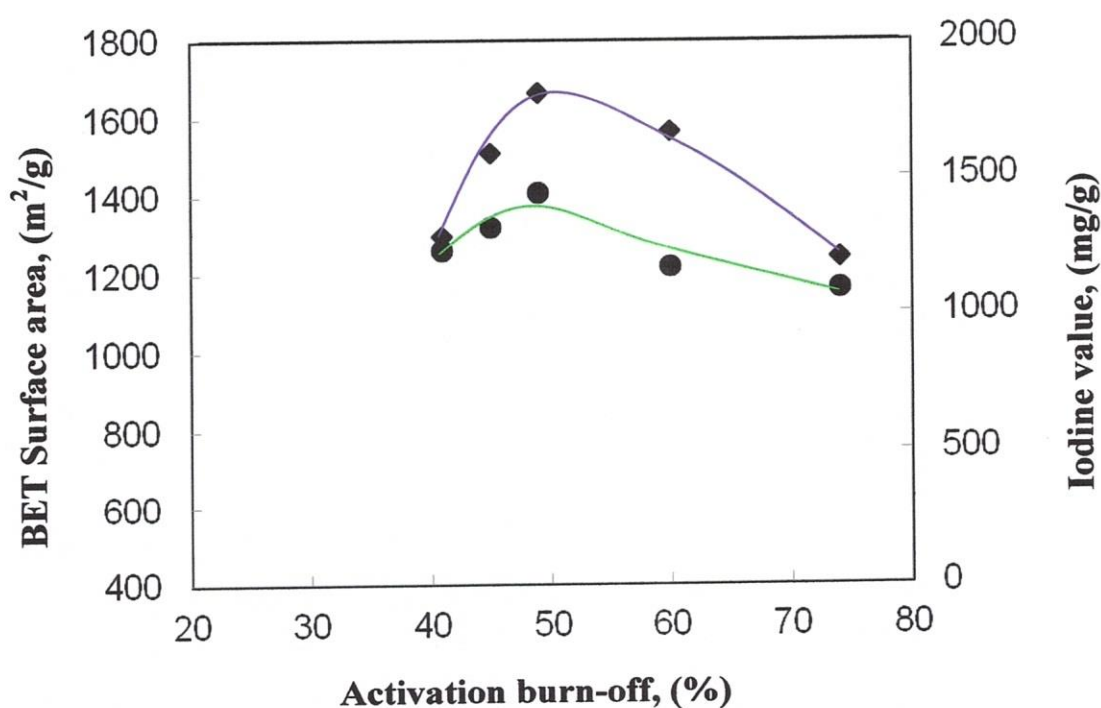


Figure 5. 8. Effect of activation burn-off on the BET surface area and iodine number of activated carbon. ●= Iodine Value, ■= BET Surface area

5.4.2. Effect of Activation Time on BET Surface Area and Iodine Number

From the above discussion it is clear that for producing high surface area activated carbon for maximum adsorption capacity, the activation burn-off should be optimized. At a particular activation temperature, the duration of

activation would have significant impact to create maximum pores and their surfaces as can be seen in Table 5.7. Figure 5.9 shows the variation of BET surface area in terms of activation time.

Table 5.7. Effect of activation time on activation burn-off, BET surface area and iodine number , Activation temperature = 500 °C, N₂ gas flow rate = 150-250 mL/min, Amount of jute stick = 5g

Activation Time (min)	Activation burn-off (wt%)	BET surface area (m ² /g)	Iodine number (mg/g)
20	35	1190	1248
40	38	1523	1275
60	50	1664	1440
80	57	1560	1210
100	60	1440	1120
120	62	1410	1050

Activation burn-off is usually a reaction limited phenomena, and thus the creation of number of pores, which reflects to the surface area gradually increased as in Figure 5.9. The maximum surface area (1664 m²/g) was obtained at 60 min activation time. The continuation of activation continuously eroded the surface of the pore walls and eventually the walls were collapsed. It resulted in bigger pore sizes, however reduced the surface area.

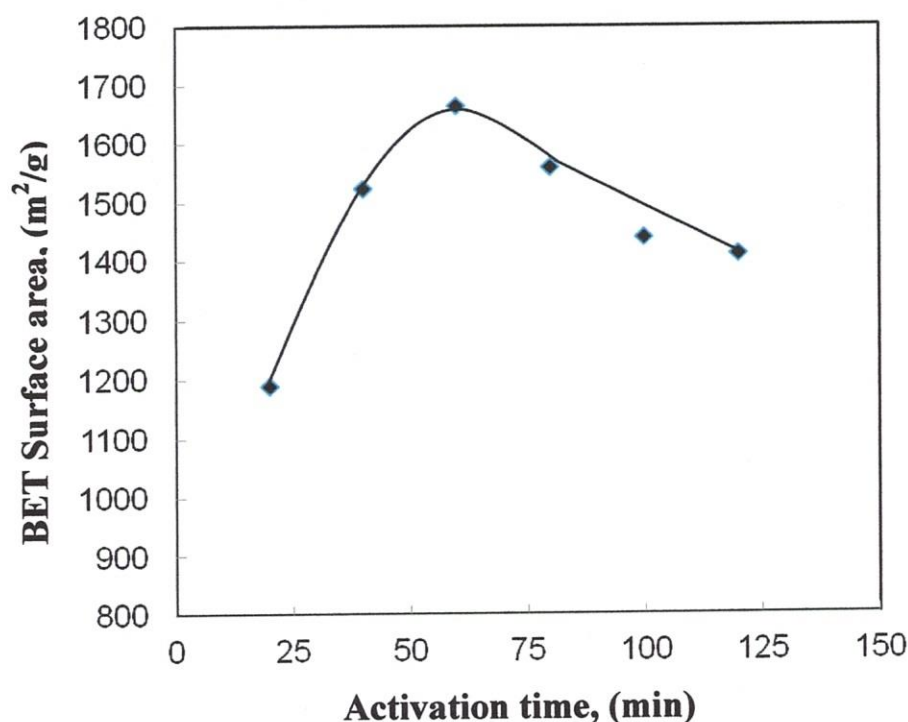


Figure 5.9. Effect of activation time on BET surface area of activated carbon.

The iodine sorption is directly proportional to the surface area as well as pore sizes. As shown in Figure 5.10, as surface area increased the iodine value is also initially increased until 60 min and then decreased with prolong time. Iodine adsorption on the adsorbent surface is usually a chemical adsorption phenomena, and thus it can form a monolayer. The monolayer in micropore can occupy more iodine than that of a monolayer in meso-pore and macro-pore structures. The higher iodine value, therefore, indicates the large micropore structure of prepared activated carbons, which eventually is desired.

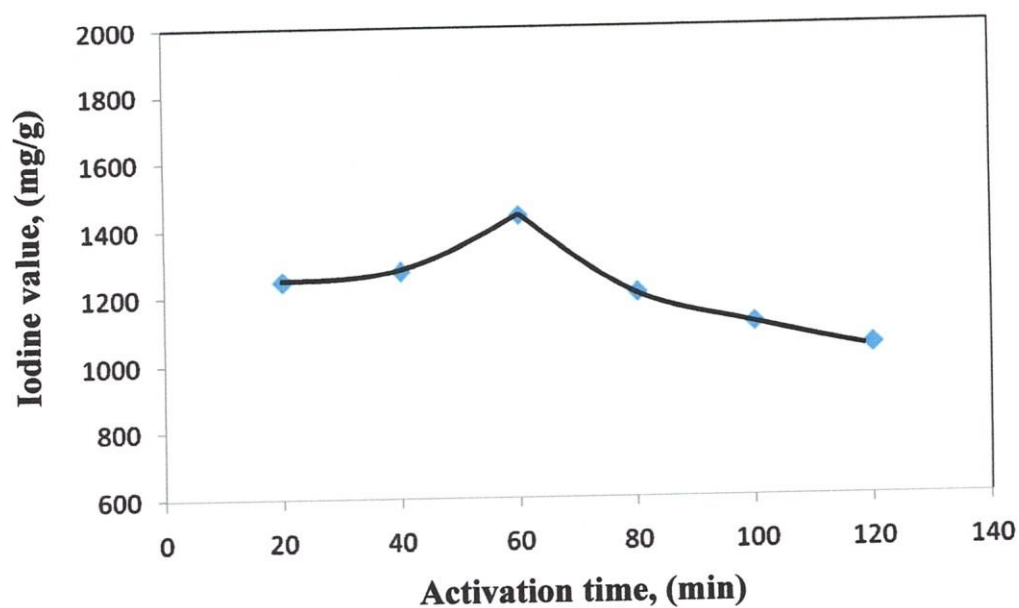


Figure 5.10. Effect of activation time on iodine value of activated carbon.

As Figure 5.11 shows, the activation burn-off is linearly increased with increasing time even until 120 min. However, the properties of the activated carbons such as BET surface area and pore volumes do not depend on the maximum activation burn-off. Around 55 wt% activation burn-off provided maximum BET surface area as well as iodine value.

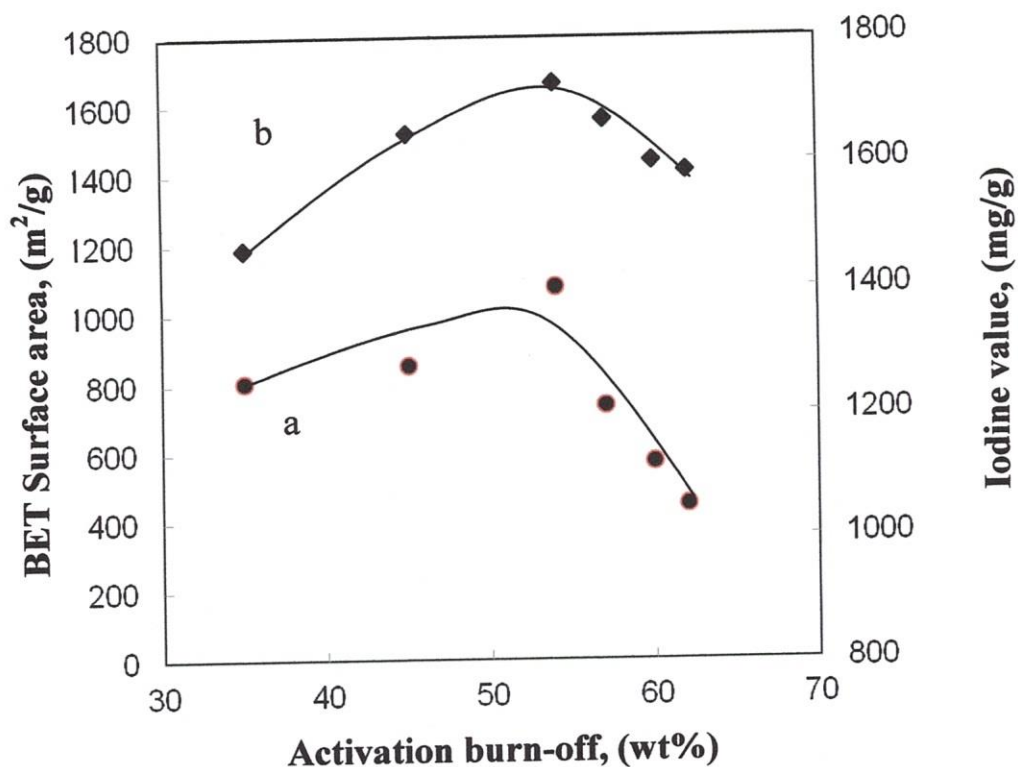


Figure 5.11. Effect of activation burn-off in terms of activation time on BET surface area and iodine value of activated carbon. (a)= Iodine Value, (b)= BET surface area.

5.4.3. Effect of Impregnation Ratio on the BET Surface Area and Iodine Number

The properties of activated carbon also depend on the H_3PO_4 impregnation ratio to jute stick. Different impregnation ratio of jute stick to H_3PO_4 ranging from 1:0 to 1:2.5 was investigated. The primary results are tabulated in Table 5.8.

Table 5.8. Effect of impregnation ratio on activation burn-off, BET surface area and iodine number.(Activation temperature, 500 °C, Nitrogen gas flow rate, 200 mL/min, Amount of jute stick, 10 g)

Jute sick :Phosphoric acid	Activation burn- off (wt%)	BET surface area (m ² /g)	Iodine number (mg/g)
1 :0.0	65	110	1041
1 :0.5	54	1024	1120
1 :1.0	50	1664	1440
1 :1.5	44	1818	1136
1 :2.0	46	1716	1098
1 :2.5	42	1654	1090

Figure 5.12 exhibits the variations of BET surface area with impregnation ratio. The jute stick to H₃PO₄ ratio 1:0 means the acid is completely absent in jute stick. In this case, the process is simply carbonization to produce charcoal at 500°C, a usual carbonization temperature. Under this condition, pore generation is limited, and thus the surface area is very low as shown in Figure 5.12. At the ratio of 1:0.5, the surface area increased to around 1024 m²/g while it is the highest at the ratio of 1:1. The surface area further decreased significantly with higher fraction of H₃PO₄. The reason is obvious that the higher concentration of acid caused an over re-polymerization of jute stick component which would have made a highly rigid materials as described in earlier section. It may assume that the pore generation in the rigid materials could be difficult.

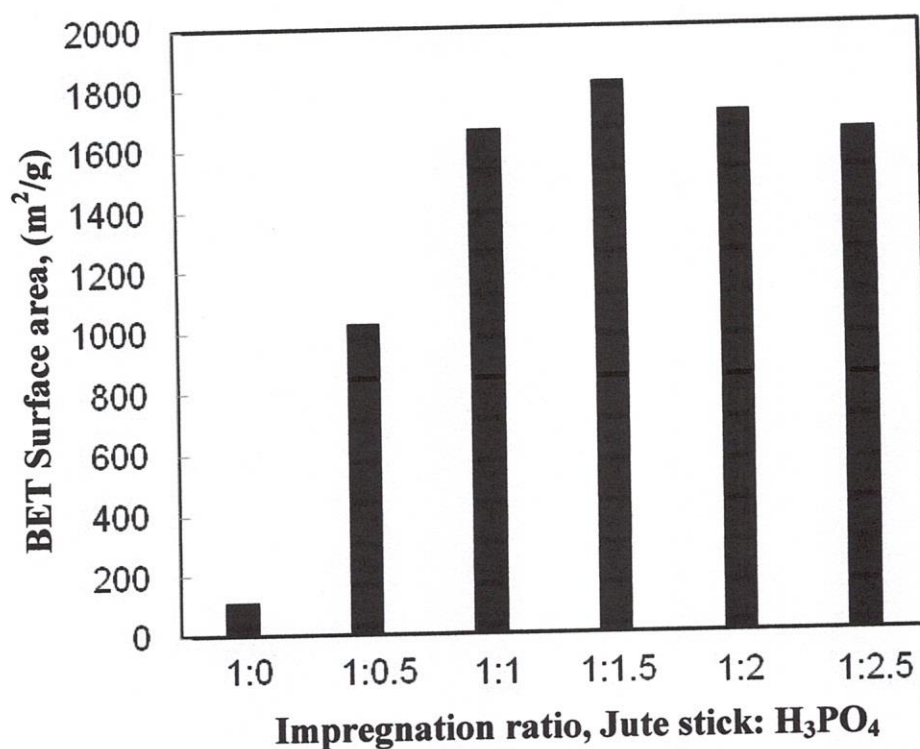


Figure 5.12. Effect of impregnation ratio on the BET surface area.

Figure 5.13 represents the variation of iodine adsorption in terms of acid impregnation ratio. As in previous section, iodine adsorption is very low by the adsorbent produced without addition of H₃PO₄. Iodine adsorption on the activated carbon surface depends on the total surface area as well as the pore size. In addition, it also depends on the surface functional groups. The presence of functional groups on the surface provides the surface potential to chemically adsorb the foreign particles. In the absence of acid, the product has abundant of surface functional groups as shown in the FT-IR spectra in the latter section. However, the porosity and surface area are insignificant, and thus the iodine value of the first sample is very low compared to other samples.

The iodine adsorption capacity is the maximum by the adsorbent produced using 1:1 ratio of jute stick and acid as of surface area. At this ratio the surface area, porosity and surface functional groups are balanced. The higher

concentration of acid may cause the over removal of surface functional groups, which in turn resulted in lower adsorption of iodine. In addition, some of the phosphoric acid may permanently combine with surface functional groups and permanently occupy some pores. This may also be the cause of lower iodine value at higher acid concentration. Sometimes, by the acidic action, the carbon skeletal may collapsed and form non-porous rigid materials. Since the activation reaction proceeded at 500 °C, which is a much lower temperature than gasification temperature (800 °C), no physical activation took place by gasification reaction of rigid carbon materials. The un-reactivity (rigidity) of the chemically activated carbon was realized from the reactivity data described in the latter section.

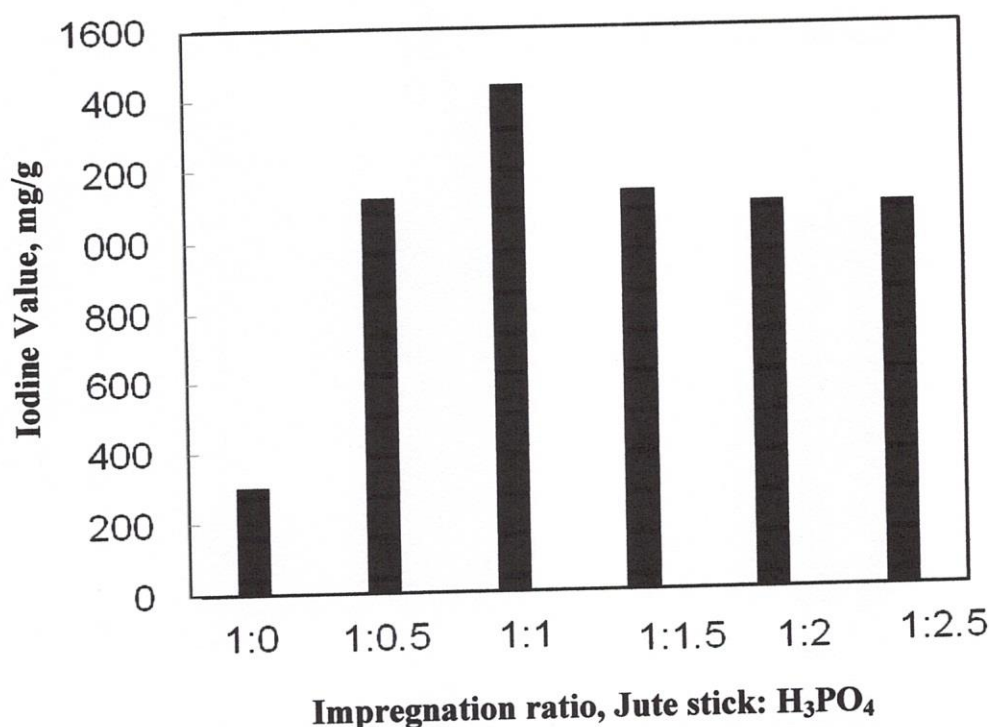


Figure 5.13. Effect of impregnation ratio on the iodine value of activated carbon.

5.4.4. Methylene Blue Dye Adsorption Study

Adsorption of solid from liquid phase can be used to determine the adsorptive capacity of activated carbon using methylene blue dye. Under standard conditions, the adsorptive capacity of activated carbon depends on adsorption time and concentration of the solution to attain the maximum saturation point. Therefore, in this study adsorption time and solution concentration were investigated in order to evaluate the potential of adsorptive property of activated carbon.

Table 5.9. Effect of adsorption time on the amount of Methylene Blue dye adsorption on activated carbon, Amount of activated carbon = 0.1 g, Temperature = 28 °C (Room temperature), Dye solution concentration = 0.3 wt%

Adsorption time (h)	Amount of dye adsorption on 0.1g activated carbon (x, g)	Amount of dye adsorption per gram of activated carbon (x/m, g/g)	x/m (mg/g)
1	0.0280	0.280	280
2	0.0310	0.310	310
4	0.0372	0.372	372
8	0.0441	0.441	441
12	0.0452	0.452	452
16	0.0463	0.463	463
20	0.0470	0.470	470
26	0.0472	0.472	472
35	0.0475	0.475	475
45	0.0474	0.474	474
60	0.0476	0.476	476
80	0.0480	0.480	480

For this measurement the standard calibration curves for Methylene Blue dye was prepared as shown in Figure 4.31. The slope obtained from the calibration curve was used for the calculation of equilibrium concentration of dye.

To ensure the equilibrium adsorption, it is necessary to know the time required to reach equilibrium adsorption. This experiment was performed under different adsorption time to obtain the equilibrium adsorption. The dye adsorption in mg per gram of activated carbon is initially small and increased with increasing time. The results are summarized in Table 5.9. Figure 5.14 shows that the Methylene Blue (0.3 wt%) adsorption reached to real equilibrium within 20 h. However, in the first 4 h, around 80% adsorption was achieved with 372 mg/g of dye which is more than double of any commercial activated carbon.

achieved with 372 mg/g of dye which is more than double of any commercial activated carbon.

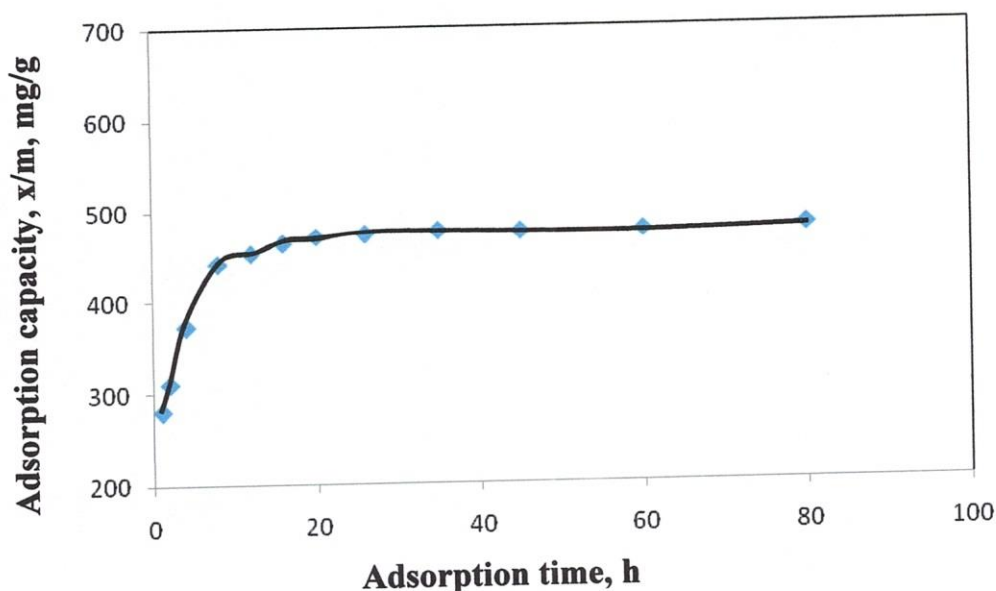


Figure 5.14. Effect of adsorption time on Methylene Blue dye removal.

The adsorption of dye from different concentration of dye solution was carried out and fitted to the Langmuir adsorption isotherm

$$C_e/(x/m) = 1/(K_L \cdot x_m) + C_e/x_m \dots\dots\dots(1)$$

and the Freundlich adsorption isotherm as follows:

$$\text{Log } x/m = \text{log } K_F + 1/n \text{ log } C_e \dots\dots\dots(2)$$

Table 5.10. Data for Langmuir and Freundlich adsorption isotherm model for Methylene Blue dye. Treatment time = 1h, Amount of activated carbon x = 0.1 g, Temperature = 28 °C (Room temperature)

Initial concentration (mmol/L)	Final concentration (mmol/L)	Equilibrium concentration (C_e) mg/L	Amount of dye adsorbed, (x, mg)	Dye adsorbed per g of adsorbent x/m (mg/g)	$C_e/(x/m)$ (mg/g)	$\text{Log}_{10} C_e$	$\text{Log}_{10} x/m$
1.40	0.054	2.67	9.61	90.00	0.029	0.427	1.95
2.80	0.665	24.94	15.26	145.00	0.172	1.397	2.16
4.20	1.228	46.50	21.25	200.10	0.232	1.667	2.30
5.62	2.457	89.95	22.50	218.21	0.412	1.954	2.34
7.02	3.200	121.79	27.22	254.32	0.478	2.085	2.41
8.43	4.300	160.89	29.39	280.41	0.573	2.206	2.45
11.23	6.552	247.35	33.36	314.45	0.786	2.393	2.50
14.04	7.592	284.74	46.48	441.01	0.645	2.454	2.65

where C_e is the equilibrium concentration of solute remaining in the solution, x/m is the quantity of solute adsorbed per unit weight of adsorbent, x_m and K_L are Langmuir constants. These constants are adsorption capacity (solute monolayer capacity) and bonding energy constant, respectively. K_F and n are the Freundlich constants.

The equilibrium concentration data is summarized in Tables 5.10. Straight line was fitted to the points as Figure 5.15 by the method of least squares, where the slope of the regression line is $1/x_m$ and the intercept is $1/K_L \cdot x_m$. The linear regression lines obtained had highly significant correlation coefficients (r), indicating a good fit to the Langmuir equation.

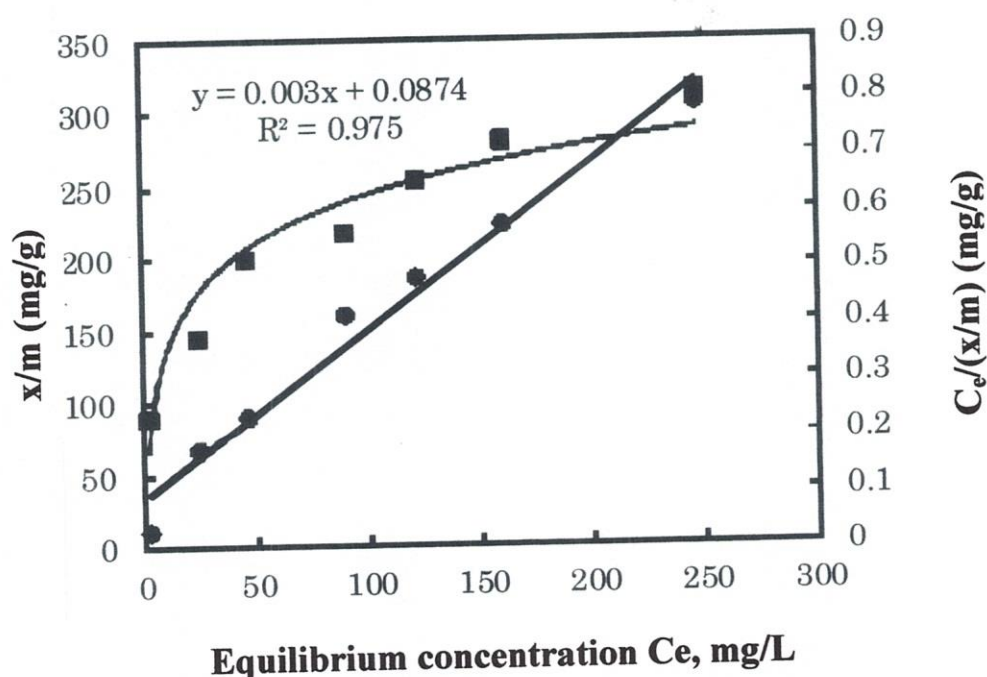


Figure 5.15. Langmuir plot for Methylene Blue dye adsorption.
 ● = Langmuir plot, ■ = Quantity of solute adsorbed curve

When the data was tested using equation (2) where they best fitted to the Freundlich model as indicated by its relatively higher linear correlation

coefficients. Figure 5.16 represents the graph fitted to the Freundlich model. The results show that activated carbons prepared from chemical activation of jute stick exhibit good capacity to remove the bulky dye molecule from aqueous solutions. This study provides the good potential of prepared activated carbon to be used for arsenic separation from water.

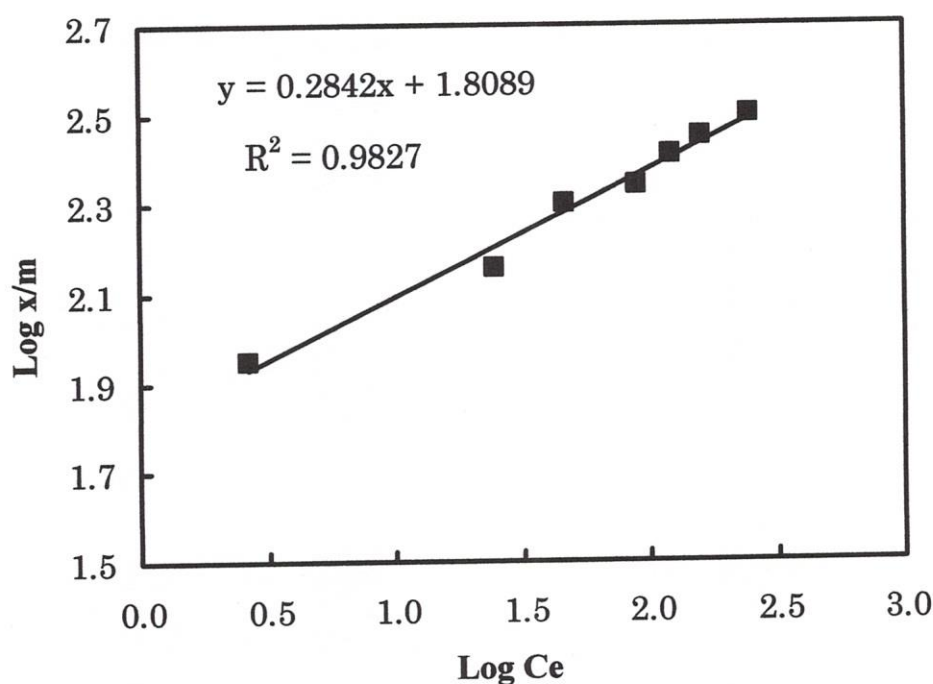


Figure 5.16. Freundlich plot for Methylene Blue dye adsorption.

5.4.5. Pore Volume, Pore Size and Surface Area Analysis of Different Activated Carbons using Multiple Theories

The varieties of ways to calculate surface area, pore volume and pore size can be used to figure out the adsorption properties of porous materials like activated carbons. The methods used in this study are described as follows:

- DFT (Density Functional Theory) method
- Multipoint BET method
- Langmuir method
- BJH (Barrett, Joyner & Halenda) cumulative adsorption method
- DH (Dollimore-Heal) cumulative adsorption method
- t- statistical thickness method external surface
- t- statistical thickness method micro pore surface
- DR (Dubinin-Radushkevich) micro pore method

The summary of the data such as surface area, pore volume and pore size obtained from different methods for different activated carbon samples prepared from jute stick are tabulated in Table 5.11.

Table 5.11. Summary data of surface area, pore volume and pore size determined by different methods

Surface area measurement method	H ₃ PO ₄ activated carbon (ACC)	5% Iron loaded on H ₃ PO ₄ activated carbon (FACC)	5% Iron loaded in jute stick and then activated (FACS)
Multipoint BET, m ² /g	1024	866	711
Langmuir Surface Area, m ² /g	1151	969	814
BJH Method Cumulative Adsorption Surface Area, m ² /g	4720	2273	1440

Continued

DH Method Cumulative Adsorption Surface Area, m ² /g	4734	2511	1480
t-Method External Surface Area, m ² /g	225	134	324
t-Method Micro Pore Surface Area, m ² /g	798	732	387
DR Method Micro Pore Area, m ² /g	1109	928	775
Pore volume measurment method			
Total Pore Volume for pores with Diameter at P/Po = 0.99588, cc/g	0.569	0.495	0.863
BJH Method Cumulative Adsorption Pore Volume, cc/g	1.152	0.670	0.913
BJH Interpolated Cumulative Adsorption Pore Volume for pores in the range of 5000.0 to 0.0 Å Diameter, cc/g	1.152	0.670	0.913
DH Method Cumulative	1.117	0.687	0.894

Continued

Adsorption Pore Volume, cc/g			
t-Method Micro Pore Volume, cc/g	0.337	0.324	0.160
DR Method Micro Pore Volume, cc/g	0.394	0.330	0.276
HK Method Cumulative Pore Volume, cc/g	0.414	0.353	0.291
Pore size measurement method			
Average Pore Diameter, Å	22.25	22.88	48.58
BJH Method Adsorption Pore Diameter (Mode), Å	6.654	6.44	7.038
DH Method Adsorption Pore Diameter (Mode), Å	6.654	6.44	7.038
DR Method Micro Pore Width, Å	19.45	17.37	13.63
DA Method Pore Diameter (Mode), Å	15.00	14.00	12.00
HK Method Pore Width (Mode), Å	3.125	3.67	3.675

The BET is the most famous gas model for multilayer gas adsorption. In the BET adsorption study, a part of the isotherm that contains the “knee”, brackets the monolayer value. Normally solved by graphical means, by plotting

$1/(V[(P_0/P)]^{-1})$ versus P/P_0 . Monolayer volume (V_m) is equal to $1/(s+i)$ where 's' is the slope and 'i' is the y-intercept. Often, BET theory is also applied to obtain the specific surface area of microporous materials, although from a scientific point of view the assumptions made in the BET theory do not take into account the micropore filling. For samples, the linear "BET" range is found usually at relative pressures < 0.1 , in contrast to the classical BET range, which extends over relative pressures between 0.05 – 0.3. Despite its inability to accurately measure the true surface area of microporous materials it is easy to apply and is widely accepted.

Figures 5.17-5.19 show the multilayer adsorption isotherms and Figures 5.20 - 5.22 represent the multipoint BET adsorption isotherms for the samples ACC, FACC and FACS. From these figures the multipoint BET surface areas of those samples are calculated as tabulated in Table 5.11.

Figure 5.17 and 5.18 indicate an inherent property of Type I isotherms, where the adsorption is limited to the completion of a single monolayer of adsorbate at the adsorbent surface. Type I isotherms are observed for the adsorption of gases on microporous solids, whose pore sizes are not much larger than the molecular diameter of the adsorbate. Complete filling of these narrow pores corresponds to the completion of a molecular monolayer. The amount of adsorption until monolayer formation is around 190 cc/gm for ACC, while it is around 160 cc/g for FACC. When the micropore is completely filled with gas molecules, the multilayer adsorption is started to form as gradually progress in Figures 5.17 and 5.18 with increasing relative pressure. The progress of multilayer adsorption continued gradually until the relative pressure reaches the saturation point.

An interesting result can be seen in Figure 5.19 for FACS. Type II adsorption isotherm is resulted and it is very similar to adsorption isotherm of iron catalyst [167]. Type II adsorption isotherm describes adsorption on meso- and macroporous adsorbent with strong adsorbent-adsorbate interaction.

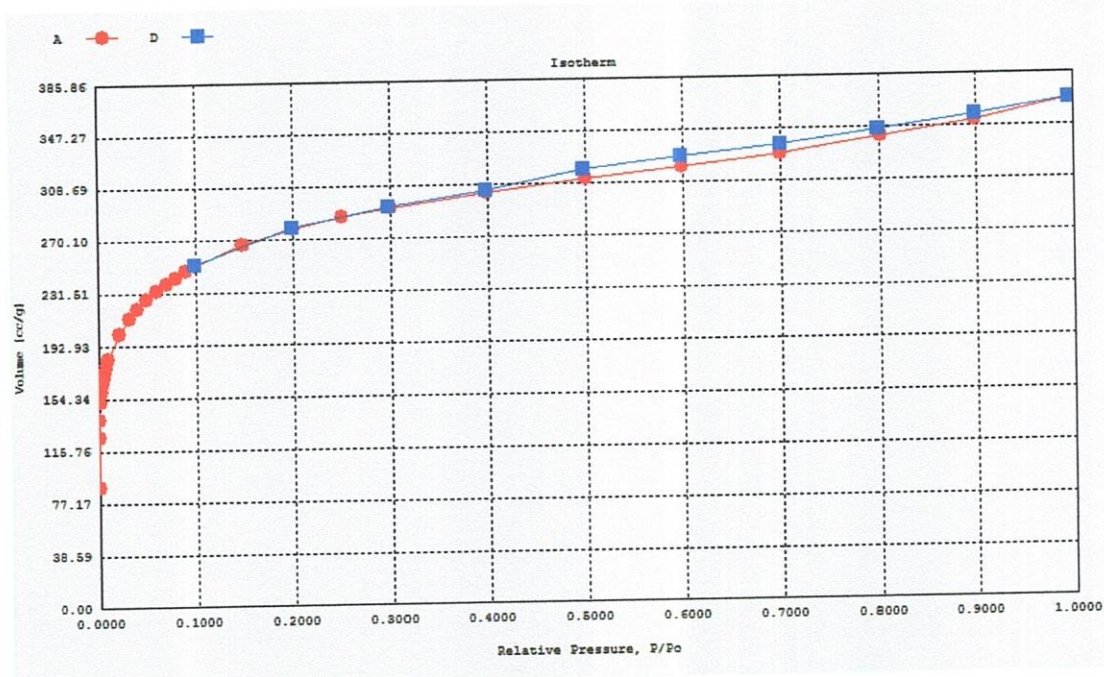


Figure 5.17. Multi-layer adsorption isotherm of ACC.

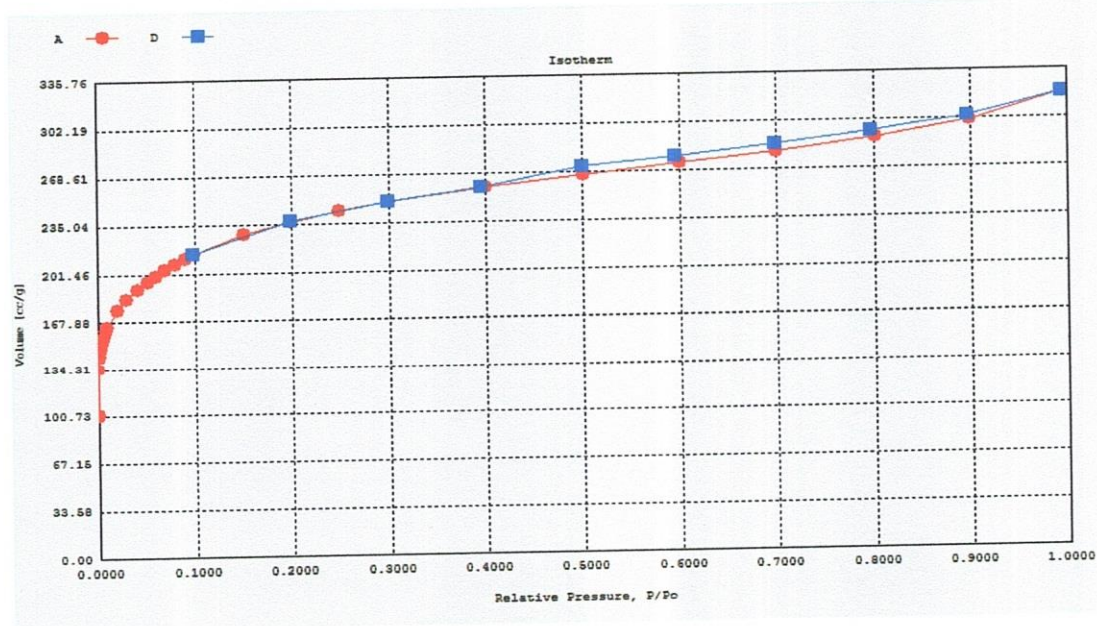


Figure 5.18. Multi-layer adsorption isotherm of FACC.

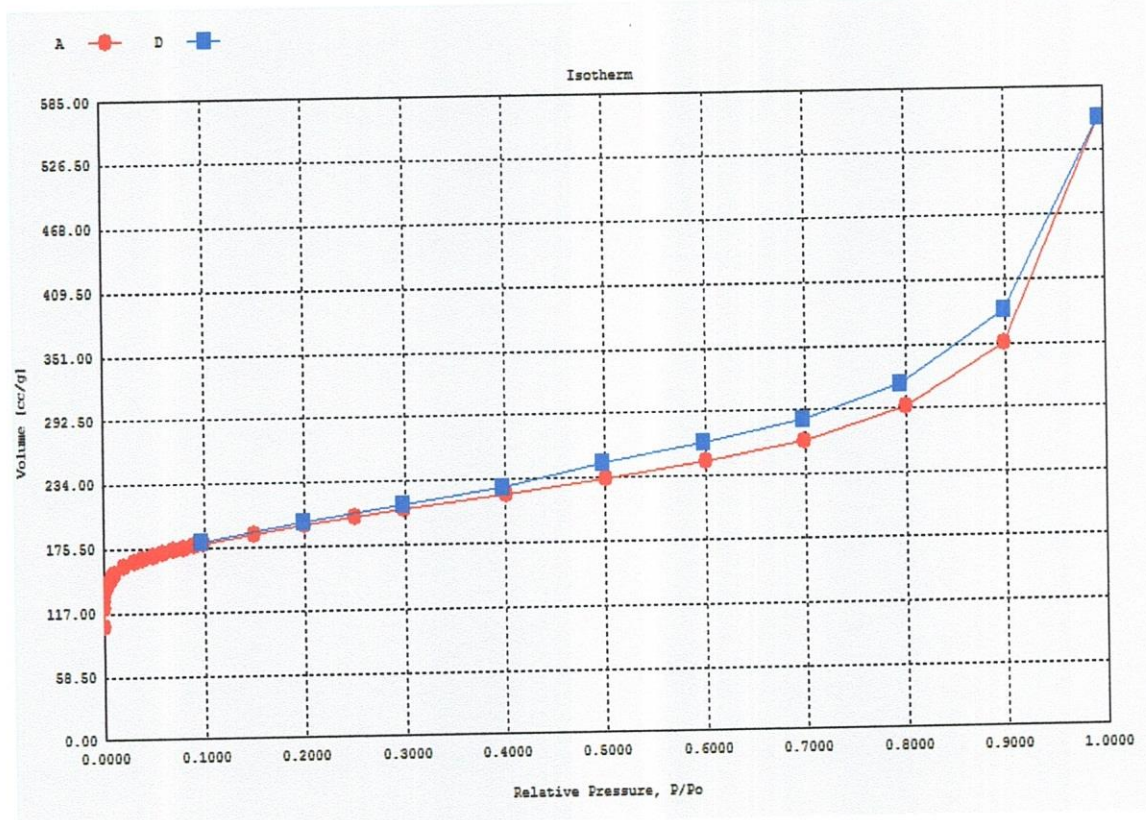


Figure 5.19. Multi-layer adsorption isotherm for FACS.

Because of the strong interaction between the adsorbent surface and adsorbate layer, infinite multilayer can be formed near the saturation relative pressure as can be seen in Figure 5.19. This finding clearly suggests that ACS poses very high macropore structure. However, the micropore structure is much more important for metal ion separation from water.

The Figure 5.20 shows the monolayer surface area $1024 \text{ m}^2/\text{g}$ for ACC until relative pressure 0.08. It is quite a big surface area for activated carbon for different applications. The multilayer adsorption is continued until the pore is completely filled with gas molecules, and thus the isotherm is gradually progressing in Figure 5.17.

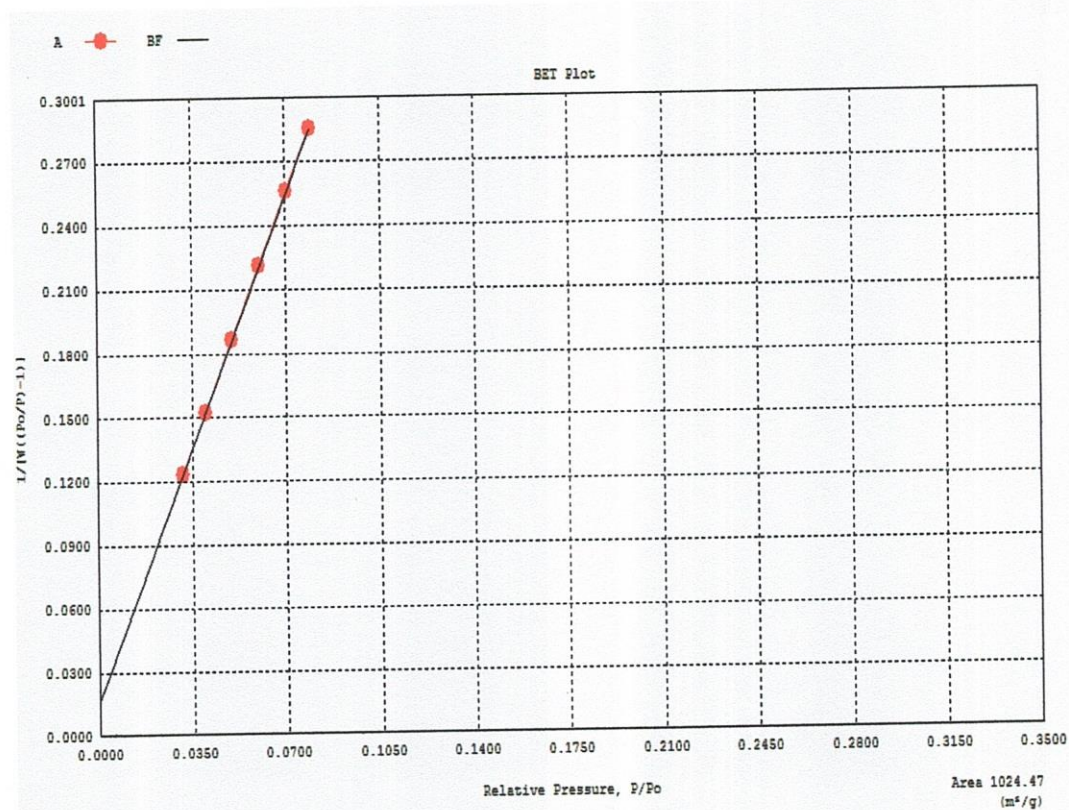


Figure 5.20. BET plot for ACC.

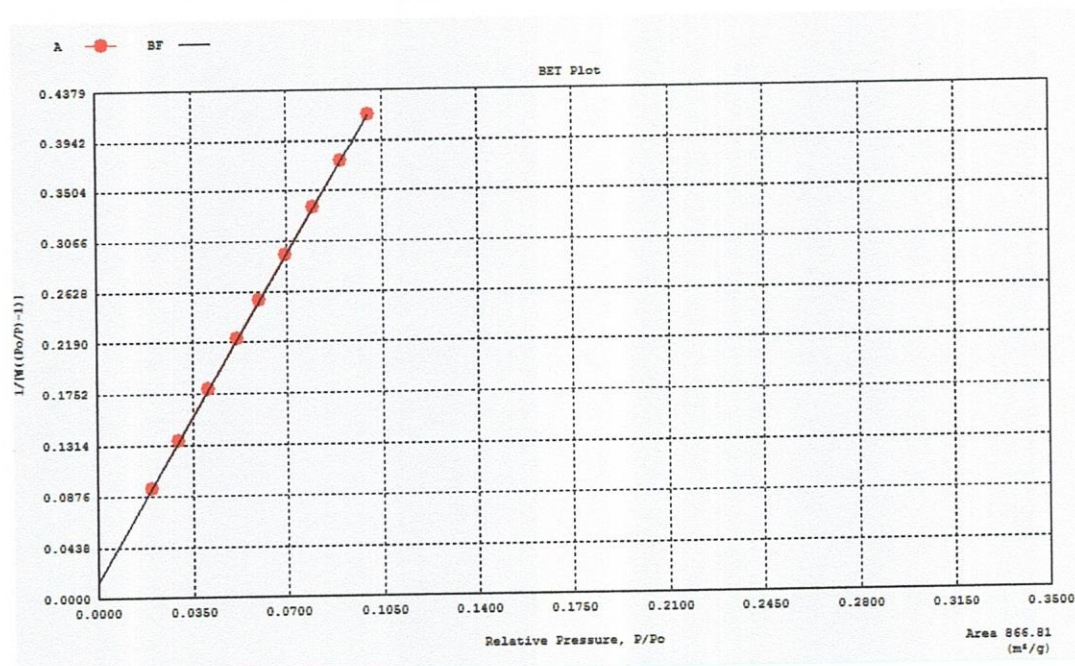


Figure 5.21. BET plot for FACC.

The surface area ($866 \text{ m}^2/\text{g}$) of 5% iron loaded activated carbon (FACC) prepared from ACC ($1104 \text{ m}^2/\text{g}$) is significantly lower than ACC (Figure 5.21). This is a clear indication of filling of some micropore with iron species. This assumption is supported with the lower t-method micropore volume and other method micropore volume as shown in Table 5.11. This means that iron species dispersed in the micropores, which in turn would be effective for arsenic separation.

Figure 5.22 shows the BET plot for ACS with surface area $711 \text{ m}^2/\text{g}$. This value is lower than ACC ($1104 \text{ m}^2/\text{g}$) and FACC ($866 \text{ m}^2/\text{g}$). The FACS is prepared by physical activation method using steam at 780°C . The iron salt (FeSO_4) was impregnated into the jute stick and then carbonized at 500°C for 1 h. After completing carbonization, the temperature was increased to 780°C , while steam was passed through the char bed for another 1 h. During this period, steam reacted with carbons, producing carbon monoxide which upon evacuation left pores of wide range. In this case iron exposed onto the micropore surface as well as meso and macropore surface. As Table 5.11, the micropore volume is very low while the total pore volume and size is much higher than that of ACC and FACC. From this results it can be revealed that the physical activation provides macropore structure, which is less important for arsenic separation.

The use of Langmuir area for microporous solids has very limited sense (and should be used only for comparisons between adsorbents). It comes from practical reasons – the shape of adsorption isotherm on microporous solids close to completion of micropores is generally more similar to Langmuir isotherm close to monolayer filling than to BET multilayer. Thus, in 0.05 – 0.2 region such experimental isotherm is more likely to follow the Langmuir than BET isotherm course. If the solid contains comparable amounts of micropores, meso- and macropores, then neither model may simulate such behavior properly. For this sample, Langmuir surface area $1151 \text{ m}^2/\text{g}$ is higher than BET

surface area, 1024 m²/g due to the consideration of higher relative pressure for Langmuir isotherm.

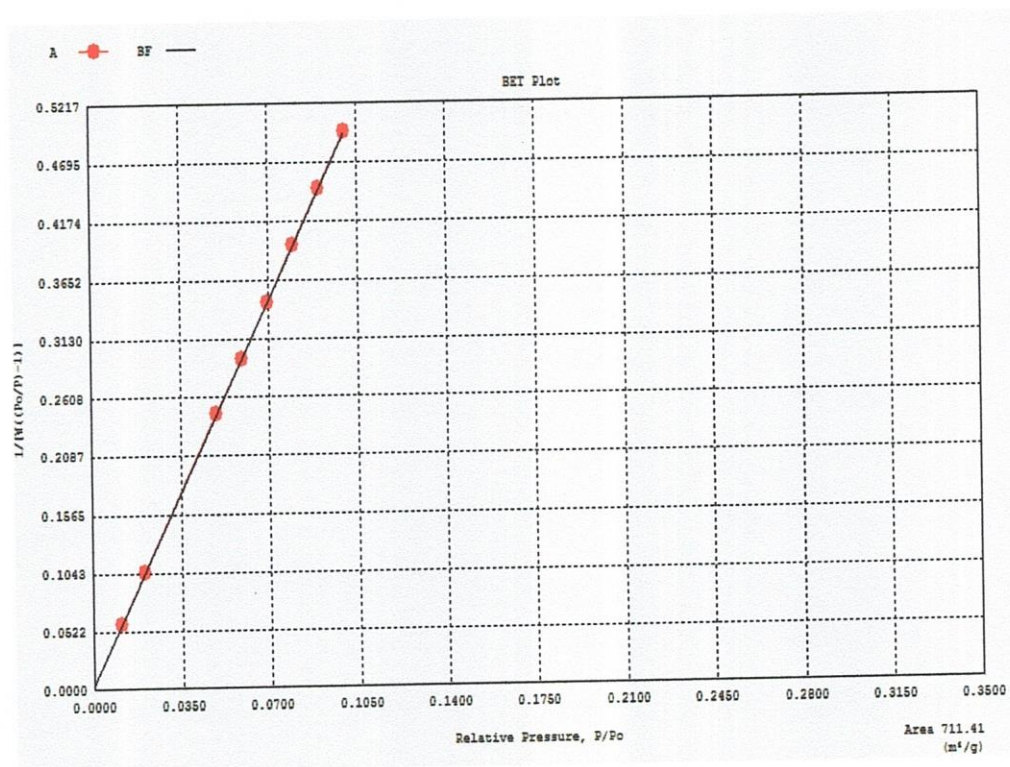


Figure 5.22. BET plot for FACS.

Figure 5.23 shows the volume of gas adsorbed vs thickness of the adsorbed layer. This is called t-plot. For physical adsorption a mono-layer thickness of nitrogen is around 1.55 Å. Based on this size the Figure 5.23 clearly indicates the multilayer adsorption.

Multi-layer formation is modeled mathematically to calculate a layer “thickness, t” as a function of increasing relative pressure (P/Po). The resulting t-curve is compared with the experimental isotherm in the form of a t-plot. That is, experimental volume adsorbed is plotted versus statistical thickness for each experimental P/Po value as shown in Figure 5.23. The linear range lies between monolayer and capillary condensation. The slope of the t-plot (V/t) is equal to the “external area”, i.e. the area of those pores that are not micropores.

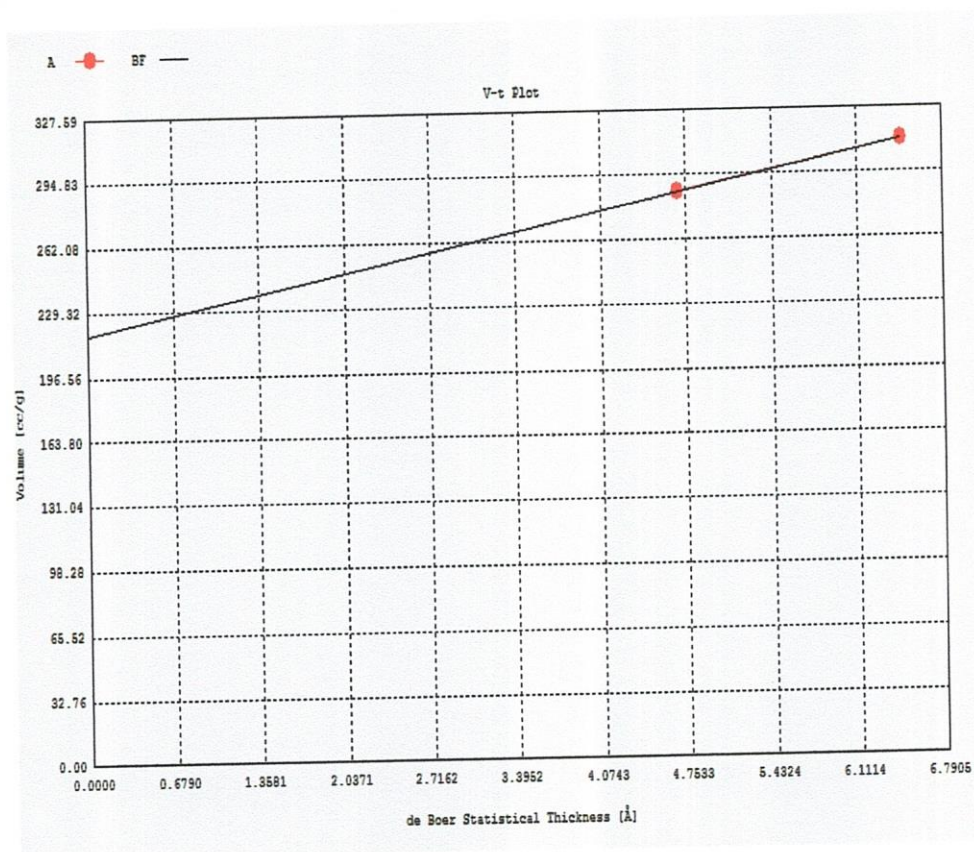


Figure 5.23. Volume –thickness plot of ACC.

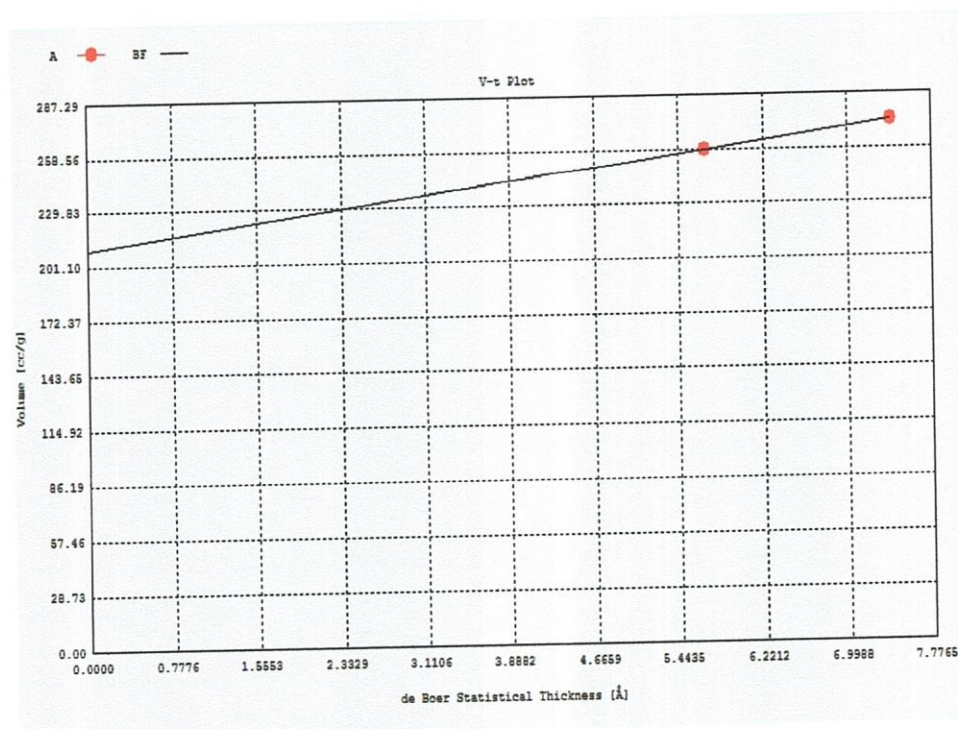


Figure 5.24. Volume –thickness plot of FACC.

The t- method measures both micropore thickness and external thickness of the adsorbate layer. Since ACC poses much higher micropore surface area and volume as can be seen in Table 5.11, it contributes in monolayer adsorption, and thus the average thickness is much lower than FACC and FACS to adsorb higher amount of gas as exhibited in Figures 5.24 and 5.25.

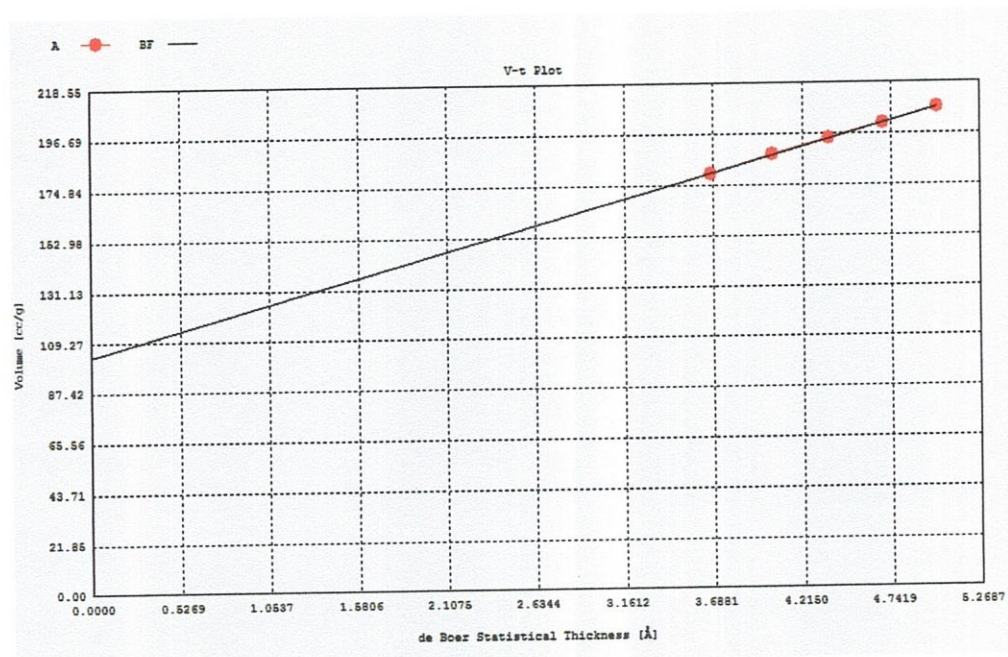


Figure 5.25. Volume –thickness plot of FACS.

Mesopores, macropores and the outside surface are able to form a multilayer, whereas micropores, which have already been filled, cannot contribute further to the adsorption process. A multilayer adsorption model with filled pores is shown in Figure 5.26. It can be seen from this model diagram that the gas molecules in the macropore are not condensed and are not contributed to measure the pore volume and surface area, and thus both of them are lower in the case of FACS.

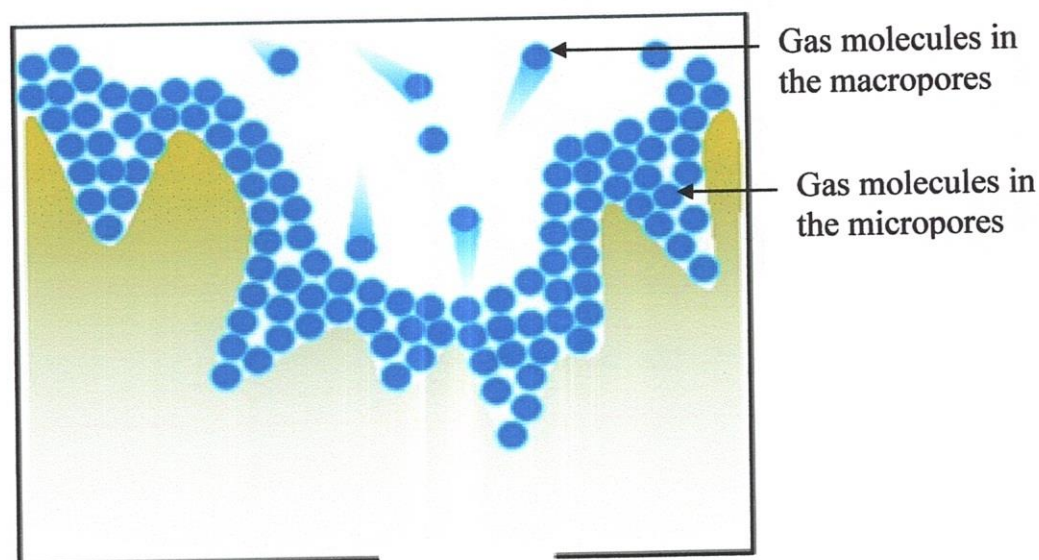


Figure 5.26. Multilayer adsorption with filled pores.

The method of Barrett-Joyner-Halenda (BJH), proposed in 1951 [168], was originally designed for determining the pore volume and total surface area of relatively wide-pore adsorbents with a wide pore size distribution. However, it was repeatedly demonstrated that it can be successfully applied to virtually all types of porous materials. The model is based on the assumption that pores have a cylindrical shape and that pore radius is equal to the sum of the Kelvin radius and the thickness of the film adsorbed on the pore wall. The desorption branch of isotherm in the pressure range $(0.4-0.967) p/p_0$, is generally used as initial data for BJH calculations (although the use of the adsorption branch is also possible). In this calculation, pores with a diameter above 60 nm are not considered.

Figure 5.27 shows the BJH cumulative adsorption pore volume against pore diameter for ACC. To calculate the pore volume, Kelvin equation is utilized in BJH prediction. In this prediction, the adsorptive gas is spontaneously condensed (and evaporated) in a cylindrical pore of a given size at adsorption pressure. Condensation occurs in pores that already have some multilayers on

the walls. Therefore, the pore size is calculated from the Kelvin equation and the selected statistical thickness (t-curve) equation.

It can be seen from the figure that cumulative adsorption pore volume is almost 1 cc/g at pore diameter 60 Å. This volume of pore is effective for solid phase adsorption from liquid. The pore volume obtained is different by different determination method. The DH method cumulative adsorption pore volume is 1.117 cc/g, t-Method micro pore volume is 0.337 cc/g, DR Method micro pore volume is 0.394 cc/g, and HK method cumulative pore volume is 0.414 cc/g. These values are significantly lower for FACC (Figure 5.28) as well as for FACS (Figure 5.29) due to lower micropore volume.

From the above discussion it can be realized that iron species are dispersed in the micropore volume of ACC which would provide strong interaction in solid phase adsorption from solution. However, in the case of FACS, it has very high pore size, and thus the monolayer of iron on the surface would not be efficient enough to condense solid species on the surface.

Figure 5.30 shows the BJH cumulative adsorption surface area against pore diameter. This surface area is 4720 m²/g, much higher than BET surface area 1024 m²/g and Langmuir surface area 1151 m²/g. This is because in the case of BET and Langmuir surface area only one layer is considered. However, in the BJH cumulative surface area, multiple layer of surface is considered. On the other hand, the cumulative surface area is significantly lower for FACC (Figure 5.31) and FACS (Figure 5.32).

Reduction of total surface area in the case of FACC does not reflect to the lower efficiency of adsorption. Indeed, the layer of iron that formed in the micropore would have strong attraction force to adsorb foreign particles. In addition, the iron particle can form complex with arsenic and can attach to the surface permanently.

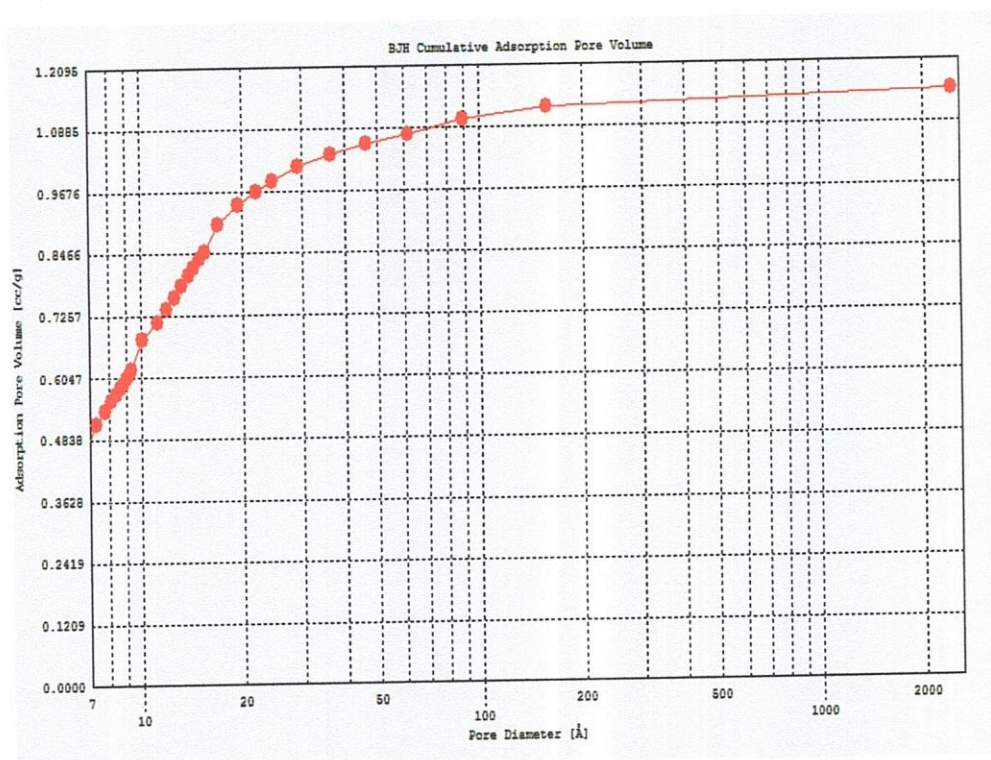


Figure 5.27. BJH plot for cumulative adsorption pore volume of ACC.

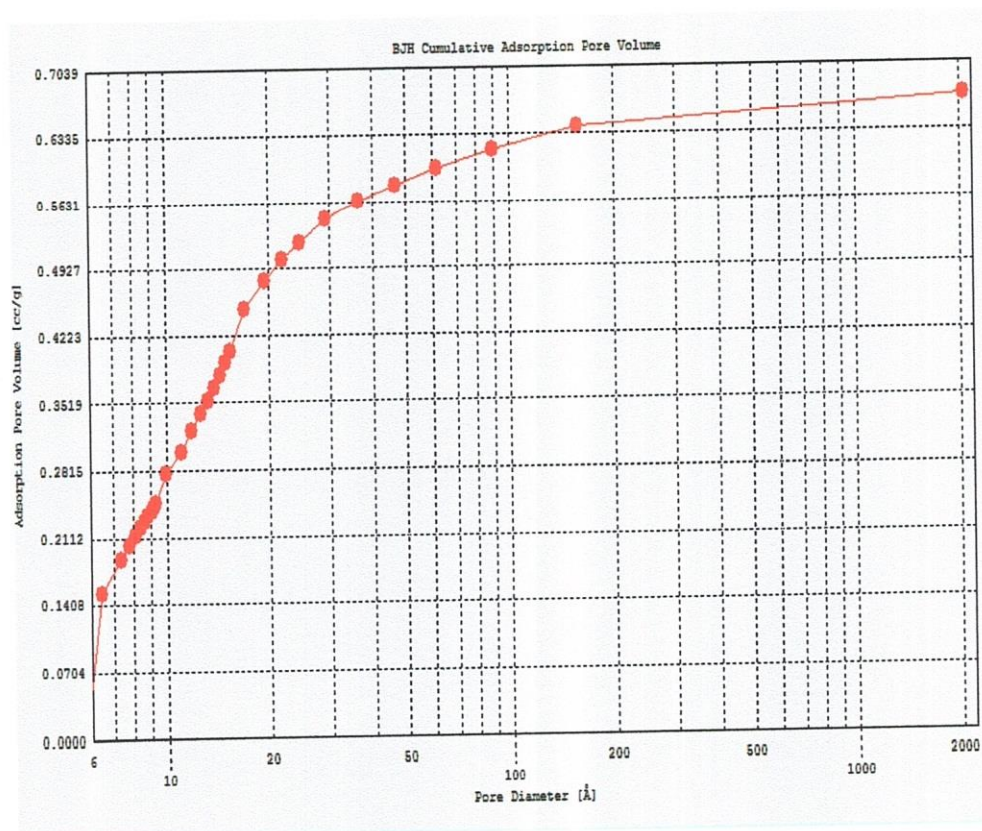


Figure 5.28. BJH plot for cumulative adsorption pore volume FACC.

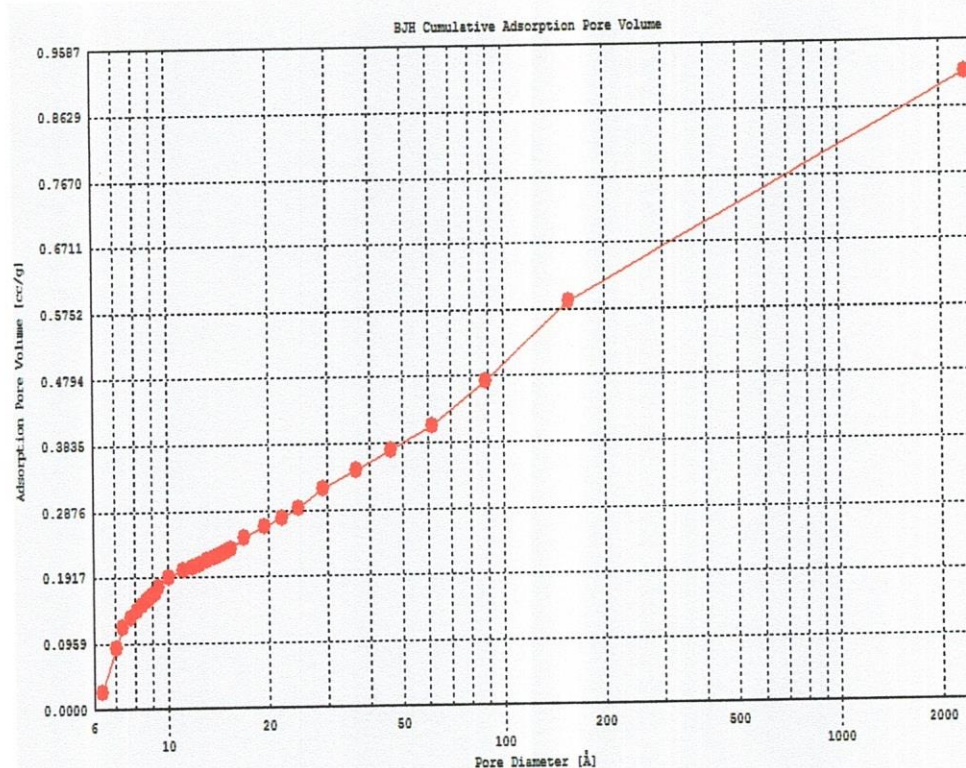


Figure 5.29. BJH plot for cumulative adsorption pore volume FACS.

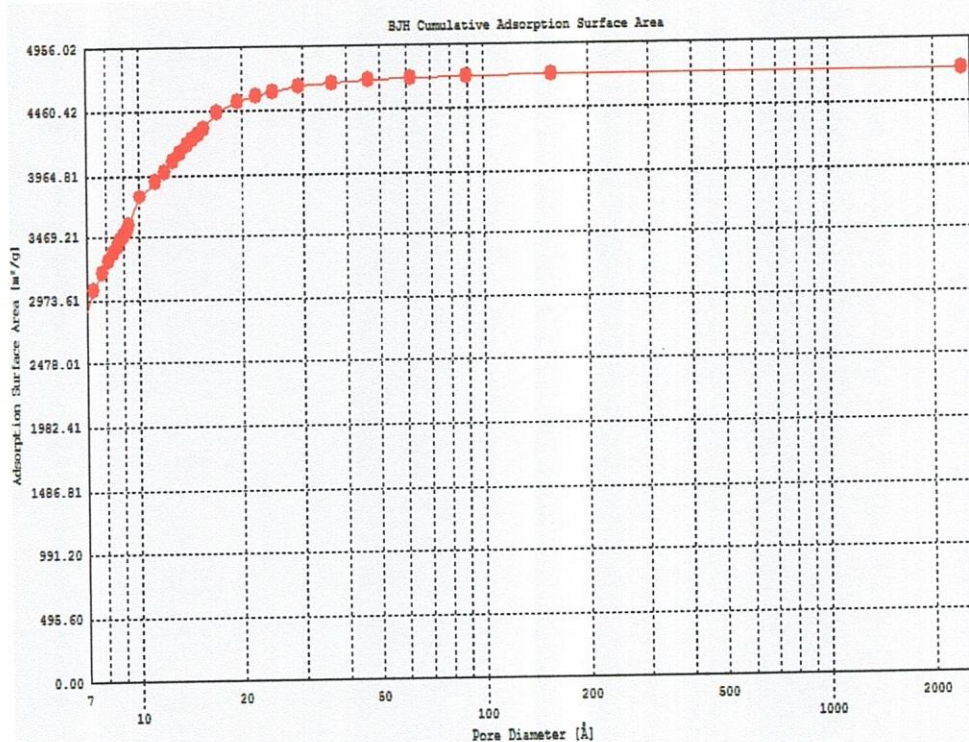


Figure 5.30. BJH plot for cumulative adsorption surface area for ACC.

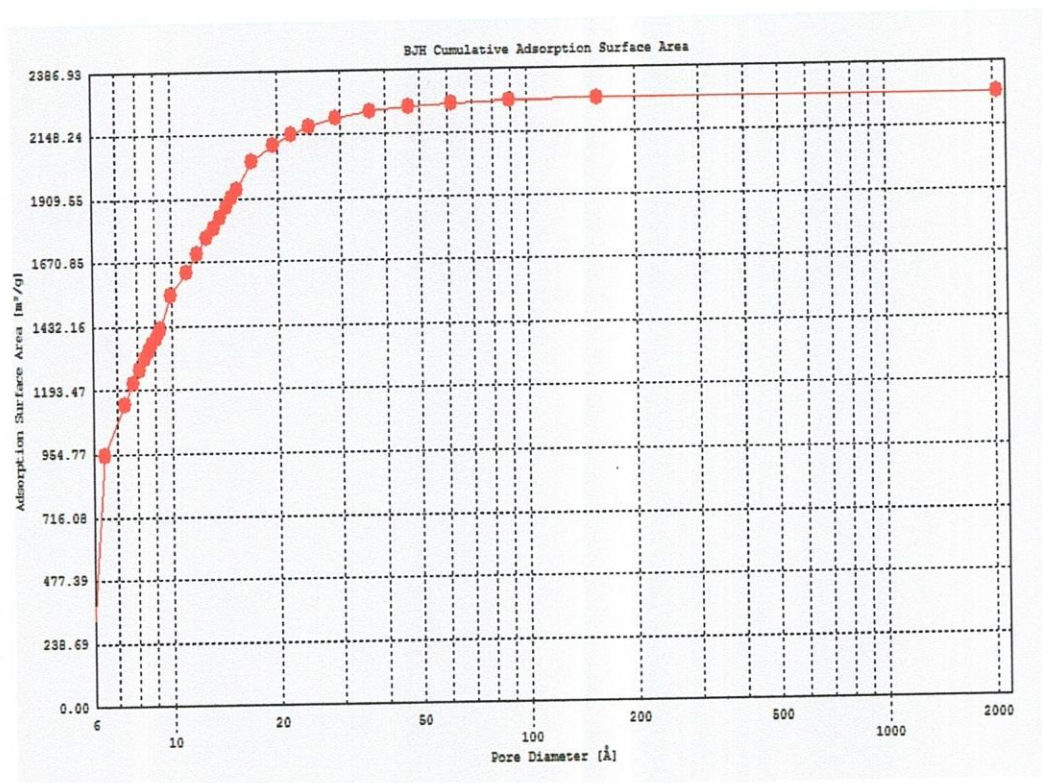


Figure 5.31. BJH plot for cumulative adsorption surface area for FACC.

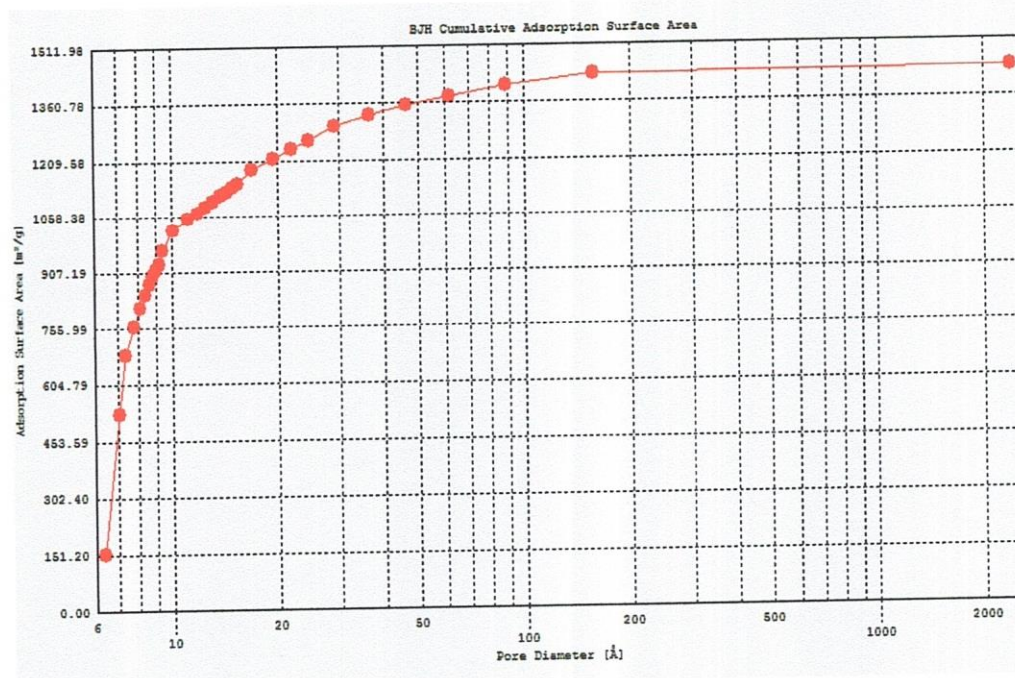


Figure 5.32. BJH plot for cumulative adsorption surface area for FACS.

5.4.6. Surface Characterization

Adsorption of solids on activated carbon surface from aqueous solution depends mainly on two typical properties as described before such as surface area and surface functional groups. The increase of surface area more likely increases the number of accessible functional groups as well as the basal plane on the surface. The activated carbon has both polar sites due to the presence of oxygen containing functional groups and non-polar basal sites [41]. Since most of the adsorbate molecules possess polar functional groups, they can preferentially be adsorbed on the polar sites of the activated carbon rather than the basal sites. It seems that the identification of surface chemical species is significant to promote the applicability of activated carbons for specific application. Although the identification of all the chemical species is not an easy task the information about the chemical nature of the carbon surfaces may be obtained by using FT-IR spectroscopy.

Figure 5.33 shows the FT-IR spectra of jute sticks, charcoal, phosphoric acid activated carbon (ACC) and steam activated carbon (ACS) over the wavelength range of $4000\text{--}400\text{ cm}^{-1}$. The spectra exhibit that the functional groups on jute stick surface significantly differ from those of charcoal, ACC and ACS. The following bands are observed on the spectrum of jute sticks (Figure 5.33(a)). The broad band at 3350 cm^{-1} was ascribed to OH^- stretching vibration in hydroxyl groups of phenols. Two bands at 2925 and 2900 cm^{-1} were represented to asymmetric and symmetric stretching vibrations of the methylene group. Their bending vibrations were observed between 1430 and 1380 cm^{-1} . These bands are quite similar to the bands of methylene group of many agricultural residues [31], [42], [43]. The strong band at 1740 cm^{-1} was attributed to carbonyl group (C=O) stretching vibration of lactones [42], [44]. Two bands at 1590 and 1510 cm^{-1} were corresponded to the stretching vibrations of aromatic C=C bonds [45]. A band at 1460 cm^{-1} was ascribed to

aromatic methyl group ($-\text{CH}_3$) [46]. The C-O stretching or $-\text{OH}$ deformation band in carboxylic acid was observed at 1430 cm^{-1} [31].

The bands at 1330 cm^{-1} could be attributed to C-O vibrations in carboxylate groups and the bands at 1240 and 1160 cm^{-1} could be attributed to esters (e.g. R-CO-O-R'), ethers (e.g. R-O-R') or phenol groups. A shoulder at 1110 cm^{-1} and a relatively intense band at 1060 cm^{-1} could be assigned to alcohol (R-OH) groups. The C-H out of plane deformation and C-H out of plane bending in benzene derivatives caused the bands at 894 and 831 cm^{-1} , respectively. Finally, the band located at 610 cm^{-1} was in-plane ring deformation [31]. From the above spectrum analysis, it can be suggested that the main oxygenated functional groups in jute sticks are phenols, carbonyls, carboxyls, alcohols, ethers and esters.

During pyrolysis of jute sticks at 500°C , most of the surface functional groups were experienced chemical transformation. As the spectra of charcoal in Figure 5.33(b), some of the functional groups were completely disappeared while some were newly generated. The strong band at 3390 is attributed to the $-\text{OH}$ group of phenol [31]. The stretching vibration of the alkenes ($=\text{C-H}$ and $=\text{CH}_2$) is located at 3040 cm^{-1} and their bending vibration is located at 876 cm^{-1} . The C-H out of plane bending in benzene derivatives caused the band at 814 cm^{-1} and the band at 752 cm^{-1} represented the C-H bending vibration in *cis*- RCH=CHR . Furthermore, the band at 2910 cm^{-1} represented the C-H stretching vibration in methyl and methylene groups. These were further confirmed by the band at 1430 cm^{-1} for $-\text{CH}_2-$ and $-\text{CH}_3$ deformation and the band at 1370 cm^{-1} for $-\text{CH}_3$ deformation. The band at 1590 cm^{-1} attributed to the C=O stretch of carbonyl group in quinone and representing γ -pyrone structure with strong vibrations from a combination of C=O and C=C [31]. A small shoulder peak at 1690 maybe represented the aryl ketone or C=N stretching vibration.

The FT-IR spectrum of chemically activated carbon (ACC) is exhibited in Figure 5.33(c). The band at 3210 cm^{-1} was assigned to OH^- stretching vibration. Two significant aspects of this band were observed. Firstly, it had been shifted to the lower wave number and secondly, it was significantly broaden. These findings apparently suggested that the $-\text{OH}$ group in the activated carbon was not free but more likely cross linked. This was due to the fact that H_3PO_4 initiated bond cleavage resulted in dehydration and elimination reactions. Consequently, a number of small molecules such as water, methanol, formic acid, acetic acid, carbon dioxide and other small molecules released from the carbon matrix, leaving behind a more aromatized, rigid, cross linked and condensed carbonaceous solids. The band at 2900 cm^{-1} in raw jute sticks was completely disappeared from the ACC, leading to the significant decrease of aliphaticity in the activated carbon. Furthermore, the band at 1740 cm^{-1} in the spectrum of raw jute sticks was also disappeared, representing the complete removal of saturated aldehydes and ketones.

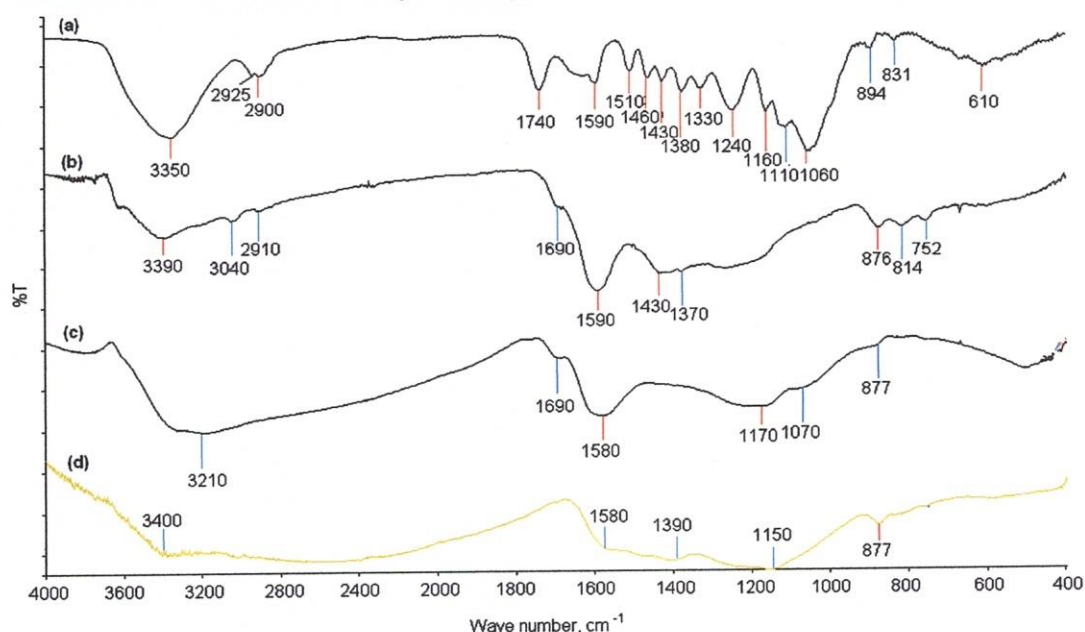


Figure 5.33. FT-IR spectra of (a) jute sticks, (b) charcoal, (c) chemical activated carbon (ACC) and (d) steam activated carbon (ACS).

The band at 1690 cm^{-1} was ascribed to stretching vibration of aryl ketone and the strong band at 1580 cm^{-1} attributed to the C=O stretching of carbonyl group in quinone structure [31]. The bands at 1170 and 1070 cm^{-1} are related to the condensed C-C-C bending. The spectrum of steam activated carbon (Figure 5.33(d)) shows much lower intensity of the peaks. This is because the steam activation was carried out at $700\text{ }^{\circ}\text{C}$, much higher than that of the treatment temperature of charcoal and ACC. Consequently, most of the IR sensitive functional groups and aliphatic groups were removed.

5.4.7. Structural Features

Figure 5.34 shows the deconvoluted Raman spectra of charcoal, ACC and ACS. The areas of each of ten Gaussian peaks as well as total peak areas for three different samples are listed in Table 5.12. The results show that the total peak area and the individual peak intensities are quite different for three different samples. As Figure 5.34 and Table 5.12 show, the peak intensities decreased in the order of charcoal > ACC > ACS. The decrease in total Raman intensities reflected to the loss of O-containing functional groups and aliphatic groups and more significantly, the growth of condensed aromatic ring systems. These results supported the FT-IR results in Figure 5.33.

The total Raman intensity is affected by the Raman scattering ability and light absorptivity of the carbon materials [47]. As the temperature increased and steam reacted with carbonaceous materials for ACS, it became increasingly aromatic. The increasing aromaticity in ACS increased the light absorptivity [48] and thus decreased the Raman intensity. However, even though ACC was treated at the same temperature as charcoal ($500\text{ }^{\circ}\text{C}$), the total Raman intensity and the intensity of each band decreased significantly. This was attributed to the elimination of O-containing functional groups and aliphatic groups by the chemical reaction of them with H_3PO_4 .

Table 5.12. Peak areas of each of 10 Gaussian bands and total peak areas of three different samples

Band name (a.u)	Description	Peak intensity		
		ACS	ACC	Charcoal
G _L	Carbonyl group C=O	21.8	170.7	474.6
G	Graphite E ² 2g; aromatic ring quadrant breathing; alkene C=C	312.7	786.5	1302.9
G _R	Aromatics with 3~5 rings; amorphous carbon structures	242.9	611.5	1499.0
V _L	Methylene or methyl; semicircle breathing of aromatic rings; amorphous carbon structures	196.0	561.0	1212.0
V _R	Methyl group; semicircle breathing of aromatic rings; amorphous carbon structures	351.5	923.3	2053.1
D	D band on highly ordered carbonaceous materials; C-C between aromatic rings and aromatics with not less than 6 rings	654.1	968.9	1594.5
S _L	Aryl-alkyl ether; para-aromatics	139.8	370.9	652.7
S	C _{aromatic} -C _{alkyl} ; aromatic (aliphatic) ethers; C-C on hydroaromatic rings; hexagonal diamond carbon sp ³ ; C-H on aromatic rings	567.4	588.2	1851.3
S _R	C-H on aromatic rings; benzene (ortho-di-substituted) ring	62.0	80.6	236.7
R	C-C on alkanes and cyclic alkanes; C-H on aromatic rings	22.1	160.2	349.2
Total peak area		2570.5	5221.7	11226.1

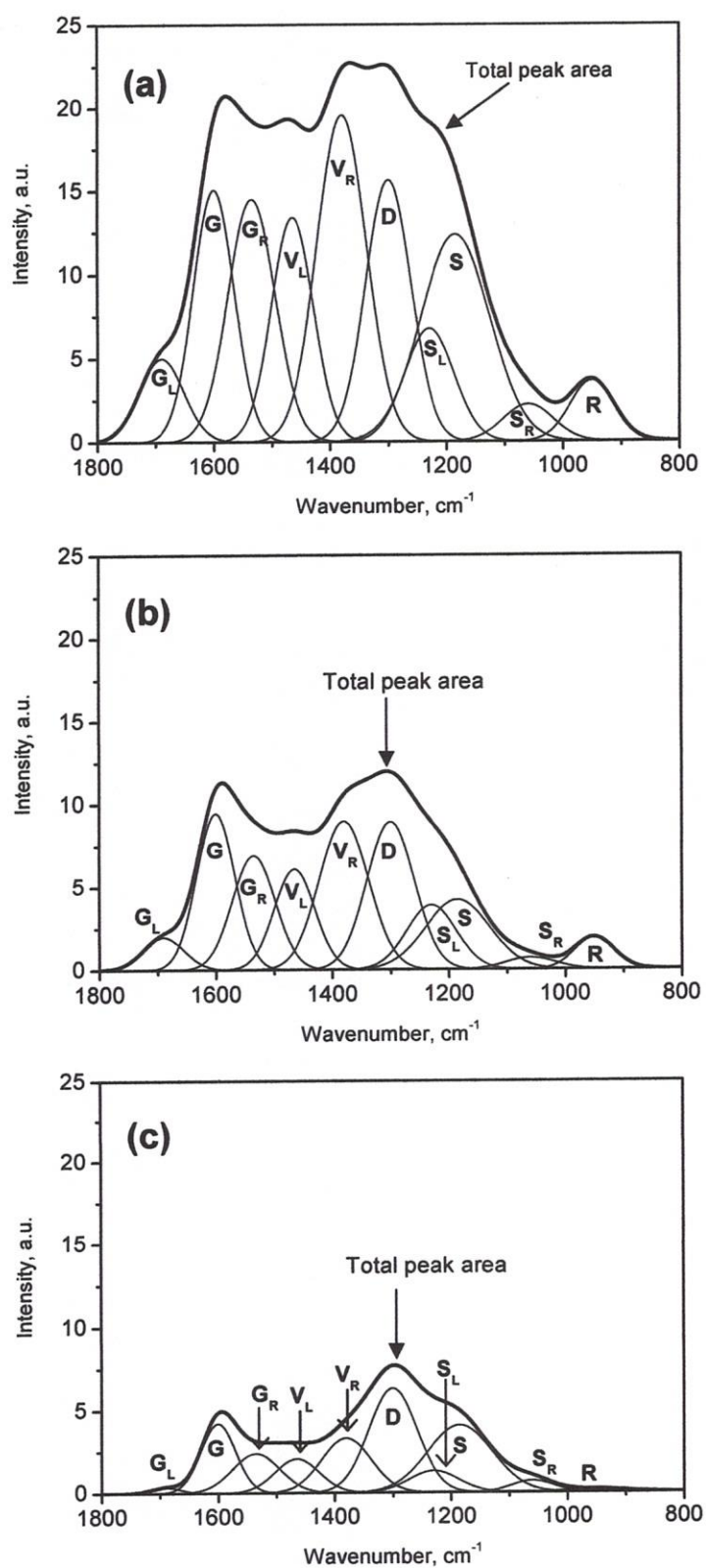


Figure 5.34. Deconvolution of Raman spectra using 10 Gaussian bands for (a) charcoal, (b) ACC and (c) ACS. Charcoal and ACC were prepared at 500 °C and ACS was prepared at 700 °C.

The D band in the Raman spectra represented the highly condensed and ordered aromatic ring systems usually equal or more than 6 fused benzene rings. On the other hand, G_R , V_L , and V_R bands mainly corresponded to the 3-5 fused benzene rings with amorphous structure. Furthermore, the band area of V_L and V_R could also be contributed by aliphatics and carboxylates. However, considering the temperature used, it was unlikely for the aliphatics and carboxylates to survive. Therefore, the ratio between the intensities of D band and the total intensities of bands G_R , V_L and V_R mainly attributed to the ratio of ordered carbons with larger ring systems to the amorphous and disordered carbons with smaller ring systems. The changes of the intensities of band area ratio between D and $G_R+V_L+V_R$ for charcoal, ACC and ACS are shown in Figure 5.35. It can be seen that the ratio $I_D/I_{(G_R+V_L+V_R)}$ decreased in the order of ACS > ACC > charcoal. The results suggested that the increase of aromatic ring condensation in ACS was mainly due to the effect of higher temperature and in ACC is mainly due to the chemical reaction with H_3PO_4 .

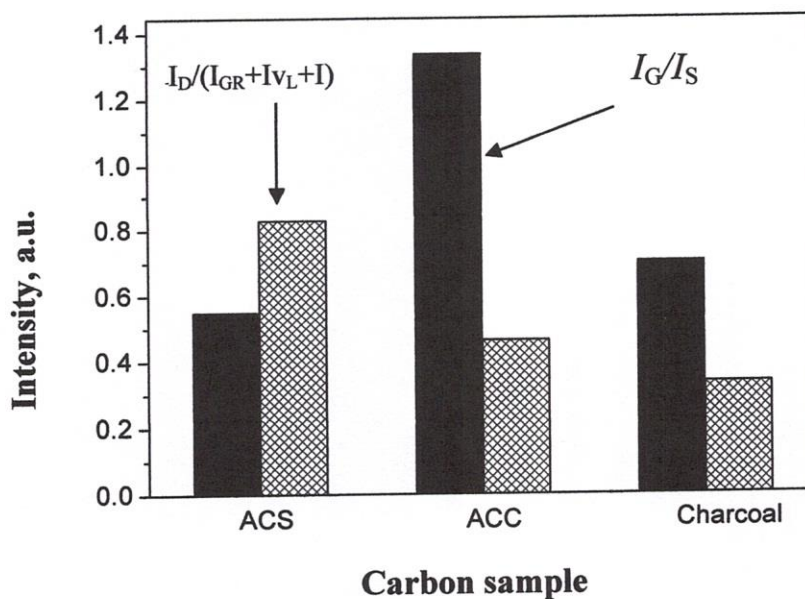


Figure 5.35. The band intensity ratio $I_D/I_{(G_R+V_L+V_R)}$ and I_G/I_S of ACS, ACC and charcoal.

Figure 5.35 also exhibits the ratio I_G/I_S of different samples, which represents the intensity ratio between the band corresponds to the sp^2 carbon structure and the band corresponds to the sp^3 carbon structure. The ratio was significantly higher for ACC than other two. These results indicated that the wider sp^2 carbon structure possibly graphite structure of carbon in ACC contributed to the high basal surface area. In addition, the π electron of sp^2 carbon can readily be delocalized. Due to electron delocalizing nature of sp^2 carbon in ACC, the surface can be more efficient to adsorb polar dye molecules.

5.4.8. Thermal Properties and Reactivity

Thermal behaviour of charcoal, ACC and ACS was investigated by TGA under nitrogen atmosphere as shown in Figure 5.36 and correlated with the results of FT-IR and FT-Raman. The ACS was prepared at 700 °C under steam atmosphere, and thus almost all of the volatiles were removed from the carbon matrix and attributed to the insignificant weight loss in TGA. The FT-IR spectrum illustrated in Figure 5.33(d) showed that the heat sensitive functional groups have almost been completely removed from ACS. In addition, the high value of $I_D/I_{(GR+VL+VR)}$ in Raman spectra (Figure 5.35) represented the condensed structure of carbon materials with more than six ring systems. Consequently, a refractive nature of ACS throughout the temperature range in TGA spectrum was observed. The charcoal prepared at lower temperature than ACS (500 °C), redeposited significant amount of volatiles in the carbon matrix and a part of which has been further evolved in TGA when it exposed at higher temperature. However, ACC showed quite a different scenario. It had also been exposed at 500 °C during activation. Nevertheless, it showed significant weight loss even though at much lower temperature than 500 °C.

The weight loss at temperature lower than 500 °C might be related to the moisture content chemically adsorbed on the micropore surface. The broad

band at 3210 cm^{-1} in FT-IR spectrum in Figure 5.33(c) also represented the hydrogen bonded hydroxyl groups, maybe due to the adsorbed water molecules. However, the constant weight loss above $500\text{ }^{\circ}\text{C}$ is more likely related to the release of organic molecules. The yield of ACC was much higher than that of the charcoal although they were prepared at the same temperature, indicating the significant redeposition of volatiles in ACC maybe due to the H_3PO_4 assisted radical reaction of O-containing compounds. The deposited tarry compounds under went further ring condensation reaction at higher temperature than $500\text{ }^{\circ}\text{C}$ and this maybe the reason of significant weight loss above $500\text{ }^{\circ}\text{C}$ for ACC.

The specific reactivity of ACC, ACS and charcoal was determined using the TGA in air at $370\text{ }^{\circ}\text{C}$ as illustrated in Figure 5.37 as a function of conversion of the sample. The specific reactivity of charcoal was much higher than that of ACC and ACS. At the beginning, it was very low for ACS and gradually increased with increasing conversion. However, for ACC, the reactivity was significantly higher at the beginning than that of ACS. It showed the maximum reactivity at around 5 % conversion level and then suddenly decreased within 10 % conversion level. After that, the reactivity gradually decreased as the conversion of ACC continuously progressed in the prolonged reaction in air. The high reactivity of charcoal may be due to the content of O-sensitive aliphatic groups in large extent as observed in IR spectra in Figure 5.33(b). It could also be realized from the lower ratio $I_{\text{D}}/I_{(\text{GR}+\text{VL}+\text{VR})}$ as in Fig. 5.35. The O-sensitive groups in ACS substantially decreased during activation at $700\text{ }^{\circ}\text{C}$ and thus the initial reactivity was very low. The reactivity of ACS gradually increased as the conversion increased. The increasing reactivity trend may be due to two reasons. Firstly, the concentration of alkali and alkaline earth metallic species such as Na, K, Mg and Ca, which catalyses the reaction gradually increased in the sample as the conversion of carbon materials

increased [35,39] and secondly, the oxygen adsorption and consumption increased as the new pores generated on the outer surface of the sample.

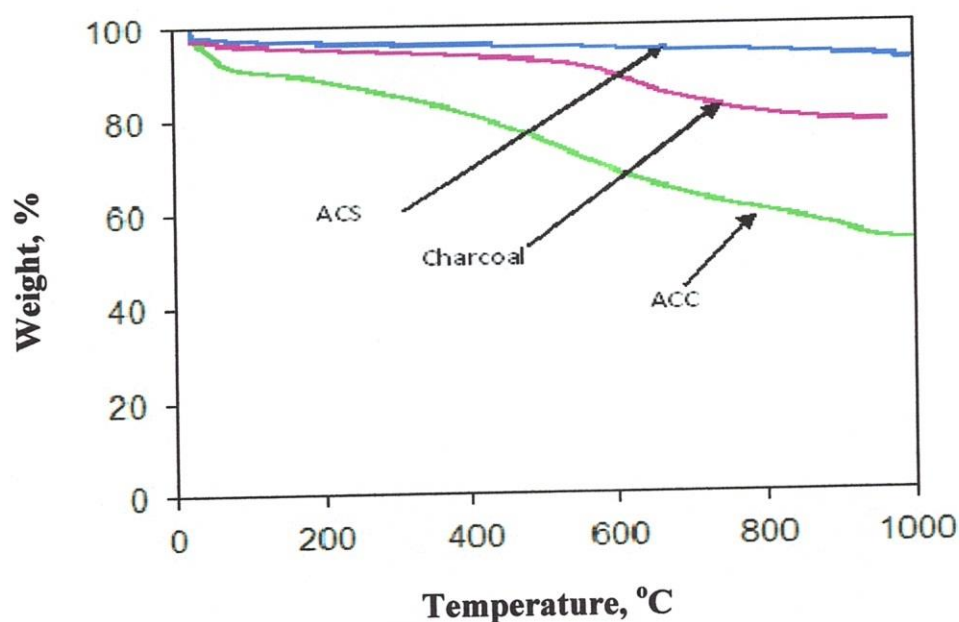


Figure 5.36. Thermogravimetric analysis curves for ACC, ACS and charcoal under nitrogen atmosphere. Nitrogen flow, 20 mL/min and temperature increasing rate, 10 °C/min.

For ACC, a quick sorption of oxygen in large extent occurred throughout the sample particles due to highly porous structure and hence the fast combustion of reactive carbon species occurred. As Figure 5.35 shows, the ratio I_G/I_S was much higher for ACC than that of ACS and charcoal, represented the large extent of highly stable graphitized carbon, which was almost refractive against oxygen at 370 °C.

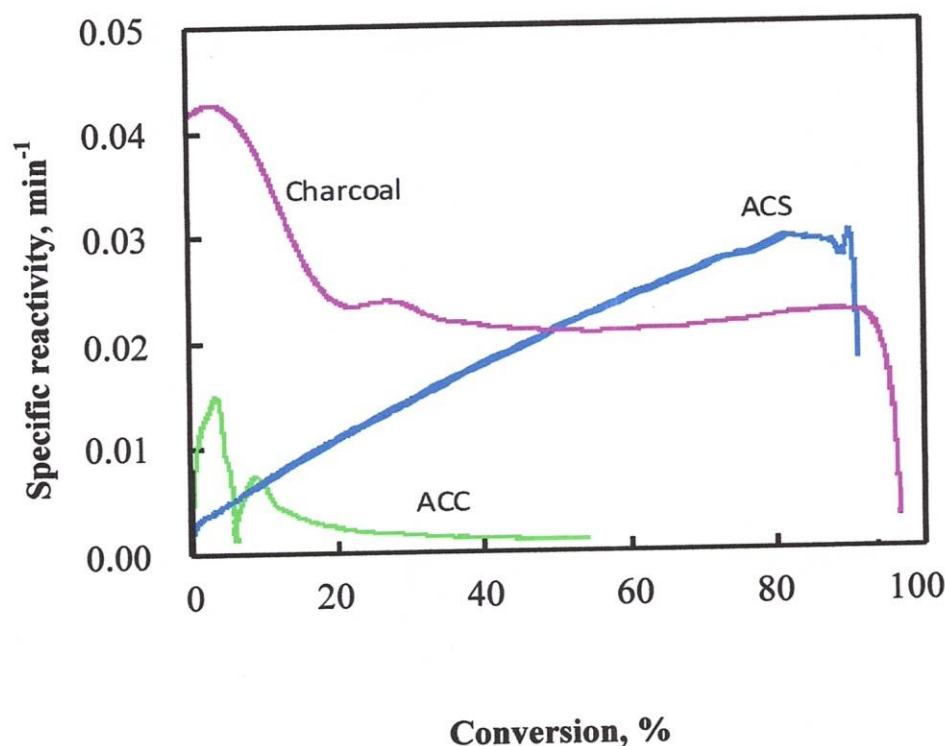


Figure 5.37 Reactivity of ACC, ACS and charcoal in air at 370 °C as a function of overall conversion of each of them.

5.4.9. Textural characterization by scanning electron microscope (SEM)

Figure 5.38 shows the SEM images of (a) jute sticks, (b) charcoal, (c) ACS and (d) ACC. The images represent the morphological changes of the carbon materials during pyrolysis and activation. The jute sticks surfaces are relatively smooth solid surface (Figure 5.38(a)) with long ridges, resembling a series of parallel lines. The surface structure is almost similar to other agricultural residues [49]. When jute sticks were subjected to pyrolyse to produce charcoal, most of the organic volatiles were evolved, leaving behind the ruptured surface of charcoal with a small number of pores.

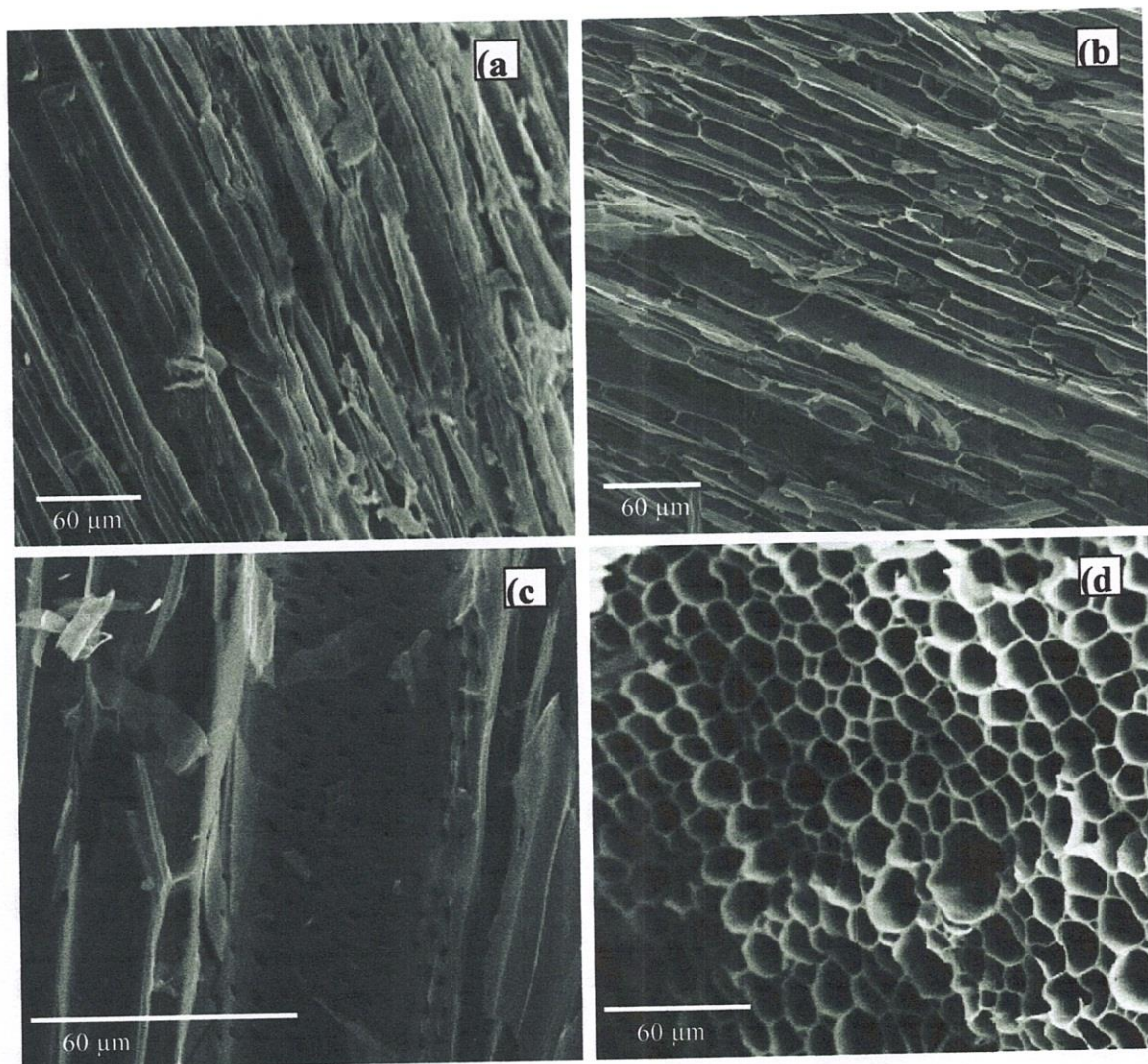


Figure 5.38. Scanning electron micrograph of (a) jute sticks, (b) charcoal, (c) ACS and (d) ACC.

The activation of charcoal with steam generated a number of different sizes of pores. This, thereby, increased the BET surface area from $80 \text{ m}^2/\text{g}$ in charcoal to $750 \text{ m}^2/\text{g}$ in ACS. From the comparison of the outer part of the charcoal and ACS with ACC, it is clear that the surface of jute sticks was deformed, resulted in well-developed pores with a honeycomb structure. This was possibly due to the extraction of some materials such as dissolution of lignin from jute sticks by activating agent during impregnation so as to create, on carbonization, a

number of large macropores on the surface, generated a honeycomb structure. Although it is not clearly seen, a number of small pores were also generated on the walls of the honeycomb, contributed in the high surface area and adsorption properties.

5.5. Arsenic Removal from Water by Using High Surface Area Activated Carbon

Of the two predominant forms of arsenic in water, arsenate As(V) and arsenite As(III), most treatment processes are effective at removing arsenate, but not arsenite, since arsenite is typically non-charged below pH 9.2. Therefore, treatment for the removal of arsenic often includes an oxidation step to convert arsenite to arsenate. This needs an extra step, making the arsenic removal process complex. However, in this work, attempts have been taken to evaluate the efficiency of the iron loaded activated carbon produced from jute stick to remove arsenite, As(III) from water. In fact, the development of materials that can provide one step filtration method both for arsenate, As(V) and arsenite, As(III) is the key step to help solve the arsenic contamination problem.

For testing activated carbon in arsenite separation, different types of As(III) solutions were prepared by using usual method in the laboratory as described in chapter 4 [169]. Then those solutions were treated to remove arsenic from water by using activated carbon. The experiments were carried out in three different methods as follows:

1. Batch method
2. Continuous column method
3. Continuous method using commercial filter.

Batch method as well as continuous method was used for evaluating pure activated carbon produced in this work for As(III) separation from water. However, the continuous column filtration and continuous filtration using commercial filter were used for evaluating iron-loaded activated carbons.

5.5.1. Batch Method for the Removal of As(III) from Water

In the batch method, 0.4 g of activated carbon was added in 20 mL of As(III) contaminated water in a 100 mL conical flask and stirred for a while. The As(III) was adsorbed on the activated carbon surface. The solution was then filtered and the water sample was analyzed using atomic absorption spectrophotometer. The results are summarized in Table 5.13.

Table 5.13. Effect of As(III) concentration on removal capacity of activated carbon in a batch system (Amount of standard solution=20 cc. , Amount of activated carbon =0.4 g, Adsorption time = 1h)

Standard solution (ppm)	Absorbance of treated solution	Concentration of treated solution (ppm)	Percentage separation (%)
0.25	0.076	0.151	35
0.20	0.070	0.127	36.4
0.10	0.030	0.055	40.0
0.08	0.016	0.045	48.0
0.06	0.010	0.027	52.2

Table 5.14 summarized the results of the effect of adsorption time on the arsenic removal capacity of the activated carbon. It can be seen that the maximum adsorption capacity can be achieved until around 52%. The

adsorption was not equilibrium even until 80 min. However, this kind of prolong adsorption time is not practical to achieve the goal of this study. From the batch study it is assumed that either the method or the activated carbon is inefficient to remove arsenic to desired level of concentration in expected time. This longer adsorption time to reach equilibrium is maybe due to the inefficient contact of the As(III) in solution to the surface of activated carbon, especially in the micropore surface.

Table 5.14. Effect of adsorption time on removal capacity of activated carbon in a batch system, (Amount of standard solution=20 cc. , Amount of activated carbon =0.4 g, Solution concentration = 0.1 ppm)

Adsorption time (min)	Absorbance of treated solution	Concentration of treated solution (ppm)	Percentage separation (%)
15	0.046	0.079	35.4
30	0.040	0.075	41.0
45	0.032	0.060	45.0
60	0.030	0.050	50.0
80	0.025	0.047	52..3

5.5.2. Arsenic Separation by Glass Column Filtration using Pure Activated Carbon

In the column filtration system the activated carbon was placed in a glass column of 20 cm long and 1.2 cm diameter. Inside the glass column a porous glass plate was set at the position of 5 cm apart from the bottom of the column. Desired amount of activated carbon was put on the porous glass plate

that made a definite height of the bed inside the column. The arsenic contaminated water was introduced from the top of the column at the rate of 5 mL/min. The contaminated water percolated through the activated carbon column. The As(III) species was adsorbed on the surface of the activated carbon and the fresh water was collected from the bottom of the column in a conical flask. The As(III) concentration of treated water was measured by AAS. The amounts of activated carbon used were 0.5, 1.0 and 1.5 g in different experiments that made different heights of activated carbon bed of 3, 6 and 9 cm, respectively. The results are summarized in Tables 5.15 to 5. 17.

Table 5. 15. Effect of As(III) concentration on the removal of activated carbon in continuous system (using 0.5 g of activated carbon Amount of activated carbon = 0.5 g, Column height = 3 cm Diameter of column = 1.2 cm, Flow rate = 5 mL/ min)

Conc. of standard solution (ppm)	Absorbance of treated solution	Concentration of treated solution (ppm)	Percentage separation (%)
0.25	0.536	0.204	18.4
0.20	0.376	0.147	26.5
0.15	0.394	0.113	30.0
0.10	0.297	0.099	35.0
0.08	0.149	0.059	37.7
0.06	0.120	0.056	35.3

From Table 5.15 it can be seen that in the continuous column filtration system, maximum of 37.7% As(III) species can be separated from water when 0.5 g of activated carbon and 0.20 ppm arsenic solution were used. The concentration of As(III) in the filtrated water was higher than the WHO specified level.

Table 5.16. Effect of As(III) concentration on the removal capacity of activated carbon in continuous system (using 1 g of activated carbon Amount of activated carbon = 1.0 g, Column height = 6 cm Diameter of column = 1.2 cm, Flow rate = 5 mL / min)

Conc. of standard solution (ppm)	Absorbance of treated solution	Concentration of treated solution (ppm)	Percentage separation (%)
0.25	0.563	0.215	20.0
0.20	0.265	0.156	26.9
0.15	0.228	0.139	27.0
0.10	0.142	0.067	31.7
0.08	0.182	0.072	35.5
0.06	0.074	0.035	45.0

From Table 5.16 and 5.17 it is observed that when the bed thickness of 6 or 9 cm was used the separation of arsenic was increased to about 48%; however, the concentration of As(III) is still higher than the accepted level. Although, some results, especially when 0.06 ppm concentration was used the concentration of treated water was lower than 0.05 ppm. The arsenic concentration in contaminated water in the most area in Bangladesh is often higher than 0.06 ppm. This study clearly indicated that the pure synthesized activated carbon was not efficient for As(III) separation from water.

Despite the presence of functional groups on the activated carbon surface the polarity of the surface is very low. As FT-IR spectra shown in previous section, the functional groups are mainly ether and quinone groups, which have limited contribution to make highly polar surface. On the other hand, arsenite As(III) is usually a non-polar species, and thus it was very difficult to trap arsenic species on the surface.

Table 5.17. Effect of As(III) concentration on the removal capacity of activated carbon in continuous system (using 1.5 g of activated carbon Amount of activated carbon = 1.5 g, Column height = 9 cm Diameter of column = 1.2 cm, Flow rate = 5 mL / min)

Conc. of standard solution (ppm)	Absorbance of treated solution	Concentration of treated solution (ppm)	Percentage separation (%)
0.25	0.520	0.208	21.0
0.20	0.233	0.173	27.1
0.15	0.203	0.133	30.4
0.10	0.138	0.065	40.0
0.08	0.129	0.067	45.0
0.06	0.070	0.032	48.0

The amount of activated carbon to treat a certain flow rate of arsenic contaminated water is another factor to be considered. In a specific diameter of the column, 0.5 g, 1.0 g and 1.5 g activated carbon formed approximately 3 cm, 6 cm and 9 cm of the bed thickness. This bed thickness affected the arsenic removal efficiency significantly as can be seen from the Figure 5.18.

Figure 5.39 shows the effect of bed thickness on the As(III) removal capacity. It is clearly seen that the removal capacity increased with increasing bed thickness. This is because, we used granular activated carbon, which usually forms some void space in the bed. This led to escape the As(III) solution without touching the solid surfaces in the micropore volume. The main adsorption area in the activated carbon is micropore volume. The penetration of any particles in the micropore usually faces some resistance and to overcome of which needs a bit longer residence time. The increasing of bed thickness substantially increases the adsorbate (arsenic) residence time in the bed, which allows As(III) to penetrate inside the micropore, and thus the As(III) separation increased with bed thickness. Finally, when 9 cm bed thickness using 1.5 g of

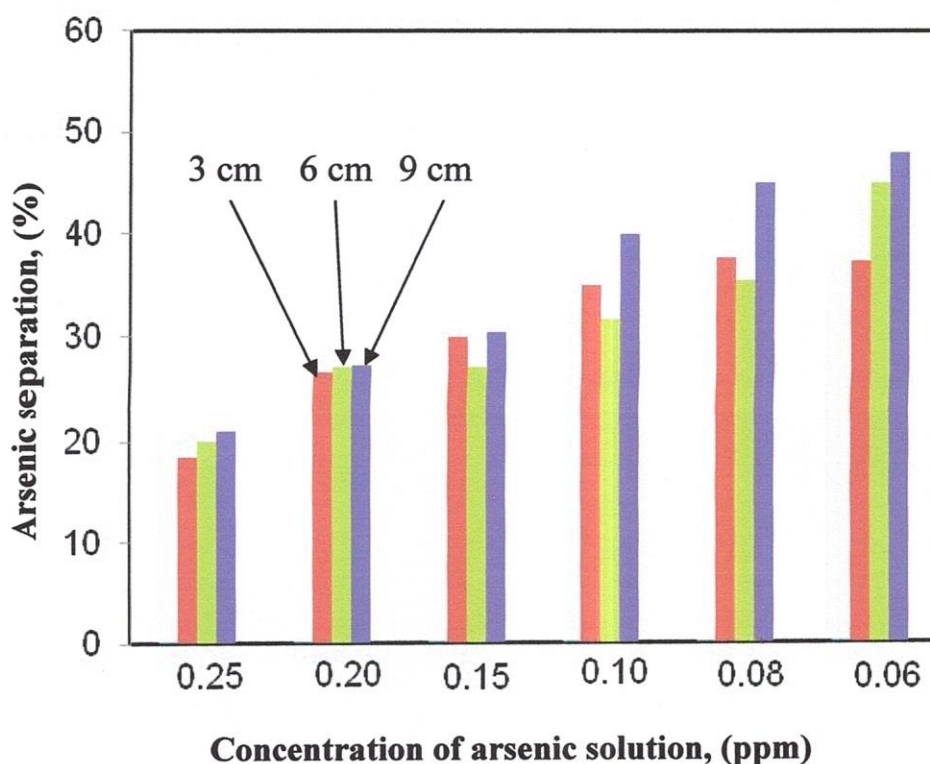


Figure 5.39. Effect of column thickness on arsenic separation using ACC.

activated carbon was used the arsenic separation was the highest in the experimental range. This figure also shows that the further increasing of the bed thickness may further increase the separation; however, the experiment was limited within the specified range.

In order to elucidate the effect of polarity, in other word, the oxidation state of arsenic on the separation by activated carbon, one attempt has been made by treating As(III) solution with KMnO_4 in order to convert As(III) to As(V). Then the solution was passed through the activated carbon column. Treatment of As(III) with small amount of KMnO_4 resulted in the formation of As(V) in the solution. When this solution was passed through the column filter almost all of the arsenic species were removed. No residual arsenic was detected either by AAS or visible spectrophotometer method even when 0.25 ppm solution was

used. The As(V) is highly polar species, and thus it has high potential to adsorb on the pure activated carbon surface.

Table 5.18. Effect of As(III) concentration on removal capacity of activated carbon after KMnO_4 treatment (Amount of activated carbon = 1 g, Column height = 6 cm Diameter of column = 1.2 cm, Flow rate = 5 mL/min)

Standard solution (ppm)	Absorbance of treated solution	Concentration of treated solution (ppm)	Percentage separation (%)
0.40	0.030	0.052	87.5
0.30	0.010	0.017	94.4
0.25	0.003	0.005	97.9
0.15	0.000	Not detected	100.0
0.10	0.000	Not detected	100.0

5.5.3. Arsenic Separation with Fe-Loaded Activated Carbon in Continuous Column Filtration

We have developed iron-containing granular activated carbon adsorbents (FACC) for arsenic removal from water. Granular activated carbon (ACC) was used as a support for ferric ions that were impregnated using aqueous ferrous sulfate solution (FeSO_4) followed by calcination at 500 °C. Carbons produced from chemical activation of jute stick using H_3PO_4 were suitable for iron impregnation and arsenic removal. The 10% iron loaded activated carbon was used for arsenic removal and the results are summarized in Tables 5.19 to 5.21.

Table 5.19. Effect of As(III) concentration on the removal capacity of Fe loaded activated carbon in continuous system (using 0.5 g FACC Amount of Fe loaded activated carbon = 0.5 g Column height = 3 cm Diameter of column = 1.2 cm, Flow rate = 5 mL / min)

Conc. of standard As (III) solution (ppm)	Absorbance of treated solution	Concentration of treated solution (ppm)	Percentage separation (%)
0.25	0.307	0.12	50.0
0.20	0.205	0.08	60.0
0.15	0.133	0.06	60.1
0.10	0.100	0.06	65.0
0.08	0.810	0.05	68.1
0.06	0.050	0.04	70.4

The layer of the iron species on the activated carbon surface inevitably improved the surface polarity, which in turn contributed to combine arsenic species more strongly than that of the naked activated carbons. In addition, iron species poses high affinity to arsenic species in order to form Fe-As complex, which also expedited the arsenic separation from water. However, it is further to mention that both of the phenomena need good contact of the adsorbent and adsorbate. It is only possible by increasing the residence time of adsorbate (arsenic species) in the adsorbent bed, and thus we have further investigated the bed thickness of FACC in the column for arsenic separation.

It can be noted in Table 5.19 that the arsenic separation is quite higher for FACC than that of naked ACC (Table 5.15 – 5.17) even when 0.5 g of FACC (3 cm column thickness) was used. Maximum around 70% arsenic was removed when 0.06 ppm solution was used. It is exactly double compared to the naked ACC (Table 5.15).

Table 5. 20. Effect of As(III) concentration on the removal capacity of Fe loaded activated carbon in continuous system (using 1 g Fe-loaded activated carbon Amount of activated carbon = 1.0 g, Column height = 6 cm Diameter of column = 1.2 cm , Flow rate = 5 mL / min)

Conc. of standard solution (ppm)	Absorbance of treated solution	Concentration of treated solution (ppm)	Percentage separation (%)
0.25	0.077	0.031	81.6
0.20	0.067	0.027	85.5
0.15	0.073	0.029	87.6
0.10	0.036	0.014	87.0
0.08	0.009	0.005	93.7
0.06	0.024	0.009	95.5

As described above the residence time increased with bed thickness, and thus around 95% arsenic separation was achieved when 1.0 g (6 cm bed thickness) activated carbon was used as stated in Table 5.20. Even though a very high concentration of arsenic solution (0.25 ppm), much higher compared to usual practical concentration (0.06-0.1 ppm) in drinking water, was used the concentration of arsenic reduced to below 0.01 ppm.

It is interesting that no arsenic was detected in the treated solution when 1.5 g (9 cm column thickness) activated carbon was used. This means that 9 cm bed thickness is quite enough to provide required residence time of adsorbate in the bed in order arsenic to be adsorbed on the adsorbent.

Table 5.21. Effect of As(III) concentration on the removal capacity of Fe loaded activated carbon in continuous system, (using 1.5 g loaded activated carbon. Amount of activated carbon = 1.5 g, Column height = 9 cm. Diameter of column = 1.2 cm, Flow rate = 5 mL / min)

Conc. of standard solution (ppm)	Absorbance of treated solution	Concentration of treated solution (ppm)	Percentage separation (%)
0.25	0.000	0.00	100.0
0.20	0.000	0.00	100.0
0.15	0.000	0.00	100.0
0.10	0.000	0.00	100.0
0.08	0.000	0.00	100.0
0.06	0.000	0.00	100.0

Figure 5.40 shows the effect of thickness of FACC bed on the As(III) removal capacity. It is clearly seen that the removal capacity increased with increasing bed thickness. The reason as described earlier is the increase of residence time of adsorbate in the adsorbent bed. From the results it can be assumed that almost all of the arsenic species have been removed from the water collected at the bottom.

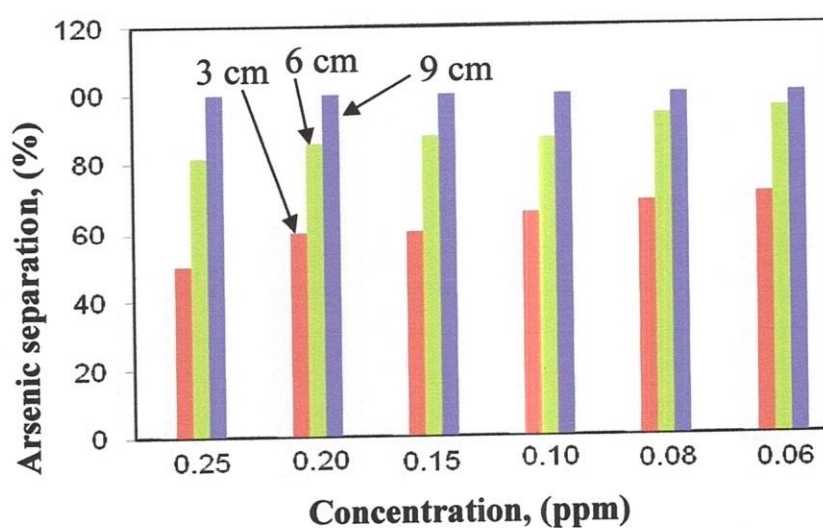


Figure 5.40. Effect of column thickness on arsenic separation using FACC.

5.5.4. Arsenic Separation with Fe-Loaded Activated Carbon in Commercial Filter

This part of the work was carried out in the Faculty of Chemical Engineering, Universiti Teknologi Mara, Malaysia. Iron loaded activated carbon exhibited high efficiency to adsorb As(III) and As(V) in the column filtration method. Arsenic concentration reduced to below WHO imposed upper limit (0.01 ppm) concentration; even it has gone to undetected level using AAS and ICP. However, in order FACC to utilize in practical filtration of arsenic contaminated water an investigation in the scale of 24 L/day of water, a minimum requirement of commercial filtration, is required. In order to investigate in that scale, a commercial filter was used. For this investigation, a commercial household filter was purchased from the local market. The ceramic candle and the materials of filter cartridge were removed. In addition, the cartridge was cut into half of the total length to maintain the thickness of the adsorbent bed in 10 cm. The FACC was loaded in the cartridge and set back into the filter. The arsenic contaminated water was percolated through the bed at a rate of 2 L/h (33 mL/min). The filtrated water was collected from the bottom of the filter and analyzed using ICP. The results are tabulate in Table 5.22.

Table 5.22. Effect of As(III) concentration on the removal capacity of different activated carbons in commercial filter method. (Amount of activated carbon = 20g, Cartridge diameter = 12 cm, Cartridge depth = 10 cm Flow rate = 33 mL / min)

Activated carbon sample	Concentration of arsenic solution (ppm)	Concentration of treated solution (ppm)	Percentage separation (%)
ACC	0.10	0.055	46
	0.15	0.077	44
FACS	0.10	0.045	62
	0.15	0.057	58
FACC	0.10	0.003	99
	0.15	0.002	99

From the data it can be seen that the maximum separation of arsenic can be achieved until 46% when 0.10 ppm solution was used using unloaded ACC (chemical activated but no iron loaded). However, in the case of iron loaded activated carbon (FACS), prepared by steam activation at 780 °C, the maximum separation was obtained to be 62% while the concentration of treated solution is higher than the 0.05 ppm. Interestingly, the arsenic concentration reduced to 0.002 ppm which is much lower than that of WHO specified concentration 0.01 ppm (currently 0.01 ppm) was achieved when FACC was used.

5.5.5. Plausible Mechanism of As Adsorption on Fe-AC surface

Most of the activated carbon contains some organic functional groups on the surface such as carboxylic groups, carbonyl groups, phenolic groups, ether groups and quinone groups [170]. These functional groups provide polarity on the surface which in turn contributes to chemical adsorption of adsorbate. However, as described in the earlier section, the pure activated carbon is not

efficient to adsorb As(III) [171]. Indeed, As(V) was efficiently adsorbed on the pure AC. This suggests that the inherent functional groups is strong enough to bind As(V), a highly charged species, onto the AC surface. However, it is contrary to fact that the drinking water from tube well in Bangladesh as well as many other countries as mentioned in the introduction chapter, is contaminated with As(III) species. In addition, As(III) is much higher toxic than As(V). These were the primary clue to load iron onto the activated carbon surface. Literature has also shown that the adsorption of As on activated carbon can be significantly increased by treating AC with various iron compounds [172], [173]. Indeed, dispersed iron species can provide much higher affinity even to the As(III) species.

Our approach was based on hypotheses that dissolved ferrous iron could diffuse deep into the internal pores of granular activated carbon, and followed by in-situ oxidation of ferrous to ferric iron, the ferric species could cross-link with various functional groups in a dispersive way on the carbon, maximizing subsequent adsorption for arsenic. The mechanisms are shown in Figure 5.41. The granular nature of activated carbon is maintained during and after the iron impregnation, so the materials would be suitable for paced-bed applications.

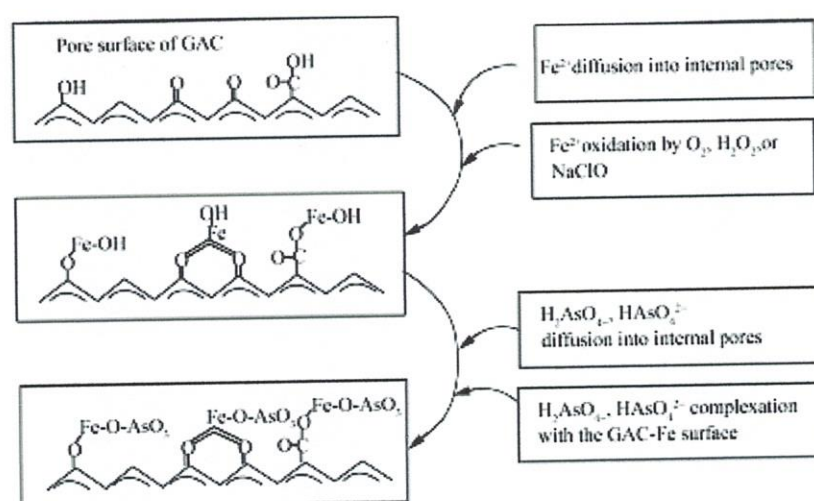
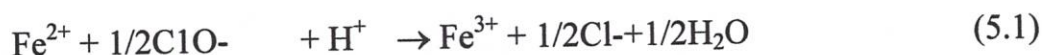


Figure 5.41. Plausible mechanism for arsenic adsorption by FACC.

AC contains several surface functional groups, and its structure can be described as a combination of carbon particles connected with a random distribution of carboxyl, hydroxyl, phenol, and quinine groups on the surfaces of the porous material [174]. Surface chemical differences and conditions influence the sorption capacity toward iron [175]. Since Fe(III) in general has stronger complexation with ligands such as carboxyl and phenol groups than Fe(II), iron impregnation should be more effective when iron is present in trivalent oxidation state. Treatment of GAC directly with Fe(III) salts such as FeCl₃, however, is not effective, because Fe(III) easily hydrolyzes to form hydroxides when pH is higher than ~3.0 (at 0.10 M) [175]. Solid forms of iron hydroxides cannot diffuse easily into the internal pores of GAC but are more likely to precipitate in the macropores and coat the outer surfaces of the particles. Use of a strong acidic solution (pH<1.0) of FeCl₃ could not be effective either, because strong competition of protons for the surface sites would diminish Fe(III) adsorption on the AC [174].

In the procedure developed in this study, Fe(II) is soluble at pH 4.5-5.0 and should be able to diffuse into the internal pores of AC, forming a weak complex with the surface ligands. Subsequent in-situ oxidation of Fe(II) to Fe(III) could result in formation of strong Fe(III) surface complexes when compared to Fe(II). Additionally, the oxidation process could modify the carbon surfaces and lead to enhanced equilibrium quantity of iron impregnated [173, 174]. Sodium hypochlorite was used for Fe(II) oxidation to Fe(III) as shown in equation 5.1 and 5.2.



CHAPTER 6

SUMMARY AND CONCLUSION

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Arsenic contamination in water is one of the most severe problems in Bangladesh. The literature survey shows that the tube well water of about 59 districts out of 64 districts in Bangladesh has been contaminated with arsenic. Arsenic concentration in most of those tube well waters has been found to be above the upper permissible limit of 0.01 mg/L set out by the World Health Organization (WHO). Because of the overwhelming dependence of the population on underground water as the main source of drinking water, there is an urgent need to adopt suitable methods for removal of arsenic from underground water.

A number of research groups from home and abroad have been investigated the presence of arsenic in underground water, effect of arsenic on the human body and mitigation of arsenic in a number of ways. However, the effective solution of arsenic problem is yet to be discovered. In this work, a low cost adsorbent, activated carbon, prepared from chemical activation of jute stick, which possesses high micropore surface area, wide micropore volume and surface functionality was used for As(III) and As(V) separation from water.

The maximum BET surface area 1664 m²/g, iodine value 1440 mg/g and methylene blue dye number 475 mg/g of chemically activated carbon (ACC) using phosphoric acid as an activating agent were achieved under optimum preparation condition. The IR spectra exhibited the wide surface functionality while Raman spectra and reactivity data implies rigid structure of ACC. In addition, the SEM analysis showed the surface morphology of charcoal, ACC and physically activated carbon (ACS) from which high degree of porosity of ACC can be realized.

In arsenic separation, around 48% of As(III) can be separated from water while almost complete removal of As(V) can be achieved using ACC. However, As(III) is the predominant species in underground water. To enhance the As(III) removal capacity, Fe compound such as FeSO_4 was loaded on the surface of ACC followed by the oxidation with NaOCl . The FeSO_4 was finally converted to Fe^{3+} , which formed FeOOH species on the activated carbon surface and was used for As(III) separation.

The FACC was found to be higher efficient than pure ACC to remove arsenic from water. Interestingly enough, almost complete As(III) removal was achieved when 9 cm filter bed thickness was used using 1.5 g of 10% Fe-AC. The treated solution was almost free of As-species in any form. Around 99% arsenic separation was also achieved in a large scale filtration, 24 L/day, a minimum requirement of commercial filter.

From the mechanistic point of view, the activated carbon contains some organic functional groups on the surface, such as carboxylic ($-\text{COOH}$), phenolic (Ph-OH), ether, quinone and etc. Our approach was based on hypotheses that the dissolved ferrous ion could diffuse deep into the internal pores of granular activated carbon, and followed by in-situ oxidation of ferrous to ferric iron, the ferric species could cross-link with various functional groups in a dispersive way on the carbon, maximizing the subsequent adsorption for arsenic. As(III) can easily be combined with Fe^{3+} complex on the activated carbon surface. Furthermore, As(III) can be oxidized by iron complex, forming As(V) species, which is reported to be readily adsorbed on the adsorbent surface.

CHAPTER 7

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CHAPTER 8

APPENDIX

APPENDIX

List of publications

- 1) **M Israt Jahan**, M Abdul Motin, M Moniuzzaman & M Asadullah,
“**Arsenic removal from water using activated carbon obtained from chemical activation of jute stick**”. Indian Journal of Chemical Technology. Vol. 15, July 2008, pp. 413-416
- 2) Mohammad Asadullah, **Israt Jahan**, Mohammad Boshir Ahmed, Pasilatun Adawiyah, Nur Hanina Malek, Mohammad Sahedur Rahman (2012), **Importance of Microporosity and Iron Loading on Activated Carbon for Arsenic (III) Removal from water**”, Journal of Environmental Management. Elsevier Editorial System. (Forth coming)
- 3) M Asadullah, M Shamim Uddin, **M Israt Jahan**, M Abdul Motin & M. Asaduzzaman, “**Catalytic conversion of propane to functionalized products**”, Indian Journal of Chemical Technology. Vol. 15, November 2008, pp. 566-571. (Communicated)
- 4) M. Asadullah, M. Shamim Uddin, **M. Israt Jahan** and M. Abdul Motin, “**Vanadium Catalyzed Partial Oxidation of Some Saturated Hydrocarbons to Functionalized Products Under Mild Conditions**”. Bangladesh J. Sci. Ind. Res. 43(3), 291-300, 2008. (Communicated)
- 5) A.T.M.K. Hasan, M. Mohiuddin, M.B. Ahmed, **I.J. poly**, M. Asadullah and M.S. Rahman, “**Production and Characterization of Bio-oil from Bio-mass by Circulating Fluidized Bed Pyrolysis Reactor**”, Bangladesh J. Sci. Ind. Res. 46(3), 313-322, 2011. (Communicated)

Notes

Arsenic removal from water using activated carbon obtained from chemical activation of jute stick

M Israt Jahan, M Abdul Motin, M Moniuzzaman & M Asadullah*

Department of Applied Chemistry and Chemical Technology,
University of Rajshahi, Rajshahi 6205, Bangladesh
Email: asad@ru.ac.bd; asadullah8666@yahoo.com

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Arsenic removal from water in the form of As(III) and As(V) was investigated using activated carbon obtained from jute stick using H_3PO_4 . Arsenic contaminated water was treated in two ways: (1) batch feeding system and (2) continuous flow system through a column filter. Removal of arsenic in continuous system was much better than that of batch feeding system. In the continuous system, where 0.15 ppm arsenic contaminated water was passed through a column packed with activated carbon, the maximum separation of As(III) was as high as 80%. In case of As(V) contaminated solution, almost complete separation of arsenic was achieved with activated carbon column filter. As(III) was converted to As(V) in the solution using very small amount of $KMnO_4$.

Keywords: Activated carbon, Adsorbent, Arsenic contamination, Water pollution

Arsenic contamination of underground water has created a big public health problem in many countries. The arsenic concentration of 0.05 mg/L in drinking water has been set by World Health Organization (WHO) as the upper permissible limit for Bangladesh. The higher concentrations of arsenic than the upper permissible limit can cause its deposition in human body and lead to serious human health problems. It takes about 8-14 years for symptoms to appear depending on the person¹. Therefore, the arsenic level in drinking water must be lowered than that of WHO recommended level. It is only possible by removing arsenic from water. Different attempts have been made to remove arsenic from water. They are: coagulation/precipitation^{2,3}, sedimentation, filtration⁴, adsorption⁵, magnetic separation⁶, ion exchange⁷, membrane/reverse osmosis⁸ etc.

Metal ion removal from water by activated carbon

is based on adsorption process on the solid liquid interface^{9,10}. High surface area of activated carbon with optimum micropore size is thus required for efficient adsorption of arsenic species from water. In addition, the ease of the production and yield of the activated carbon also play important roles for economic separation of arsenic from water. These lead to optimise the production conditions and characterization of activated carbon.

To meet the requirement for effective separation of arsenic from water, the aim of the present work is to develop suitable adsorbent from agricultural residues such as jute stick, which is available in many countries such as India, Bangladesh etc. In this work the high surface area activated carbon was targeted to be used as an arsenic removing material from drinking water. The jute stick was considered as raw material for high surface area activated carbon production. The activated carbon was produced by chemical activation process using H_3PO_4 as an activating agent. Before using the activated carbon for arsenic separation from water, it was characterized by measuring the specific surface area, iodine number and methylene blue number.

Experimental Procedure

After collection of jute stick, it was dried to less than 10% moisture content and cut into pieces to about 0.5 cm in size. In the previous work the jute stick was characterized by evaluating the proximate and ultimate analyses¹¹. According to the proximate analysis, the volatile fraction, fixed carbon and ash yield of jute stick were found to be 76-78, 21.4-23.4, and 0.62 wt%, respectively. From the ultimate analysis, the elemental composition of jute stick has been found to be: C, 49.79; H, 6.02; O, 41.37; N, 0.19; Cl, 0.05 and S, 0.05 wt%. Phosphoric acid (E-Merk, India, 99%) was used as an activating agent. Iodine (99.5%, Loba Chemical, India), potassium iodide (99.9%, Loba Chemicals, India), sodium thiosulphate (99.9%, Loba Chemicals, India), potassium dichromate (99.5, Loba Chemicals, India), activated carbon (Laboratory Reagent, Thomas Baker Chemicals Ltd.), and methylene blue dye (99.9%, Aldrich) were also used in the investigation.

Local made but highly precised temperature controlled stainless steel reactor was used for activated carbon production. Oven (Gallenkamp Regd, Model OV-445), Muffle furnace (Type MV2 220V 2-6kW CV3612/1973), spectrophotometer (Ogawa Seiki, Model-ANA-75), Brunauer-Emmett-Teller (BET) instrument (Model-Gemini Micrometrics 2360) and atomic absorption spectrophotometer (Shimadzu, AA-6200) were also used.

Preparation of activated carbon

Required amount of dry jute stick was mixed with 60% phosphoric acid in 1:1 ratio and kept for 12 h. Then the material was transferred into a carbonization reactor made of stainless steel with the height of 25 cm and the internal diameter of 5 cm. The temperatures of the inside and out side of the reactor were controlled by means of a temperature controller through thermocouples. The reactor was set horizontally. The nitrogen gas was passed through the reactor at the rate of 200 mL/min. The reactor temperature was kept at 200°C for 15 min and then the temperature was increased to different activation temperatures ranging from 400 to 700°C to optimize the activation temperature. After completing the activation, the products were washed with hot distilled water repeatedly in order to remove H_3PO_4 until the pH of solution reached at 6.5 and finally washed with 1% NaOH solution to completely neutralize the sample. Residual NaOH was washed out with further washing with distilled water. Then the samples were dried at 110°C for 24 h and stored in desiccators. The BET surface area of activated carbon was determined by nitrogen adsorption method at -196°C by a Gemini Micrometrics-2360. Iodine number of activated carbon was determined at 25°C based on the Standard Test Method (ASTM D4607-86)¹².

Two methods are applied for removal of arsenic from water samples. They were as follows:

(a) Batch method: About 0.1 g of activated carbon was introduced in a conical flask containing 20 mL of standard As(III) solution. The solution was stirred with magnetic stirrer for about 30 min. Then the concentration of arsenic was determined by AAS.

(b) Continuous method: About 0.5 to 1.5 g of activated carbon was loaded in a 1 cm diameter glass column. The standard As(III) solution was percolated from the top of the column and the treated water was collected from the bottom of the column in a conical flask. The arsenic concentration was measured by AAS.

The separation of As(V) was performed by the following steps: 150 mL of standard As(III) solution was taken in a 500 mL beaker. About 10 mg of $KMnO_4$ was added into the solution and the mixture was stirred with a glass rod for 10 min. Then this mixture was allowed to rest for 5 min. After that the solution was passed through a glass column filter as described above.

Results and Discussion

During the activation period at temperature 475°C, H_3PO_4 reacted with oxygen, hydrogen and other elements in the functional groups present in the jute stick, so as to produce volatile compounds such as H_2O , NO_x , SO_x and some of CO and CO_2 . These gaseous compounds released the solid mass leaving behind the porous structure of activated carbon. The activated carbon was produced at different temperatures in view to optimize the process. The mass decreased during activation was called activation burn-off and this varied with varying activation temperatures. The yields and properties of activated carbons at different temperatures are summarized in Table 1. The steam produced in the activation process subsequently takes part in the reforming reaction of char; forming carbon monoxide and hydrogen¹³.

The yield of activated carbon decreased with increasing temperature due to the increase of activation burn-off. This was because the elevated temperature facilitated the activation burn-off and

Table 1—Effect of temperature on the yield and properties of activated carbon

Activation temperature (°C)	Yield of activated carbon (wt%)	BET surface area (m ² /g)	Iodine number (mg/g)
400	67.0	1790	1115
450	61.0	1875	1175
475	51.0	1910	1205
500	52.0	1795	1095
550	51.0	1470	887
600	50.0	1209	692
700	49.0	959	601

thus, the total mass of activated carbon decreased. On the other hand, the BET surface area and iodine number of the activated carbon derived from jute stick initially increased with increasing temperature until 475°C. Higher activation temperatures than 475°C caused the decrease of BET surface area as well as iodine number. The maximum BET surface area and iodine number were found to be 1910 m²/g and 1205 mg/g, respectively. Lower activation temperature than 475°C resulted in incomplete activation burn-off, which is attributed to the high yield but low surface area as well as iodine number of activated carbon. The higher activation temperature than 475°C also resulted in lower surface area and iodine number. High temperature activation may cause high pore volume due to the high activation burn-off; however, it may cause the destructive effect to pores, resulting in decrease of surface area and iodine number. The methylene blue dye adsorption from solution of different equilibrium concentrations on activated carbon was also studied. The results are recorded in Table 2. The amount of dye adsorption increased with increasing equilibrium concentration. The equilibrium adsorption was attained when equilibrium concentration was 8.2×10^{-4} mol/L. At the equilibrium, the dye adsorption was 399 mg/g. This amount was much higher than reported results¹⁴.

Of the two predominant forms of arsenic in water, arsenate As(V) and arsenite As(III), most treatment processes are effective for removing arsenate, but not arsenite, since arsenite is typically non-charged¹⁵ below pH 9.2. Figure 1 shows the effect of concentration on the arsenate separation capacity in batch feeding system. Although the amount of arsenic removal decreased with decreasing the concentration of As(III) due to the decrease of total amount of As(III) in the solution, the percentage separation

increased with decreasing concentration as clearly seen in Fig. 1. In this experiment the maximum removal was about 60% when 0.06 ppm standard solution was used.

The effects of concentration and the amount of adsorbent on the percentage separation in continuous flow system are shown in Fig. 2. The arsenic separation capacity increased with decreasing the solution concentration as well as with increasing the amount of adsorbent. It can be seen that in the continuous column filtration system about 80% of As(III) species can be separated from water when 1.0 g of activated carbon and 0.08 ppm arsenic solution with the flow rate of 15 mL/min were used. The concentration of As(III) in the filtrated water was as low as 0.001 ppm. This value was much lower than

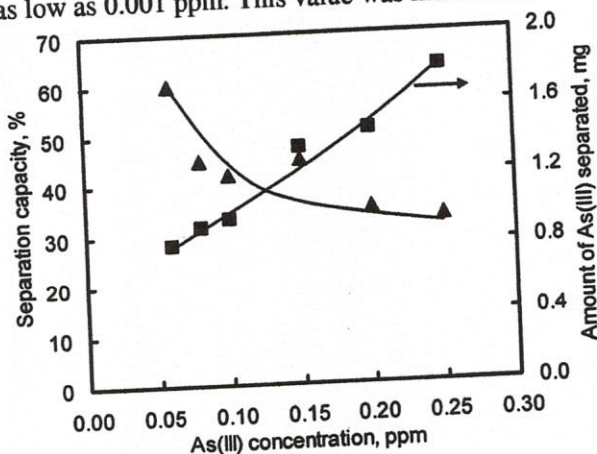


Fig. 1—Effect of As(III) concentration on separation capacity in batch feeding system at 30°C.

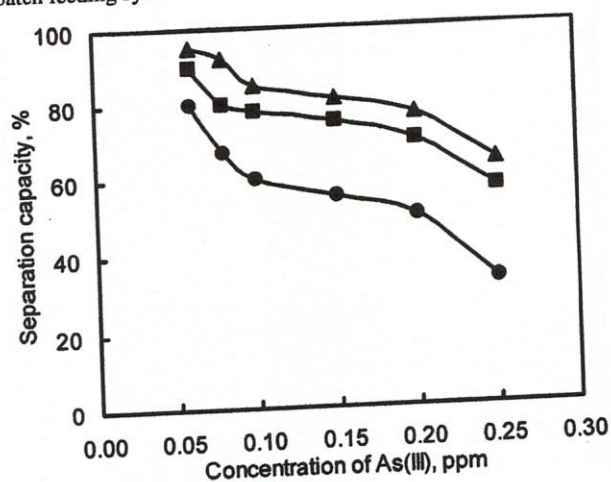


Fig. 2—Effect of As(III) concentration on separation capacity in flow system at 30°C. Amount of activated carbon ●, 0.5g; ■, 1g; and ▲, 1.5g

Table 2—Methylene blue dye adsorption on activated carbon from various concentrations at 30°C

Amount of activated carbon (m, mg)	Equilibrium concentration (10^{-5} mol/L)	Amount of dye adsorbed (x, mg)	x/m $\times 10^{-3}$
0.10	1.1	9.8	97.9
0.11	3.2	19.6	184.7
0.10	13.7	28.3	282.4
0.10	78.2	30.5	301.3
0.10	82.1	39.9	399.0
0.10	162.3	42.9	370.0
0.10	273.0	36.6	366.0
0.11	342.0	41.4	382.0
0.11	437.0	43.2	379.0
0.10	508.6	37.9	379.0

Table 3—Effect of As(V) concentration generated from As(III) by treating with KMnO_4 on removal capacity of activated carbon

Concentration of arsenic (ppm)	Flow rate (mL/min)	Arsenic concentration in filtrate (ppm)	Percentage separation (%)
0.40	40	0.027	93.5
0.30	40	0.007	97.7
0.2	40	0.000	100.0
0.15	40	0.000	100.0
0.10	40	0.000	100.0

that of WHO recommended upper permissible limit. The recommended limit of 0.05 ppm was also achieved even when 0.1 ppm solution, which is the usual arsenic concentration in tube well drinking water, was used. The difference between the separation using 1.5 g and 1 g of activated carbon with the same flow rate was very close and thus, further increase of the amount of adsorbent was not necessary.

The separation of arsenic as As(V) was also performed in the same column filter and the results are presented in Table 3. Before filtration the arsenic solution was treated with KMnO_4 in order to convert As(III) to As(V). When As(V) solution was passed through the column almost all of the arsenic in the solution was removed. No residual arsenic in the treated water was found either by AAS or by visible spectrophotometer method even when 0.25 ppm solution was used. The pink colour of KMnO_4 completely disappeared. The As(III) species is neutral in charge, thus the adsorption of this species on activated carbon is not chemisorption but a physical adsorption. However, the As(V) is a charged species and thus, it was adsorbed effectively on the activated carbon.

Conclusion

High surface area activated carbon is produced from jute stick using H_3PO_4 as activating agent. This activated carbon is used for arsenic separation from

water. In the continuous column filtration system, the activated carbon produced from jute stick is highly efficient to separate both As(III) and As(V) species from water. About 80% of As(III) and 100% of As(V) are removed from 0.15 ppm arsenic solution. This is also dependent on the amount of activated carbon used. More than 85% As(III) is removed from the contaminated solution when 1.5 g of activated carbon is used in the column. The complete removal of arsenic is achieved (100% separation) when the solution is pretreated with KMnO_4 even when very high concentration of arsenic solution (0.4 ppm) is used. This is due to the fact that upon oxidation the As(III) is converted to the As(V) which is highly polar species and can easily be adsorbed on the surface of the activated carbon.

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