"Activation of gasifier based waste to remove heavy metals from wastewater"

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"Activation of gasifier based waste to remove heavy metals from wastewater"

Major Project

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Master of Technology in Chemical Engineering (ENVIRONMENTAL PROCESS DESIGN)

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Declaration

This is to certify that

i)   The thesis comprises my original work towards the degree of Master of Technology in Chemical Engineering at Nirma University and has not been submitted elsewhere for a degree.

ii)   Due acknowledgement has been made in the text to all other material used.

Shalin Patel

Certificate

This is to certify that the Major Project entitled "Activation of gasifier based waste to remove heavy metals from wastewater" submitted by Patel Shalin (07MCH006), towards the partial fulfillment of the requirements for the degree of Master of Technology in Chemical Engineering of Nirma University of Science and Technology, Ahmedabad is the record of work carried out by him under my supervision and guidance. In my opinion, the submitted work has reached a level required for being accepted for examination. The results embodied in this major project, to the best of my knowledge, haven't been submitted to any other university or institution for award of any degree or diploma.

Prof. (Dr.) J.P.Ruparelia   Prof. A.P.Vyas

Guide, Professor,   Professor and Head,

Department Chemical Engineering,   Department of Chemical Engineering,

Institute of Technology,   Institute of Technology,

Nirma University, Ahmedabad   Nirma University, Ahmedabad

Dr K Kotecha

Director,

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Abstract

India being a petroleum starved nation, the utilization of biomass based gasifier has increased tremendously because of easy availability of agricultural based biomass. (The ministry for Non-Conventional Energy Sources has assesses that nearly 500 million tons of biomass is generated every year from crop residue, bagasse, agro residue and forest sources. Out of this, only 170 million tons are used for power generation.) Under the National Biomass Gasifier Program in India 1,074 gasifier system have been installed in different states for various modes of applications including mechanical, electrical, thermal heating, and cooking besides village electrification. However, this route of generation of energy can leave large foot print on the environment because of significant quantity of solid waste generated. In this research an attempt has been made to prepare sorbent from gasifier based solid waste.

Among various pollutants in drinking and wastewaters, inorganic species are major, and difficult to remove because of smaller size, low concentration and competition with nontoxic species. In this work, activated carbon has been prepared by chemical activation from gasifier based waste to study the effect of preparation variables and metal removal capacity. Characterizations were done for the observation of surface area, surface functional groups and its acidity. The Fourier transform infrared (FTIR) spectroscopy study has revealed that the functional groups (C=O, S=O,–OH) present on the sorbent surface. Application was tested through batch adsorption in single solutes solutions and fitting the equilibrium data to various equilibrium and kinetic models. Prepared carbons show very high adsorption capacities for borderline and soft metal ions like Lead(II), Cadmium(II), Chromium(VI) and As(V). The developed activated carbon is expected to be useful in removing borderline and soft metal ions as well as ionic or nonionic soft ligands of metalloids present in drinking and wastewaters. The adsorption parameters were estimated using both the Freundlich and Langmuir models. The experimental results indicated that the gasifier based waste can be used as a suitable sorbent and may easily replace activated carbon in wastewater treatment process. Max.% Removal efficiency achieved at optimized pH and single solute solution: lead II (96%), cadmium II (94%), chromiumVI (93%), arsenic V (88%).

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List of Symbols

°C	-	Degree Celsius
C_0	-	Initial concentration
Ce	-	Equilibrium concentration
cm	-	Centi meter
g	-	Gram
L	-	Liter
M	-	Molar
meq	-	Mili equivalent
mg	-	Mili gram
min	-	Minute
ml	-	Mili Liter
mm	-	Mili meter

List of Abbreviations

AAS   -   Atomic absorption spectrophotometer

BET   -   Brunauer, Emmett and Teller

CAC   -   Commercial activated carbon

DDW   -   Distilled deionized water

FTIR   -   Fourier transform infrared spectrophotometer

GBAC   -   Gasifier based activated carbon

GAC   -   Granular activated carbon

IUPAC   -   International Union of Pure and Applied Chemistry

MB   -   Methylene Blue

PAC   -   Powered activated carbon pp

SEM   -   Scanning electron microscope

TGA   -   Thermogravimetric analysis

UV   -   Ultra violet

VOCs   -   Volatile organic compounds

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Chapter 1

Introduction

It is well known that activated carbon is produced from a wide variety of carbon rich raw materials including wood, coal, peat, coconut shells, nutshells, bones and fruit stones [1,4,5]. Many agricultural by-products such as grain sorghum [6], jackfruit peel waste [7] and Waste tea [2], have been discovered to be suitable precursors for activated carbon due to their high carbon and low ash contents. Agricultural wastes are considered to be a very important feedstock because of especially two facts: they are renewable sources and low cost materials [3].New materials are currently under investigation as sources for the production of activated carbon. For example, gasifier based waste charcoal can be a potential new candidate as a source of activated carbon.

Biomass gasification is basically conversion of solid Biomass (Wood, agriculture residues etc.) in to a combustible gas mixture normally called "Producer Gas" (or low Btu gas). The process involves partial combustion of Biomass. Partial combustion is carried out in absence of air or less air than the stoichiometric requirement of air for completes combustion. Partial combustion produces Carbon Monoxide (CO) as well as hydrogen (H_2) which are both combustible gas. Solid Biomass fuels, which are usually inconvenient and have low efficiency of

```
            biomass
            \|/
150°C                          → gas

           drying zone      – removal of
                              humidity
400°C
           pyrolysis zone   tar and other liquids
                            are driven off
600°C
           reduction zone      C + 2H₂ -> CH₄

950°C                          C + H₂O -> CO + H₂

                               C + CO₂ -> 2CO
           combustion zone     C + O₂ -> CO2
1300°C
  air →

            ashes
```
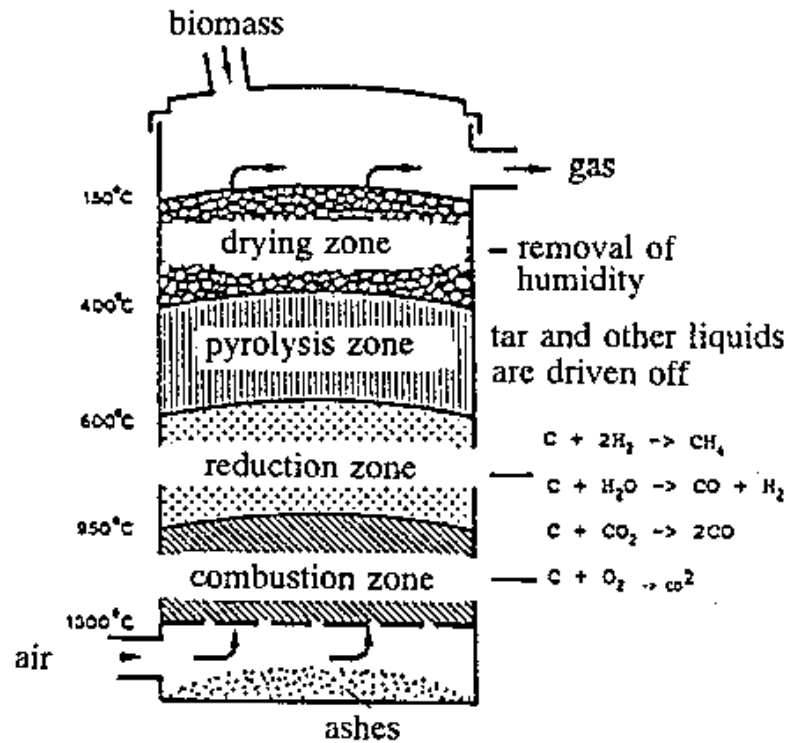
Figure 1.1 schematic of gasifier arrangement

utilization can thus, be converted in to a high quality gaseous fuel with associated convenience etc.In Indian market generally downdraft gasifiers are available due to utilization of mechanical mode. In this type air intake and biomass is fed at the top. Biomass moves down as the process proceeds. The first stage consists of drying through pyrolysis oxidation and reduction. The hot gas coming out of the Gasifier has significant carry over of ash and soot particles. The gas is passed through cyclone and scrubber for cleaning and cooling. The clean and cool gas is than further passed through fine filter and fed into a diesel generating set to run the engine or for direct heat application. The diesel generating set operates on dual-fuel mode (typically 20% Diesel and 80% producer gas.)

1.1 Technological description of gasifier

A complete Biomass gasification includes a fuel metering bin, the reactor/gasifier, the combustion tube and chamber, the gasifier cooling water system, water cooled ash discharge conveyors, multi-zoned combustion air supply, rotary feeders and instrumentation required to provide automatic control over the process. The entire gasification/combustion process, from in-feed to ash discharge, can be controlled manually or by computer. The gasifier basically a vertical cylindrical steel shell reduced in diameter in the upper portion and lined with a refractory capable of withstanding temperature as high as 1560°C in a reducing atmosphere. The cross sectional area of the upper portion of the gasifier is reduced to provide the turbulence required to ensure proper mixing of the product gas and the combustion air introduced in to the combustion tubes in this area of the gasifier.

Fuel is metered to the gasifier from the fuel-meter in bin. This bin is equipped with an in-feed conveyor that delivers fuel to the gasifier. The speed of the out-feed conveyor is automatically adjusted by the automatic control system to maintain a preset temperature in the first stage gasifcation zone. The gasification process is controlled by the proportional application of gasification and combustion air in a manner that supports efficient gasification. Residence time in the gasifier is varied by a residence control system that is adjusted to achieve a target quality of the ash residue. In the gasification zone of the gasifier, approximately 10 to 12 percent of the stoichiometric air requirement is admitted into the gasification air distribution area. The application of gasification air is multi-zoned and is controlled to maintain the proper temperature required to volatize the Biomass and allow partial combustion of the fixed carbon. Temperatures in this zone are controlled between 600°C and 800°C, depending on the particular biomass fuel and the required ash quality. A low gasification air flow rate (0.1 m/s) through the gasification zone, coupled with a low feed stock entry point and continuous ash discharge minimizes the amount of the particulate matter entrained in the gasifier exhaust.

1.2 Aims and Objectives

Present research trends showed that many lignocellulosic materials are good precursors especially for scavenging borderline and soft metal ions. Since India is rapidly moving towards the concept of safe drinking water, so huge amounts of activated carbon precursors are needed to be testified as metal ions scavenger.

The processing industries have increasingly been generating heavy metals of which the production of copper, lead and zinc had increased tremendously with a tenfold increase by the years between 1850 and 1990. We have seen borderline metals form relatively stable complexes with both hard and soft donor ligands. The first row *d*-block transition metal ions in the periodic table fall mainly into the group of borderline. Their stability order in complexes can be shown from Irving-Williams series. Cadmium, Nickel and lead are the highly toxic (toxic to all life forms even in low concentrations) metals among all borderline and marginal soft metals. Thus, the divalent cations of lead, cadmium are given priority for the removal using activated carbon from the toxicity and environmental standpoint as well as from the underlying adsorption mechanism. The anions of chromium(VI) and the non-ionic species of arsenic(III) are taken into adsorption experiment to observe the suitability of the prepared activated carbon in the removal of highly toxic anionic and non-ionic species.

1.2.1 Problem Identification

Arat chemicals (Bapunagar), Ahmedabad using gasifier for the generation of producer gas for thermal application their own purpose, produces waste coal after biomass combustion.Its Biomass Consumption is 64-80 Kg/hr and waste charcoal produced is 6-8% of the total biomass. With a view to there daily usage of gasifier this produced lower economic waste charcoal is a headache for the industry. More than 300 units are operating based on gasifier in Gujarat. These number is increasing day by day due to the higher cost of LDO, F.O., PNG and electricity. Also the use of gasifier is increasing day by day for rural electrification. So, ample

amount of waste charcoal is available having lower ecomonic value. So, present study is an effort to investigate gasifier based waste as a precursor for the preparation of activated carbon and as a metal ions adsorbent.

1.3 Objectives

The main objectives of this study are:

- ✓ Activation of waste charcoal
- ✓ Effect of concentration of activating agent, activation temperature on the charecteristics of activated carbon.
- ✓ Characterization-Analysis of the pore structures of the resulting carbons by N_2 adsorption, FT-IR Spectrum.
- ✓ To conduct the batch adsorption to remove heavy metal ions from waste water using activated carbon as a adsorbent.

1.4 Thesis Organization

Today's concern over the presence of inorganic species necessitates a cost effective and eco-friendly treatment process to remediate these contaminants from drinking water and wastewater. Present research trend demonstrates gasifier based waste material as promising precursor in the removal of borderline and soft metal ions. Since India is moving rapidly towards the concept of safe drinking water, wastes are needed to be testified for the same. Thus the present work consisted of adsorbent activation and preparation, followed by subsequent adsorption studies that determined the suitability of prepared adsorbents as scavengers for borderline and soft ionic or non-ionic species. The findings of this work are described in this thesis that contains five chapters including a concise introduction, problem identification and objectives in Chapter 1.

Chapter 2 provided the thorough literature review of activated carbon, like- how its use increse form colour removal to cansugar purification to wastewater treatment and as a air pollution controller. Research regarding its characteristics development and findings of number of authers are also covered.

Chapter 3 provides the description of processing gasifier based waste to obtain activated carbon suitable for removing borderline and soft metal ions. This chapter also includes chemical method of activation and the effect of preparation variables like concentration of acid/base, temperature of activation on the characteristics of activated carbons were studied extensively while physical characterizations were conducted to determine porous structure, ultimate and proximate analysis.

Chapter 4 shows the suitability of prepared activated carbons for the removal of Pb(II), Cd(II), Cr(VI), As(v) through adsorption equilibria and kinetics studies. Although the technique is simple and the basis of the idea is originated from the very old concepts of Lewis acid-base and Pearson's hard and soft acids and bases. The adsorption experimental parameters are also well discussed.

Finally, in chapter 5 concluding remarks and scope for future work is presented.

Chapter 2

Literature Survey

2.1 Introduction

One of the most important environmental problems in the world is water pollution. Fecal pollution of natural water and drinking water has frequently caused waterborne diseases. In general, waterborne diseases have been well controlled, especially in developed countries. Today, toxic chemicals pose a great threat to the safety of water supplies in developed and developing countries alike. There are many sources of toxic chemicals in the environment, such as badly designed landfills, industrial pollution and pesticide runoff. However, industrial wastewater is an important point source of water pollution. Thus, there is an increasing global demand for the treatment of industrial wastewater to protect the limited water resources. Microbial degradation, chemical oxidation and photolysis are used in the treatment of industrial wastewater. However, many hazardous organics in water are either non-biodegradable or refractory by-products. Some of these organics can be removed by adsorption on an active solid surface. Activated carbons are the most common adsorbent used for this purpose. Activated carbon is extensively used to remove pollutants from gaseous and liquid process streams. It is produced by chemical or physical activation of carbonaceous materials. The features of carbons

such as porosity, surface area, density, and mechanical stability govern the use of activated carbons as adsorbents. Wood, coal, lignite, coconut shell, and peat are some of the raw materials currently used to produce activated carbons. Nutshells have also been used to produce activated carbons. Their advantages as carbon feed stocks include high density, availability as renewable resources, low cost, low ash content, and they are capable of producing activated carbons of high adsorption capacity The widespread use of a particular raw material as a source of activated carbon is limited by the supply of that material. As a result, wood is by far the most common source of activated carbon followed by coal, coconut shells and peat. The raw material from which a given activated carbon is produced often has large effect on its porosity distribution and surface area. New materials are currently under investigation as sources for activated carbon. Almost any organic matter with a large percentage of carbon could theoretically be activated to enhance its sorptive capacity. In practice however, the best candidates for activated carbon should satisfy the following conditions (1) Contain a minimum amount of organic material, (2) Have a long storage life, (3) Consist of hard structures to maintain their properties under usage conditions, and (4) Can be obtained at a low cost.

2.2 Historical Aspect of Carbon

The application of powdered charcoal goes back to prehistoric times. The use of charcoal in medicine was reported in an Egyptian papyrus as early as 1550 B.C.. A Swedish chemist Karl Wilhelm Scheele, an apothecary by profession, was the first to discover the adsorptive properties of charcoal in 1773 when an experiment, consisted of the adsorption of gases, was conducted. The power of charcoal in removing colour from solution was first observed by the Russian academician Lovits in 1785. A few years later in 1794, wood char was employed to purify cane sugar in England. During the nineteenth century, much research had done to develop decolourizing carbons from various source materials such as bone, blood, cocoanut, flour, tar etc. with a special preference to be used in sugar industry. The chemicals generally used in these preparations were potash, magnesium carbonate, phosphate etc. In 1862, Lipscombe manufactured a carbon for the treatment of drinking water. In 1900 and 1901, two activation processes were developed and patented by Ostrejko to manufacture activated carbon from

vegetable material. These patents make the basis for the development of modern activated commercial carbon. In one process metallic chlorides were used as activating agent whereas in another process carbon dioxide was used as selective oxidizing agent. Elevated carbonization temperature was applied for activation with carbon dioxide. In 1909, a plant was built for the first time to manufacture powdered activated carbon on industrial scale following Ostrejko's patents. In 1911, the same plant produced new kinds of activated carbon from peat by activation with steam. In1915 during World War I, preparation of granular activated carbon was developed by Germany as filtering material in gas masks to protect the soldiers against chlorine gas used by the German soldiers. Coconut shell was emerged then as promising raw material for the production of granular activated carbon. During the past decades, activated carbons have been produced from a variety of raw materials by employing different processes. Manufactured carbons have been found numerous applications in the industry. Although many of ancient preparations make the basis of today's industrial process, they were not then developed on a commercial scale. The reason is assumed in the difficulties in process engineering as well as in the lack of knowledge in diversifying its application.

2.3 Structure of Activated Carbon

Activated carbons are highly porous materials with surface areas of up to 3000 $m^2.g^{-1}$. The surface area of a typical activated carbon is about 1000 $m^2.g^{-1}$. These high surface areas are the result of development of mainly micro and mesopores while a little contribution is also come from macropores. According to the IUPAC classification, pores having the radii less than 2 nm are called micropores whereas pores having the size of radii in between 2 to 50 nm are identified as mesopores. Macropores are defined as pores having the radii size above 50 nm. Cokes, chars and activated carbons are often termed as amorphous carbon. X-ray diffraction and electron microscopy have shown that these materials have crystalline characteristics, even though they may not show certain features, such as crystal angles and faces, usually associated with the crystalline state. The existence of submicroscopic dimensions in so called amorphous carbons makes the microcrystal structure known as crystallites. It was evident that amorphous carbon consists of graphitic flat plates in which the carbon atoms are arranged in a hexagonal lattice,

each atom, except those at the edge, is held by covalent linkages to three other neighboring carbon atoms. The crystallites formation is the result of the stacking of two or more of these plate-structures with an interlayer distance of 3.6 Å. The diamagnetic anisotropy is the highest in activated carbon among known materials. The structure of delocalized π-electrons is similar to that of aromatic hydrocarbons. Each basal layer can be considered a unique macromolecule. The various basal layers in the lattice, having delocalized electron structures, are markedly separated from one another. The relatively large distance between layers and the weak forces that hold the layers together make it possible for atoms, ions or molecules to enter the interlayer spaces. The adsorbates make room for themselves if necessary by forcing the sheets farther apart.

2.3.1 Surface Functional Groups

The adsorption of acids and bases on carbon was found to be controlled by the concentration of surface-oxygen. This finding led to study the effect of oxygen in contact with carbon at different temperatures and pressures. It was observed that graphite, carbon black, and activated carbon can adsorb molecular oxygen. Elevated temperature is needed to remove once chemisorbed oxygen. It has been reported that when oxygen contacts carbon surfaces some sort of oxygen-carbon complex is formed. It is not known what surface functional groups are formed during the carbon activation process. In general, acidic oxides are predominantly formed in carbon when it is prepared under moist air at 300 to 500°C, and basic oxides in those carbons prepared at 800 to 900°C in air, steam, or carbon dioxide. Amphoteric properties are found in carbons prepared between 500 to 800°C. The activated carbons prepared at low activation temperature, below 500-600°C, adsorb OH^- ions primarily are called L-carbons. Those activated carbons are prepared at above 500-600°C and adsorb H^+ ions are called H-carbons. Almost every type of functional group in organic chemistry has been suggested to be present on activated carbons surface. The ones suggested most often acidic functional groups are: carboxyl, phenolic-hydroxyl, and quinone-type carbonyl groups (Figure 2.1) while other suggested groups are ether, peroxide and ester groups in the forms of normal lactones and fluorescein-like lactones, carboxylic acid anhydrides and the cyclic peroxide (Figure 2.2). On the other hand, proposed basic surface

Normal lactones

Fluorescein type lactones

Carboxylic acid anhydrides

Cyclic peroxide
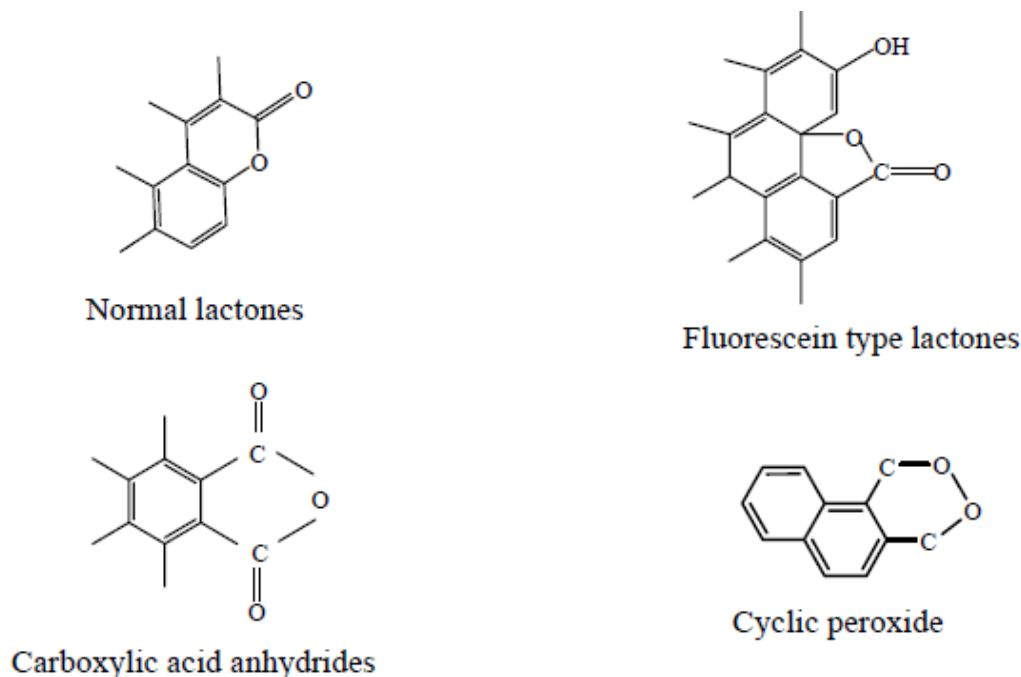
Figure 2.1 Structures of carboxyl, phenolic hydroxyl and quinone type carbonyl groups.

groups include chromene and pyrone. Typical identification reactions of organic chemistry were employed by Boehm (2002) to characterize oxygen chemisorbed on carbon as comprising four types of acidic surface groups:

1) a strongly acidic carboxyl group which is neutralized by $NaHCO_3$, Na_2CO_3, NaOH, and $NaOC_2H_5$,

2) a more weakly acidic carbonyl group which is neutralized by Na_2CO_3 or stronger bases such as NaOH and $NaOC_2H_5$; but not by $NaHCO_3$,

3) a phenolic hydroxyl group which is neutralized by NaOH and $NaOC_2H_5$,

4) a carbonyl group which is neutralized by $NaOC_2H_5$ only.

The type and number of surface groups on activated carbon will influence the extent and rate at which organic and inorganic compounds/species are adsorbed. It had been observed that acidic

surface oxides reduce the adsorption capacity of phenol and nitrobenzene on activated carbon. There are a couple of explanations for the role of acidic surface oxygen groups in their inhibition of adsorption of phenol and nitrobenzene molecules. A major portion of these oxygen bearing
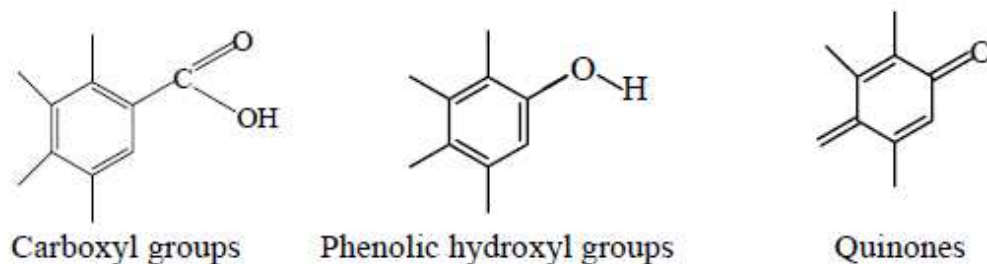
Figure 2.2 Structures of lactones, acid anhydrides and cyclic peroxide.

functional groups is located on the edges of the layer planes of carbon and they are not expected to be interfered by the adsorbed organic molecules on the basal planes from the view of steric sense.

2.4 Preparation and characteristics

Almost any carbonaceous material can be converted into activated carbon [32], whether it is occurring naturally such as coal (e.g. peat, lignite and all forms of coal) and lignocellulosic materials (e.g. wood, coconut shell, fruit stones, nut kernels etc) or prepared synthetically such as organic synthetic polymers (e.g. synthetic resins, rayon, polyacrylonitrile, polyvinylidene chloride, waste resins, textile wastes, rubber,dumped gangue etc). Bansal, Donnet and Stoeckil (1988) summarized the principal commercial carbon feedstocks as: coal, lignite and peat 52%; wood 35%; coconut shell 10% and others 3%. The development of pores and their size-distributions mainly depends upon the precursor type and the process of preparation. Acid treatment can be performed after activation to control the ash content in the resulted carbon. The process, activation of carbonaceous material, comprised of either physical or chemical activation method. Based on the required properties of the activated carbon, the proper raw material and

most importantly the activation process are utilized. Low temperature activation processes are adopted in presence of air or oxidizing materials to prepare carbon having acidic characteristic to remove preferably metal cations.

Physical activation consists of controlled or partial gasification of carbonaceous raw material. This uses gaseous flow, at high temperature, of mild oxidizing agents such as steam and CO_2 or a combination of these. Partial gasification eliminates unorganized carbon and non-carbon volatile matters as respective oxides. The process usually carried out in two steps: thermal Carbonization of carbonaceous precursor in presence of an inert gas (such as N_2) atmosphere followed by activation of the resulting char in a mild oxidizing gaseous (CO_2 and steam) atmosphere. The use of catalyst (e.g. K-, Na-salts) for the partial gasification of carbon is a variation of physical activation [38,39].

Chemical activation process consists of impregnation followed by carbonization. The impregnation process is applied in order to achieve a good contact of a solid with a solution containing activating chemical, such as $ZnCl_2$, H_3PO_4, or KOH etc. to be deposited on the surface. Carbonization is carried out by heating at a relatively low temperature under the atmosphere of nitrogen. Chemical activation is generally applied to uncarbonized feedstock containing cellulosic materials while activation is based on the dehydration of the feedstock. The more extensive impregnation produces weaker cellular structure and a large development of mesoporosity. A combination of both, physical and chemical, processes may also be practiced [38,39].

Carbonization is the pyrolysis or thermal decomposition process to remove most of the non-carbon elements (hydrogen, oxygen, traces of sulphur and nitrogen) from a carbonaceous material in gaseous form in the absence of air and without the addition of chemical agents. This enriches the carbon content and creates an initial porosity in the resulting char. The free valancies of released carbons are satisfied to group them into organized crystallographic formations known as elementary graphitic crystallites. The mutual arrangement of these crystallites is irregular, so that free interstices remain between them and, apparently, as the result

of deposition and decomposition of tarry substances, these become filled or blocked by disorganized carbon. Therefore, the resulting carbonized product needs activation to enhance its adsorption capacity. Activation process further develops the porosity and creates some ordering of the structure to generate a highly porous solid as the final product. Chemical impregnation of lignocellulosic carbon precursor results degradation of the cellulosic material while carbonization produces dehydration. The former results in charring and aromatization of the carbon skeleton whereas the latter creates the pore structure. The common feature of all substances used in the chemical activation process is that they are dehydrating agents that influence pyrolytic decomposition and inhibit formation of tar. As a result, higher yield is obtained with a high bulk densitysuitable for use in column. It is believed that dehydration, due to impregnation, proceeds by the partial dissolution of biopolymers together with the cleavage of either bonds between the lignin and cellulose, followed by recombination reactions in which layer structural units are formed, which ultimately derived a rigid crosslinked solid . Then, in the next step, thermal treatment of the impregnated feedstock modifies the morphology and dimensions of the cellular units existing before impregnation [38,39].

There is first an expansion of the cellular structure at impregnation state, then a subsequent contraction during carbonization at a temperature above 450°C. Coals are widely used as conventional feed stock for the manufacture of activated carbons and the process usually followed is physical activation: carbonization at about 600-650°C to prepare char, followed by partial gasification of carbon, called activation, using steam or carbon dioxide at 800-950°C to develop pore structure. The use of chemical activation of wood, sawdust, with phosphoric acid has been known for many decades and has been applied to different cellulosic and lignocellulosic materials to prepare high surface area activated carbons [39]. Phosphoric acid is used to provide oxidation environment. The phosphoric acid activation process was independently developed in America and Europe by Hudson and Urbain respectively. Although a good number of works have been found regarding preparation of activated carbon from oil palm kernel shell, the publications regarding preparation variables and application in removing metal ions from aqueous solution are still rare. So it would be our prime focus to utilize oil palm shell as low cost local raw materials for the preparation and modification of activated carbon and subsequent

adsorption studies for the removal of metal ions. As huge amounts of coconut shells are also produced as agricultural wastes, focus would also be given to utilize them as precursor as well as to study their suitability in removing metal ions.

Table 2.1 Sub-seuqent review of activation methods, activating agents and raw materials

Raw material	Preparation	remarks	Ref.
Bituminous coal	chemical activation with Potassium hydroxide and zinc chloride and also by physical activation with carbon dioxide.	Increasing the carbonization temperature upto 700°C enhances surface area and pore volumes of KOH-activated carbon, it destroys carbon structure in the $ZnCl_2$ carbon series if more than 500°C	[8]
Coconut shell	Chemical activation using zinc chloride ($ZnCl_2$).	Activated carbon made by has a high density, high purity, and are virtually dust-free, since they are harder and more resistant to attrition. Also, the pore structure is very uniform, with the majority of pores falling in the micro-pore range, particularly effective for decontamination, VOCs and industrial pesticide residual removal.	[3]
Waste tyres	Physical activation using steam and KOH	Production of tyre derived activated carbons using carbon dioxide, these generally have surface areas in the range of 270–980 m^2/g. Wet chemical activation using KOH has achieved a surface area of 820 m^2/g at an activation temperature of 850°C.	[9]

Molasses	Chemical activation using sulfuric acid (H_2SO_4).	These results have shown that it possible to produce high quality activated carbon from molasses. The highest surface area ($1214 m^2/g$) and the important maximum adsorption capacity of methylene blue (435 mg/g) and iodine (1430 mg/g) were found by activation of mixture (molasses/sulphuric acid) in steam at 750°C.	[10]
Cherry stones	chemical activation with $ZnCl_2$	When using the 4:1 impregnation ratio, the specific surface area (BET) of the resultant carbon is as high as 1971 m^2/ g. The effect of the increase in the impregnation ratio on the porous structure of activated carbon is stronger than that of the rise in the carbonization temperature.	[11]
Mesocarbon microbeads (MCMB)	chemical activation microwave (MW) heating	MWheating method can provide an efficient way to prepare activated carbons with high surface area. The activated carbons prepared by MWheating method present higher SBET compared to those prepared by EF heating method when KOH/MCMB ratio is the same.	[12]
jackfruit peel waste	chemical activation by H_3PO_4	It has been reported that well-developed pores are produced at activation temperature of 450°C and 550°C By increasing activation temperature (at the same impregnation ratio) the amount of acidic functional groups decreases while the basic surface groups of the carbon are increase.	[7]

Activated sludge obtained from the secondary precipitator	Activation with KOH solution and carbonization in the atmosphere of steam	Results indicated that 99.7% coloration and 99.6% total organic carbon (TOC) were removed after 15 min adsorption in the synthetic solution of Acid Brilliant Scarlet GR with initial concentration of 300 mg/L of the dye and 20 g/L activated carbon.	[13]
Waste tea	chemical activation with microwave energy and then carbonization	Reported results shows that microwave heating reasonably influenced the micropore,surface area of the samples as well as the BET surface area and also shortens the activation time considerably.	[2]

2.4.1 Brunauer, Emmett and Teller (BET) Surface Area

Surface area is one of the key indicators attributed to the adsorptive properties of porous materials. The most commonly used model in the determination of that parameter was developed by Brunauer et al. It is evaluated through N2 adsorption at 77 K, using an Autosorb Quantachrome instrument. The BET (Brunauer–Emmet and Teller) model could be applied to fit nitrogen adsorption isotherm and evaluate the surface area (SBET) of the sorbent [1,14,21].

2.4.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a spectroscopy method that enables us to study the types of bonding in a molecule as well as the interaction of bonding in a solid matrix or a mixture. The infrared light refers to the electromagnetic wave within the frequency region of 3´1012 to 3´1014 Hz or the wave number of 10000 cm^{-1} to 100 cm^{-1}. The basic principles of FTIR analysis is based on the fact that every molecule vibrates at a certain frequency. When the

frequency of an infrared light is in resonance with the frequency of the molecular vibration, the molecular vibration can absorb the infrared light. The frequency of the absorbed infrared light is characteristic of the bonds existing in the molecule. For example, the absorbance at region 1300-1000 cm^{-1} indicates the vibration of a C-O bond, while the absorbance at 3500-3200 cm^{-1} is characteristic of an O-H bond. Thus by obtaining infrared spectrum of the activated carbon, we can identify the chemical bonds that exist in the activated carbon. It can be determined whether the raw material is converted completely to pure carbon. We can determine too the functional groups present in the activated carbon [15,16,18].

2.4.3 Field Emission Scanning Electron Microscopy (FESEM)

Field Emission Scanning Electron Microscope (FESEM) is an instrument that can produce images of the sample surface up to 1000× and even 10000 × magnifications. In a scanning electron microscope, a beam of highly energetic electrons is emitted towards the surface of sample. The interaction between the electrons and the surface can produce signals which are in the form of electrons. The signals will be detected and be used to produce a point-by-point reconstruction of the surface image of the sample. Thus SEM does not produce the real image of the sample surface. However the reconstructed image of the surface is good enough for scientists to study the surface morphology of their samples [17,18,23].

2.4.4 Thermogravimetry Analysis (TGA)

Thermogravimetry is an analytical technique in which the mass (weight) of sample is monitored versus time or temperature while the temperature of sample is programmed under certain atmosphere. The result of detection is presented graphically as a plot of weight % versus time or temperature. Such plot is known as a thermogram. From the thermogram, we are able to determine the steps of reaction when sample undergoes heating, the thermal stability, the temperature at which certain reaction takes place etc. In this study, TGA is important in determining the optimum activation temperature for the production of activated carbon, and also to ensure that the conversion of bamboo to activated carbon is complete [19].

2.4.5 Nitrogen Adsorption Analysis

In nitrogen adsorption analysis, dry gas nitrogen will be flowed through the sample. The volume of nitrogen adsorbed on the sample will be monitored versus the gas pressure. The result will be presented as a plot of volume of gas adsorbed at 77 K versus relative pressure (*P/P0*). Such plot is known as an adsorption isotherm. From the shape of the isotherm, the type, shape and size of the pores in the sample can be determined. With the adsorption data obtained, the surface area, pore volume and pore size distribution of the sample can also be calculated [19,20,22].

2.5 Adsorption at Solid-Liquid Interface

The adsorption phenomenon at solid-liquid interface is rather complex compared with that at solid-gas interface. Two isotherm models, namely Freundlich isotherm and Langmuir isotherm, are widely employed to study the adsorption property at solid-liquid interface. In this study, the solid-liquid interaction between bamboo activated carbon and surfactant solutions is investigated.

2.5.1 Freundlich Isotherm

Freundlich model is an empirical equation based on the distribution of solute between the solid phase and aqueous phase at equilibrium. The equilibrium relationship for adsorbent can be stated using Freundlich equation when two conditions are fulfilled. The first condition is that when molecules are adsorbed onto the surface, no combination or dissociation of molecule occurs. The second condition is that the adsorption must occur by means of physical adsorption but not by chemical adsorption.

The basic Freundlich equation is:

$$\log(\frac{x}{m}) = \log q_e = \log K_F + \frac{1}{n}\log C_e$$

(1.4)

where

x = weight of solute adsorbed

m = weight of adsorbent

Ce = equilibrium concentration of surfactant

K_F and n = empirical constant

Eq. 1.4 can be rearranged into a linear form:

$$x/m = q_e = K_F\, C_e^{1/n}$$

A plot of log (x/m) versus log Ce will give a straight line of which the slope equals to $1/n$ and the intercept equals to log K_F. The value of n and K_F will provide information about the capacity of the activated carbon or the amount required to remove a unit mass of adsorbate [31].

2.5.2 Langmuir Isotherm

The Langmuir model is the simplest model that can be used to describe monolayer adsorption. It assumes a uniform surface and a single layer of adsorbed molecules at constant temperature. If a system deviates from this model, the deviation may be due to the irregularity of the surface or maybe there are interactions between the adsorbed molecules. The adsorbed molecules on the surface can cause other molecules to be adsorbed more difficult or easier on the nearby sites.

The Langmuir equation is as follows:

$$\frac{m}{x} = \frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{bq_{max}C_e}$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \tag{1.5}$$

where

$b =$ Langmuir constant related to the affinity of the binding site

$q_{max} =$ maximum adsorption at monolayer coverage

Above equation can be rearranged to a linear form:

$$\frac{x}{m} = q_e = \frac{bq_{max}C_e}{1 + bC_e} \tag{1.6}$$

When *Ce/qe* is plotted against *Ce*, a straight line graph is obtained with the slope of graph gives the value of 1/*qmax* and the intercept gives the value of 1/(*b qmax*). By such, we can determine the value of *b* and *qmax* from the graph plotted [30].

2.6 Heavy Metals

The classification of some elements as heavy metals does not have a rigorous scientific basis or a chemical definition. But they have widespread usage among professionals and laymen for over the past two decades. They constitute a group name for the transition and post-transition metals long with metalloids, arsenic and selenium, that has been associated with contamination and potential toxicity or ecotoxicity [33]. No relation can be drawn with specific gravity and toxicity. Even then, they are so called only because of their significantly heavier specific gravity, usually

greater than five though exceptions remain, in comparison to sodium, calcium and other light alkali and alkali-earth metals [25].

2.6.1 Pollution and Remediation Approaches

Today, the cry of "Pollution" is heard from all nooks and corners of the globe and it has become a major threat to the very existence of mankind on the planet earth. Heavy metal pollution affects flora, fauna and other abiotic components of the ecosystem. Metal leads to various metabolic alterations and undesirable changes, which in many cases may cause severe injury and health hazards. There are several factors like human population explosion, unplanned urbanization, deforestation, profit oriented society and technological advancement etc., whose cumulative effect is responsible for the origin of pollution crisis on the earth. The ecological crisis of environmental pollution has been blamed on many different things and one of the major things is the pollution due to metals or their species in the environment. The presence of heavy metals, strictly speaking 'the species of heavy metals', in the environment is of increasing major, worldwide concern for the last few decades. The toxicity and threat of heavy metal species to human life and environment came into the limelight in 1970s especially after the disclosure of mercury poisoning by the Minamata disaster in Japan [34]. Since then, World Health Organization (WHO) set up various permissible limits on the discharge of heavy metals into the environment. According to WHO, aluminium, chromium, magnesium, iron,cobalt, nickel, copper, zinc, cadmium, mercury and lead are the most toxic metals. Toxic metal pollution can be a much more serious and insidious problem, as these are intrinsic components of the environment. At high concentrations, all the metal species are toxic to both animals and plants [25]. Heavy metals are continually released into the aquatic environment from natural processes, such as volcanic activity and weathering of rocks, as hidden pollutant. Arsenic, another hidden common trace inorganic contaminant in drinking water, is extremely detrimental to human beings. Leaching from geological formations is a major natural source of arsenic in the ground water. Thus the presence of toxic elements or ionic/nonionic species particularly in ground water makes the so-called safer water unsafe at least in some part of the world and those are not affected, still in risk. Metals are also released into environment from a wide spectrum of

anthropogenic sources such as smelting of metallic ores, industrial fabrication and commercial application of metals, agrochemicals, pesticides as well as burning of fossil fuels. These metals are redistributed in the biosphere and dispersed in the air, soil, water and consequently in human beings through food chain bio-magnification causing chronic ailments.

Precipitation, sedimentation, coagulation, oxidation, filtration, sorption and membrane processes are generally employed to reduce heavy metal ions from the contaminated water. No doubt, the toxicity effects of these elements are largely a function of concentration. The widely used treatment method for the removal of heavy metal ions from wastewater is chemical precipitation using hydroxide, carbonate or sulphide or some combination of these chemicals. The most common processes use hydroxide precipitation, because the theoretical minimum solubility of metal hydroxides is low and the treatment cost is lower when lime is used. Ion exchange sorption and membrane processes such as reverse osmosis are capable of reducing metal concentrations to very low levels. But these are expensive and subject to operation problems such as fouling [35].

Thus, to mitigate the present problem of lowering the heavy metal contamination to the permissible level, an introduction of cost-effective, eco-friendly highly efficient sorption technology is needed to impose as down stream treatment process preferably to be used at the point of use or in house hold filtering unit. The term high efficiency is used to mean that the process would be selective towards the target species and capable of treating them to a safe level. To meet the cost-effective criteria, the process should be based on locally available low cost material and unlike ion exchange synthetic polymeric resin, should be eco-friendly. Thus the majority of people especially rural people might benefit from the innovative adoption of existing knowledge of advanced water treatment.

The necessity of selectivity is highly desired in removing heavy metal cations from water and wastewater streams while using sorption/adsorption based process. Because, selective removal of minor (0.01-10 $mg.L^{-1}$) to trace (<0.01 $mg.L^{-1}$) concentration of the heavy metals in the presence of other competing non-toxic, non regulated ions such as Ca^{2+}, Mg^{2+}, Na^+ etc certainly makes the process efficient and cost effective. Otherwise, treatment cost would be very high due to premature exhaustion of the sorbent by the above mentioned non-regulated ions. As for example,

in a conventional ion exchanger, Ca^{2+} ion is preferred over heavy metal cations such as Zn^{2+}, Co^{2+}, Cu^{2+} and Ni^{2+}. The heavy metal cations of mercury and lead are preferred marginally over Ca^{2+} [33]. The lower selectivity towards target heavy metal ions makes the commonly used cation exchangers uneconomical and unfavourable.

Any elemental species with a net positive charge behaves as a Lewis acid. Most of the heavy metal cations such as Cu^{2+}, Hg^{2+}, Pb^{2+}, Ni^{2+}, Cd^{2+} and Zn^{2+} being transition-metal ions exhibit fairly strong Lewis-acid characteristics due to the presence of incomplete *d*-orbital. Their electron clouds are readily deformable by the induction effect of electric field of other species. They favour to form fairly strong complexes with Lewis bases, organic and inorganic ligands, in the aqueous phase through inner sphere complexes by coordinated with donor electrons. Heavy metal cations thus can serve as good electron accepters. In other words, they are relatively 'soft' cation.

In contrast, cations of light metals, such as alkali and alkali-earth metals, having the inert gas configuration are not good electron acceptors and hence poor Lewis acids. Their electron clouds are not readily deformable by the electric field of other species. Thus they are less polar and commonly referred to as 'hard' cations. They form only outer sphere complexes with aqueous-phase ligands containing primarily oxygen donor atoms through columbic force of attraction. Hence, the simple ion exchange sorption-desorption processes are applicable to remove, preferentially, these hard ions. Pearson (1968) first showed that most cations are Lewis acids and anions are Lewis bases, while he expressed their strengths and affinity to acid-base-complexation in his famous principle of 'hard and soft acids and bases' (HSAB) using the property of ions as 'soft' and 'hard'.

The interaction of metallic species with living systems and adsorbents can be demonstrated better by the properties of metal ions as Lewis acids. Thus, the classification of metals by their Lewis acidity would be consistent in the assessment of toxicity and in the remediation approach.

		Class A Hard		Class AB Border line			Class B Soft											
1																		
H	2												13	14	15	16	17	
Li	Be												B	C	N	O	F	
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl		
K	Ca	Sc	Ti	V	Cr	Mn	Fe(III) Fe(II)	Co	Ni	Cu(II) Cu(I)	Zn			As	Se	Br		
Rb	Sr	Y	Zr					Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I		
Cs	Ba	†	Hf					Ir	Pt	Au	Hg	Ti	Pb(IV) Pb(II)	Bi	Po	At		
Fr	Ra	#	Rf	Db	Sg	Bh	Hs	Mt	110									

†Lanthanide	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

# Actinide	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 2.3 The periodic table showing classification of metals based on Lewis acidity as: Class A-hard metals (black), Class B-soft metals (light grey), Class AB-borderline (dark grey) (IUPAC, 2002).

This classification divided metals into three groups based on their observed affinity for different ligands, as Class (a)-'hard metals', Class (b)-'soft metals' or borderline- 'difficult to distinguish as hard or soft'. It should be noted that this classification, being based on observed chemical behaviour, is empirical. This is why, the same metal ion is found into different classes in literatures. As hard and soft metals are also denoted as Class A and Class B, the term Class AB is conveniently introduced for the borderline metals throughout this

thesis. Figure 2.3 shows the periodical table classifying metals as Class A- hard, Class B- soft and Class AB- borderline metals (IUPAC, 2002).

Although the term 'heavy metals' is used by the legal regulations, it has no sound terminological or scientific basis in the interpretation of toxicity and has never been defined by authoritative body like IUPAC- International Union of Pure and Applied Chemistry. Since no relationship can be drawn between density and toxicity or eco-toxicity, a classification based on their chemical properties is put forward in this work to abandon the classification of some metal ions as heavy metals and to follow the guideline of IUPAC. A theoretical basis of classification of metals as Class A and Class B has been introduced by Klopman (cited in IUPAC, 2002) depending on the calculated orbital electronegativity of cations or anions. Metals with calculated orbital electronegativities above 1.45 all belong to Class A, while those have the orbital electronegativity below -1.88 are all Class B.

2.7 Lead

Table 2.2 Chemical properties of lead

Atomic number	82
Atomic mass	207.2 $g.mol^{-1}$
Density	11.34 $g.cm^{-3}$ at 20°C
Melting point	327 °C
Boiling point	1755 °C

Lead is a bluish-white lustrous metal. It is very soft, highly malleable, ductile, and a relatively poor conductor of electricity. It is very resistant to corrosion but tarnishes upon exposure to air. Lead isotopes are the end products of each of the three series of naturally occurring radioactive elements [26].

2.7.1 Applications

Lead pipes bearing the insignia of Roman emperors, used as drains from the baths, are still in service. Alloys include pewter and solder. Tetraethyl lead ($PbEt_4$) is still used in some grades of petrol (gasoline) but is being phased out on environmental grounds. Lead is a major constituent of the lead-acid battery used extensively in car batteries. It is used as a coloring element in ceramic glazes, as projectiles, in some candles to threat the wick. It is the traditional base metal for organ pipes, and it is used as electrodes in the process of electrolysis. One if its major uses is in the glass of computer and television screens, where it shields the viewer from radiation. Other uses are in sheeting, cables, solders, lead crystal glassware, ammunitions, bearings and as weight in sport equipment [26].

2.7.2 Lead in the environment

Native lead is rare in nature. Currently lead is usually found in ore with zinc, silver and copper and it is extracted together with these metals. Lead occurs naturally in the environment. However, most lead concentrations that are found in the environment are a result of human activities. Due to the application of lead in gasoline an unnatural lead-cycle has consisted. In car engines lead is burned, so that lead salts (chlorines, bromines, oxides) will originate. These lead salts enter the environment through the exhausts of cars. The larger particles will drop to the ground immediately and pollute soils or surface waters, the smaller particles will travel long distances through air and remain in the atmosphere. Part of this lead will fall back on earth when it is raining. This lead-cycle caused by human production is much more extended than the natural lead-cycle. It has caused lead pollution to be a worldwide issue [26].

2.7.3 Health effects of lead

Lead is a soft metal that has known many applications over the years. It has been used widely since 5000 BC for application in metal products, cables and pipelines, but also in paints and pesticides. Lead is one out of four metals that have the most damaging effects on human health. It can enter the human body through uptake of food (65%), water (20%) and air (15%).

Foods such as fruit, vegetables, meats, grains, seafood, soft drinks and wine may contain significant amounts of lead. Cigarette smoke also contains small amounts of lead. Lead can enter (drinking) water through corrosion of pipes. This is more likely to happen when the water is slightly acidic. That is why public water treatment systems are now required to carry out pH-adjustments in water that will serve drinking purposes. For as far as we know, lead fulfils no essential function in the human body, it can merely do harm after uptake from food, air or water.

Lead can cause several unwanted effects, such as:
- Disruption of the biosynthesis of haemoglobin and anaemia
- A rise in blood pressure
- Kidney damage
- Miscarriages and subtle abortions
- Disruption of nervous systems
- Declined fertility of men through sperm damage
- Diminished learning abilities of children
- Behavioural disruptions of children, such as aggression, impulsive behavior and hyperactivity

Lead can enter a foetus through the placenta of the mother. Because of this it can cause serious damage to the nervous system and the brains of unborn children [26].

2.7.4 Environmental effects of lead

Not only leaded gasoline causes lead concentrations in the environment to rise. Other human activities, such as fuel combustion, industrial processes and solid waste combustion, also contribute.

Lead can end up in water and soils through corrosion of leaded pipelines in a water transporting system and through corrosion of leaded paints. It cannot be broken down; it can only converted to other forms. Lead accumulates in the bodies of water organisms and soil organisms. These

will experience health effects from lead poisoning. Health effects on shellfish can take place even when only very small concentrations of lead are present. Body functions of phytoplankton can be disturbed when lead interferes. Phytoplankton is an important source of oxygen production in seas and many larger sea-animals eat it. That is why we now begin to wonder whether lead pollution can influence global balances. Soil functions are disturbed by lead intervention, especially near highways and farmlands, where extreme concentrations may be present. Soil organisms than suffer from lead poisoning, too. Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains [26].

2.8 Cadmium

Table 2.3 Chemical properties of cadmium

Atomic number	48
Atomic mass	112.4 g.mol^{-1}
Density	8.7 g.cm^{-3} at 20°C
Melting point	321 °C
Boiling point	767 °C

Cadmium is a lustrous, silver-white, ductile, very malleable metal. Its surface has a bluish tinge and the metal is soft enough to be cut with a knife, but it tarnishes in air. It is soluble in acids but not in alkalis. It is similar in many respects to zinc but it forms more complex compounds [27].

2.8.1 Applications

About three-fourths of cadmium is used in Ni-Cd batteries, most of the remaining one-fourth is used mainly for pigments, coatings and plating, and as stabilizers for plastics. Cadmium has been used particularly to electroplate steel where a film of cadmium only 0.05 mm thick will provide complete protection against the sea. Cadmium has the ability to absorb neutrons, so it is used as a barrier to control nuclear fission.

2.8.2 Cadmium in the environment

Cadmium can mainly be found in the earth's crust. It always occurs in combination with zinc. Cadmium also consists in the industries as an inevitable by-product of zinc, lead and copper extraction. After being applied it enters the environment mainly through the ground, because it is found in manures and pesticides.

Naturally a very large amount of cadmium is released into the environment, about 25,000 tons a year. About half of this cadmium is released into rivers through weathering of rocks and some cadmium is released into air through forest fires and volcanoes. The rest of the cadmium is released through human activities, such as manufacturing. No cadmium ore is mined for the metal, because more than enough is produced as a byproduct of the smelting of zinc from its ore, sphelerite (ZnS), in which CdS is a significant impurity, making up as much as 3% [27].

2.8.3 Health effects of cadmium

Human uptake of cadmium takes place mainly through food. Foodstuffs that are rich in cadmium can greatly increase the cadmium concentration in human bodies. Examples are liver, mushrooms, shellfish, mussels, cocoa powder and dried seaweed. An exposure to significantly higher cadmium levels occurs when people smoke. Tobacco smoke transports cadmium into the lungs. Blood will transport it through the rest of the body where it can increase effects by potentiating cadmium that is already present from cadmium-rich food. Other high exposures can occur with people who live near hazardous waste sites or factories that release cadmium into the air and people that work in the metal refinery industry. When people breathe in cadmium it can severely damage the lungs. This may even cause death.

Cadmium is first transported to the liver through the blood. There, it is bond to proteins to form complexes that are transported to the kidneys. Cadmium accumulates in kidneys, where it damages filtering mechanisms. This causes the excretion of essential proteins and sugars from the body and further kidney damage. It takes a very long time before cadmium that has accumulated in kidneys is excreted from a human body [27].

Other health effects that can be caused by cadmium are:

- Diarrhoea, stomach pains and severe vomiting
- Bone fracture
- Reproductive failure and possibly even infertility
- Damage to the central nervous system
- Damage to the immune system
- Psychological disorders
- Possibly DNA damage or cancer development

2.8.4 Environmental effects of cadmium

Cadmium waste streams from the industries mainly end up in soils. The causes of these waste streams are for instance zinc production, phosphate ore implication and bio industrial manure. Cadmium waste streams may also enter the air through (household) waste combustion and burning of fossil fuels. Because of regulations only little cadmium now enters the water through disposal of wastewater from households or industries. Another important source of cadmium emission is the production of artificial phosphate fertilizers. Part of the cadmium ends up in the soil after the fertilizer is applied on farmland and the rest of the cadmium ends up in surface waters when waste from fertilizer productions is dumped by production companies. Cadmium can be transported over great distances when it is absorbed by sludge. This cadmium-rich sludge can pollute surface waters as well as soils. Cadmium strongly adsorbs to organic matter in soils. When cadmium is present in soils it can be extremely dangerous, as the uptake through food will increase. Soils that are acidified enhance the cadmium uptake by plants. This is a potential danger to the animals that are dependent upon the plants for survival. Cadmium can accumulate in their bodies, especially when they eat multiple plants. Cows may have large amounts of cadmium in their kidneys due to this.

Earthworms and other essential soil organisms are extremely susceptive to cadmium poisoning. They can die at very low concentrations and this has consequences for the soil structure. When

cadmium concentrations in soils are high they can influence soil processes of micro organisms and threat the whole soil ecosystem. In aquatic ecosystems cadmium can bio accumulate in mussels, oysters, shrimps, lobsters and fish. The susceptibility to cadmium can vary greatly between aquatic organisms. Salt-water organisms are known to be more resistant to cadmium poisoning than freshwater organisms. Animals eating or drinking cadmium sometimes get high blood-pressures, liver disease and nerve or brain damage.

2.9 Chromium

Table 2.4 Chemical properties of chromium

Atomic number	24
Atomic mass	51.996 g.mol^{-1}
Density	7.19 g.cm^{-3} at 20°C
Melting point	1907 °C
Boiling point	2672 °C

Chromium is a lustrous, brittle, hard metal. Its colour is silver-gray and it can be highly polished. It does not tarnish in air, when heated it borns and forms the green chromic oxide. Chromium is unstable in oxygen, it immediately produces a thin oxide layer that is impermeable to oxygen and protects the metal below [28].

2.9.1 Applications

Chromium main uses are in alloys such as stainless steel, in chrome plating and in metal ceramics. Chromium plating was once widely used to give steel a polished silvery mirror coating. Chromium is used in metallurgy to impart corrosion resistance and a shiny finish; as dyes and paints, its salts colour glass an emerald green and it is used to produce synthetic rubies; as a catalyst in dyeing and in the tanning of leather; to make molds for the firing of bricks. Chromium (IV) oxide (CrO_2) is used to manufacture magnetic tape. Chromium is mined as chromite ($FeCr_2O_4$) ore [28].

2.9.2 Health effects of chromium

People can be exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. In drinking water the level of chromium is usually low as well, but contaminated well water may contain the dangerous chromium(IV); hexavalent chromium. For most people eating food that contains chromium(III) is the main route of chromium uptake, as chromium(III) occurs naturally in many vegetables, fruits, meats, yeasts and grains. Various ways of food preparation and storage may alter the chromium contents of food. When food in stores in steel tanks or cans chromium concentrations may rise. Chromium(III) is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much chromium(III) can cause health effects as well, for instance skin rashes. Chromium(VI) is a danger to human health, mainly for people who work in the steel and textile industry. People who smoke tobacco also have a higher chance of exposure to chromium. Chromium(VI) is known to cause various health effects. When it is a compound in leather products, it can cause allergic reactions, such as skin rash. After breathing it in chromium(VI) can cause nose irritations and nosebleeds [28].

Other health problems that are caused by chromium(VI) are:
- Skin rashes
- Upset stomachs and ulcers
- Respiratory problems
- Weakened immune systems
- Kidney and liver damage
- Alteration of genetic material
- Death

The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in this product) is of low toxicity. The hexavalent form is toxic. Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions. Inhalation of hexavalent chromium compounds can result in ulceration

and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch [28].

2.9.3 Environmental effects of chromium

There are several different kinds of chromium that differ in their effects upon organisms. Chromium enters the air, water and soil in the chromium(III) and chromium(VI) form through natural processes and human activities. The main human activities that increase the concentrations of chromium (III) are steal, leather and textile manufacturing. The main human activities that increase chromium(VI) concentrations are chemical, leather and textile manufacturing, electro painting and other chromium(VI) applications in the industry. These applications will mainly increase concentrations of chromium in water. Through coal combustion chromium will also end up in air and through waste disposal chromium will end up in soils.

Most of the chromium in air will eventually settle and end up in waters or soils. Chromium in soils strongly attaches to soil particles and as a result it will not move towards groundwater. In water hromium will absorb on sediment and become immobile. Only a small part of the chromium that ends up in water will eventually dissolve. Chromium(III) is an essential element for organisms that can disrupt the sugar metabolism and cause heart conditions, when the daily dose is too low. Chromium(VI) is mainly toxic to organisms. It can alter genetic materials and cause cancer. Crops contain systems that arrange the chromium-uptake to be low enough not to cause any harm. But when the amount of chromium in the soil rises, this can still lead to higher concentrations in crops. Acidification of soil can also influence chromium uptake by crops. Plants usually absorb only chromium(III). This may be the essential kind of chromium, but when concentrations exceed a certain value, negative effects can still occur.

Chromium is not known to accumulate in the bodies of fish, but high concentrations of chromium, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal. In animals chromium can cause respiratory problems, a lower ability to fight disease, birth defects, infertility and tumor formation [28].

2.10 Arsenic

Table 2.5 Chemical properties of arsenic

Atomic mass	74.9216 g.mol^{-1}
Electronegativity according to Pauling	2.0
Density	5.7 g.cm^{-3} at 14°C
Melting point	814 °C (36 atm)
Boiling point	615 °C (sublimation)

Arsenic appears in three allotropic forms: yellow, black and grey; the stable form is a silver-gray, brittle crystalline solid. It tarnishes rapidly in air, and at high temperatures burns forming a white cloud of arsenic trioxide. Arsenic combines readily with many elements. The metallic form is brittle, tharnishes and when heated it rapidly oxidizes to arsenic trioxide, which has a garlic odor. The non metallic form is less reactive but will dissolve when heated with strong oxidizing acids and alkalis [29].

2.10.1 Applications

Arsenic compounds are used in making special types of glass, as a wood preservative and, lately, in the semiconductor gallium arsenade, which has the ability to convert electric current to laser light. Arsine gas AsH_3, has become an important dopant gas in the microchip industry, although it requires strict guidelines regarding its use because it is extremely toxic. During the 18th, 19th, and 20th centuries, a number of arsenic compounds have been used as medicines; copper aceto arsenite was used as a green pigment known under many different names [29].

2.10.2 Arsenic in the environment

Arsenic can be found naturally on earth in small concentrations. It occurs in soil and minerals and it may enter air, water and land through wind-blown dust and water run-off. Arsenic in the atmosphere comes from various sources: vulcanoes release about 3000 tonnes per year and

microorganisms release volatile methylarsines to the extent of 20.000 tonnes per year, but human activity is responsible for much more: 80.000 tonnes of arsenic per year are released by the burning of fossil fuels.

Despite its notoriety as a deadly poison, arsenic is an essential trace element for some animals, and maybe even for humans, although the necessary intake may be as low as 0.01 mg/day. Arsenic is a component that is extremely hard to convert to water-soluble or volatile products. The fact that arsenic is naturally a fairly a mobile component, basically means that large concentrations are not likely to appear on one specific site. This is a good thing, but the negative site to it is that arsenic pollution becomes a wider issue because it easily spreads. Arsenic cannot be mobilized easily when it is immobile. Due to human activities, mainly through mining and melting, naturally immobile arsenics have also mobilized and can now be found on many more places than where they existed naturally [29].

2.10.3 Health effects of arsenic

Arsenic is one of the most toxic elements that can be found. Despite their toxic effect, inorganic arsenic bonds occur on earth naturally in small amounts. Humans may be exposed to arsenic through food, water and air. Exposure may also occur through skin contact with soil or water that contains arsenic. Levels of arsenic in food are fairly low, as it is not added due to its toxicity. But levels of arsenic in fish and seafood may be high, because fish absorb arsenic from the water they live in. Luckily this is mainly the fairly harmless organic form of arsenic, but fish that contain significant amounts of inorganic arsenic may be a danger to human health.

Arsenic exposure may be higher for people that work with arsenic, for people that live in houses that contain conserved wood of any kind and for those who live on farmlands where arsenic-containing pesticides have been applied in the past.

Exposure to inorganic arsenic can cause various health effects, such as irritation of the stomach and intestines, decreased production of red and white blood cells, skin changes and lung irritation. It is suggested that the uptake of significant amounts of inorganic arsenic can intensify

the chances of cancer development, especially the chances of development of skin cancer, lung cancer, liver cancer and lymphatic cancer. A very high exposure to inorganic arsenic can cause infertility and miscarriages with women, and it can cause skin disturbances, declined resistance to infections, heart disruptions and brain damage with both men and women. Finally, inorganic arsenic can damage DNA. A lethal dose of arsenic oxide is generally regarded as 100mg. Organic arsenic can cause neither cancer, nor DNA damage. But exposure to high doses may cause certain effects to human health, such as nerve injury and stomachaches [29].

2.10.4 Environmental effects of arsenic

The arsenic cycle has broadened as a consequence of human interference and due to this, large amounts of arsenic end up in the environment and in living organisms. Arsenic is mainly emitted by the copper producing industries, but also during lead and zinc production and in agriculture. It cannot be destroyed once it has entered the environment, so that the amounts that we add can spread and cause health effects to humans and animals on many locations on earth.

Plants absorb arsenic fairly easily, so that high-ranking concentrations may be present in food. The concentrations of the dangerous inorganic arsenics that are currently present in surface waters enhance the chances of alteration of genetic materials of fish. This is mainly caused by accumulation of arsenic in the bodies of plant-eating freshwater organisms. Birds eat the fish that already contain eminent amounts of arsenic and will die as a result of arsenic poisoning as the fish is decomposed in their bodies [29].

Chapter 3

Materials and Methods

3.1 Chemicals and Reagents

The reagents used to impregnate the raw materials were phosphoric acid, H_3PO_4 (88%); sodium carbonate, Na_2CO_3 (99.5%); sodium hydroxide (NaOH) pellet (99%) supplied by NICE chemical Pvt. Ltd. Various metal ion solutions and reagents were prepared using the following chemicals and reagents: lead (II) nitrate, $Pb(NO_3)_2$; potassium dichromate, $K_2Cr_2O_7$; sodium arsenate, $Na_2HAsO_4.7H_2O$; nitric acid, HNO_3 (65%); and hydrochloric acid, HCl (36.5%). Commercial activated carbon was supplied by NICE chemical Pvt. Ltd.. Glasswares like Round bottom flask, measuring cylinder, beakers and conical flasks were washed by immersing in 10% HNO3 followed by washing with distilled water.

3.2 Instruments

The following instruments were used to prepare, modify and characterize activated carbons as well as to conduct batch adsorption studies: mechanical grinding machine by sun instruments; muffle furnace (Lab Fine manufacturers); hot air oven (Lab Fine manufacturers); BET surface area and Pore Size Analyzer (Nova 1000e); Fourier transform infrared spectrophotometer, FTIR

(IRPrestige-21, Shimadzu, Japan); mechanical shaker (Sedko laboratory equipments); Digital pH meter (Systronics Pvt. Ltd.); atomic absorption spectrophotometer (AAS-6300, Shimadzu, Japan); Ultraviolet--visible spectrophotometer(UV-1800, Shimadzu, Japan); Arsenic kit supplied by Transchem Agritech Limited.

3.3 Activated carbon Preparation

Various activated carbons had been successfully prepared with the optimization of the preparation variables through studying the effect of process variables such as concentration of activating agent, and activation temperature.

```
┌─────────────────────────────────────────┐
│         Raw materials as collected        │
└─────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────┐
│   Crushed and sieved to selected particle │
│   sizes, 2.36-1.18 and 1.18-0.60 mm       │
└─────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────┐
│   Impregnation with KOH / H₃PO₄ solution  │
│   having specific concentration in a      │
│   round bottom                            │
└─────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────┐
│   Washing with water to remove acid/base  │
│   and ash content                         │
└─────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────┐
│   Filtration for cake formation and       │
│   drying using hot air oven               │
└─────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────┐
│   Carbonization at 400-700°C either in a  │
│   muffle furnace                          │
└─────────────────────────────────────────┘
```
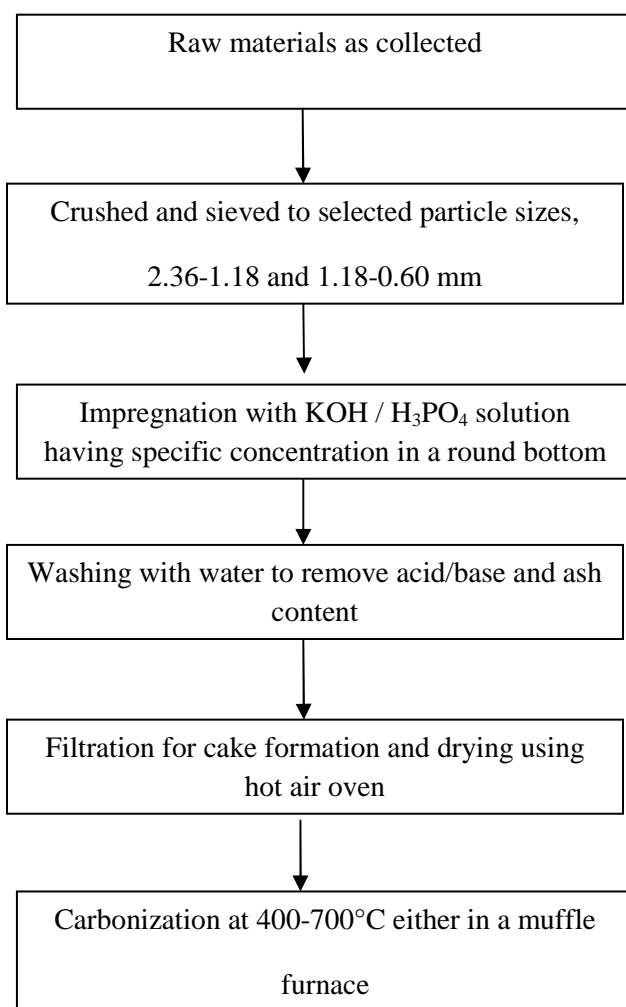
Figure 3.1 A flow diagram of activated carbon preparation.

In this work, different concentration of KOH / H_3PO_4 aqueous solution was used in the chemical treatment to enhance surface acidity and porosity.To maximize the development of internal surface area as well as to enhance the development of various acidic surface groups, pretreatment was also explored with range of temperature.

Gasifier based solid waste collected from (Arat electochem Pvt. Ltd, Bapunagar), were crushed using a mechanical grinding machine and sieved to the selected particle sizes of 75-150 microns. After sieving and selecting, crushed particles were mixed with KOH / H_3PO_4 solution in a round bottom flask with condesor at 100°C and whole lab set up was properly adjusted and flow of water was maintained. in aqueous solution of either 0.5N-5N KOH and 5-15% phosphoric acid , for a period of 4-6 hours. Finally, the particles were thoroughly washed with distilled water in a 2 lit beakers and filtrate for the cake formation; and dry using hot air oven to eliminate moisture.

Figure 3.2 Preparation activated carbons activated either in a muffle furnace using KOH and H_3PO_4 activated carbon

3.4 Characterization of Activated and Composite Carbon

Prepared activated and modified carbons were subjected to physical characterization. The porous property of the prepared activated carbons, raw solid waste and a commercial activated carbon was analysed to determine the surface area. Fourier transform infrared (FTIR) spectroscopy was used to identify and quantify the acidic surface groups on prepared activated carbons. Proximate and ultimate analysis of different carbons was carried out.

Table 3.1 Activated Carbon Analysis

Sr.	Particulars	Units	CAC	GBC	GBC (CT)	GBC (TT)	GBC (CT+TT)
1.	Ash	%	1.09	9.837	1.05	8.75	3.02
2.	Moisture	%	3.2	4.85	4.1	3.87	3.8
3.	Volatile organic matter	%	9.42	12.95	9.19	10.31	9.3
4.	Carbon	%	86.3	72.32	85.64	77.02	83.86
5.	Matters soluble in water	%	0.79	0.27	0.95	0.18	0.85
6.	Hydrogen	%	2.58	3.88	2.59	1.43	2.45
7.	Nitrogen	%	0.42	2.91	0.65	2.58	1.33
8.	Sulphur	%	0.95	0.82	0.98	0.68	0.72
9.	Oxygen	%	9.73	18.47	10.14	17.91	11.56
10.	Specific surface area	m2/gm	512	237	551	398	715
11.	Conductivity	µs/cm	351	159	313	124	322

CAC= Commercially available carbon

GBC= Gasifier Based Charcoal

GBC (CT)= Gasifier Based Charcoal (Chemically Treated (1.5 N KOH))

GBC (TT)= Gasifier Based Charcoal (Thermally Treated)

GBC (CT+TT)= Gasifier Based Charcoal (Chemically Treated (1.5 N KOH) + Thermally Treated)

3.4.2 Measurement of iodine-adsorption capacity (ASTM D4607)

It is a simple and quick test, giving an indication of the internal surface area of the carbon; in many activated carbons the iodine number (expressed as milligrams of iodine per gram of carbon). In this method, the 0.5g activated carbon is boiled with 5% HCl and, after cooling, a 0.1N iodine solution is added and shaken for 30 s; after filtration, the filtrate is titrated with O.1N sodium thiosulfate solution, with starch as indicator.

Table 3.2 Properties of KOH/ H_3PO_4 activated GBC (CT+TT)

KOH activated GBC

0.5 N Solution (Iodine Number/Temp/hr)	1.5N Solution (Iodine Number/Temp/ hr)	2.5N Solution (Iodine Number/Temp/ hr)	5N Solution (Iodine Number/Temp/ hr)
1398/500°C /3	1423/500°C /3	1612/550°C /4	2100/550°C /4
1479/650°C /3	1612/650°C /3	1977/750°C /4	2050/750°C /4
1697/800°C /3	1784/800°C /3	2114/920°C /4	-

H_3PO_4 activated GBC

5% Solution (Iodine Number/Temp/hr)	10% Solution (Iodine Number/Temp/ hr)	15% Solution (Iodine Number/Temp/ hr)
1238/500°C /3	1411/500°C /3	1946/550°C /4
1328/650°C /3	1563/650°C /3	2215/750°C /4
1512/800°C /3	1649/800°C /3	2506/920°C /4

The capacity of a carbon for any adsorbate is dependent upon the concentration of the adsorbate in solution. The concentrations of the standard iodine solution and filtrates must be specified or known. This is necessary to determine an appropriate carbon weight to produce final concentrations agreeing with the definition of iodine number. The amount of carbon sample to be

used in the determination is governed by the activity of the carbon. If filtrate normality (C) are not within the range of 0.008 N to 0.040 N, repeat the procedure using different carbon weights.
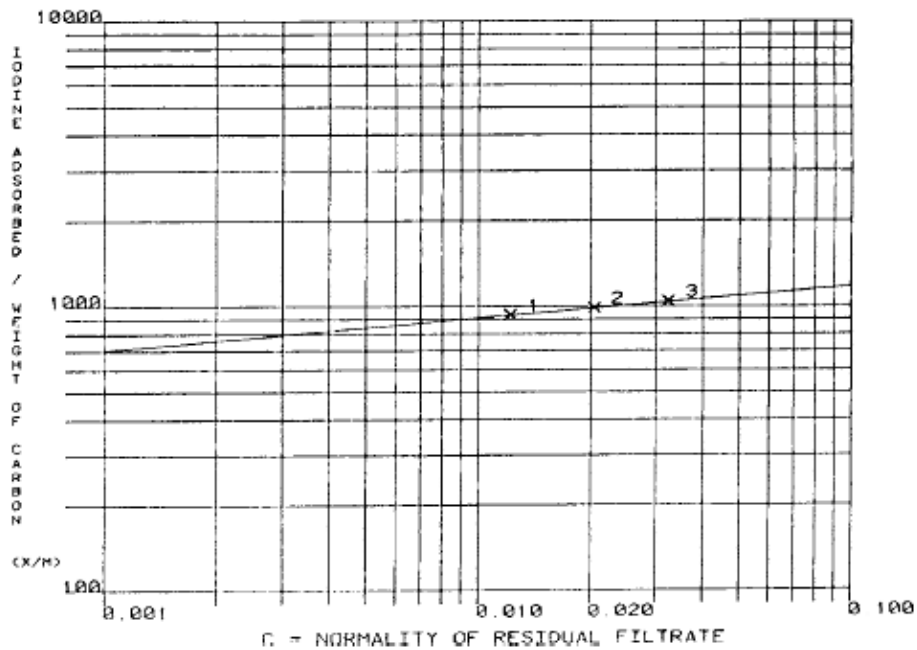
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TDB NO. 604 PAGE 22
TECH. PRP

POINT 1		
X/M	–	932
C	–	0.012
POINT 2		
X/M	–	964
C	–	0.020
POINT 3		
X/M	–	1040
C	–	0.032

Fig. 3.3 Activated Carbon Iodine Adsorption Isotherm

Two calculations are required for each carbon dosage, as *X/M* and *C*.

To calculate the value of *X/M*, first derive the following values:

$A = (N_2)(12693.0)$

where:

N1 = sodium thiosulfate, N

DF = (1+ H)/F

where:

DF = dilution factor,

I = iodine, mL

H = 5 % hydrochloric acid used, mL, and

F = filtrate, mL.

For example, if 10 mL of HCl and 50 mL of filtrate are used:

DF = (100 + 10)/50 = 2.2.

Calculate the value of X/M as follows:

X/M =[A –(DF)(B)(S)] / M

where:

X/M = iodine absorbed per gram of carbon, mg/g,

S = sodium thiosulfate, mL, and

M = carbon used, g.]

Calculate the value of C as follows:

C =(N1·S) / F

where:

C = residual filtrate, N,

N1 = sodium thiosulfate, N, and

F = filtrate, mL.

3.4.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy in the wave number range of 4000-400 cm^{-1} and potassium bromide (KBr) pellet technique were used to detect the surface functional groups present in the activated carbon. About 1-3 mg of finely ground sample was well mixed with about 200 mg of KBr powder. The mixture was then pressed continuously at a pressure of 10 tonnes for 1 min. to form a transparent pellet using a Perkin Elmer hydraulic press. During pellet preparation, the system was kept under evacuation. The pellet was analysed immediately after being prepared [15,16,18].

GBC (CT+TT), prepared from 1.5N KOH pretreated gasifier based waste charcoal precursor showed the following absorption bands:

i) $3486 cm^{-1}$: O–H stretching in hydroxyl groups;

ii) $3450 cm^{-1}$: O–H stretching vibrations in hydroxyl functional groups;

iii) $2972 cm^{-1}$: =C–H stretching in unsaturated hydrocarbon;

iv) $2917 cm^{-1}$: –C–H vibration stretching in saturated hydrocarbon;

v) $2342 cm^{-1}$: a sharp characteristic peak of CO_2 while the absorbance arose from its resonance structure of carbon triply bonded oxygen stretching ;

vi) $1701 cm^{-1}$: C=O stretching in ketones and carboxylic acids;

vii) $1690 cm^{-1}$: C=O stretching in ketones and/or in carboxylic acids;

viii) $1559 cm^{-1}$: C=P stretching;

ix) $1168 cm^{-1}$: C=O stretching in ketones and carboxylic acids;

GBC (CT+TT), prepared from 5% H_3PO_4 pretreated gasifier based waste charcoal precursor showed the following absorption bands:

The activated carbon, PSW-P-500, prepared from wet feedstock of H_2SO_4 pretreated
palm shell precursor displayed the following bands:

i) $3413 cm^{-1}$: O–H stretching in hydroxyl groups;

ii) $2972 cm^{-1}$: =C–H stretching in unsaturated hydrocarbon;

iii) $2917 cm^{-1}$: –C–H vibration stretching in saturated hydrocarbon;

iv) $2342 cm^{-1}$: a sharp characteristic peak of CO_2 while the absorbance arose from its resonance structure of carbon triply bonded oxygen stretching ;

v) $1690 cm^{-1}$: C=O stretching in ketones and/or in carboxylic acids;

vi) $1168 cm^{-1}$: C=O stretching in ketones and carboxylic acids;

vii) $995 cm^{-1}$: P–O stretching in phosphonic acid groups; P–O–C asymmetric stretching.

The probable main acidic groups present on the surface of both GBC(CT+TT) were phenols, carbonyl groups, carboxylic and phosphorous acid groups. Here, it is supposed that chemical treatment enhanced the development of carboxylic groups in PSW-P-500 and PSW-P-ad-500. The hydroxyl groups either in phenols and/or in phosphorous acid groups were well developed in case of both GBC(CT+TT).

After preliminary study of methylene blue adsorption and due to the problems like, higher settling time sticky in nature) and cost of the chemical GBC(CT+TT) treated with 1.5N KOH was used for the all further study.

3.4.4 Methylene Blue adsorption and colour removal capacity of GBC(CT+TT)

Methylene blue in commercial purity was used without further purification. The dye stock solution was prepared by dissolving accurately weighed dye in distilled water to a concentration of 500 mg/l. The experimental solution was obtained by diluting the dye stock solution in accurate proportions to different initial concentrations [36,37].
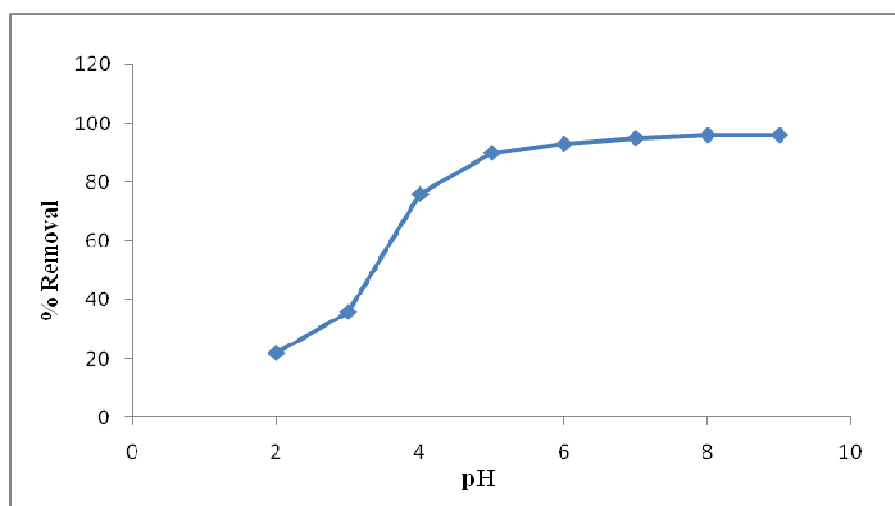

Figure 3.4 Effect of pH on the adsorption(%) of methylene blue 100 ppm using activated carbon; Condition: contact time = 120 minutes, adsorbent dose=0.2gm/50ml
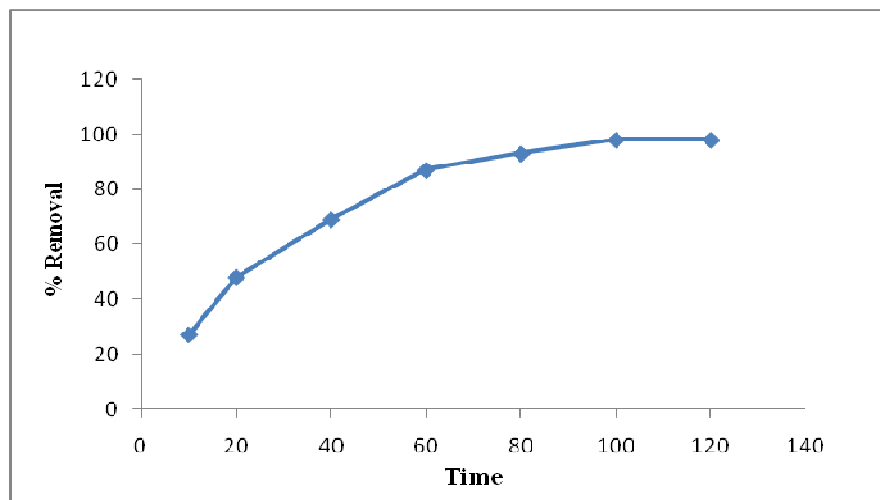
Figure 3.5 Effect of time on the adsorption(%) of methylene blue 100 ppm using activated carbonConditions: initial pH of MB solution = 5.5; contact time = 120 minutes, adsorbent dose=0.2gm/50ml

Adsorption of methylene blue (MB) on activated carbon was carried out using a bath experiments method in a mechanical shaker. The effect of contact time, solution pH and adsorbent dosage were investigated. The adsorption process was carried out with two different initial concentrations at 100 ppm MB. In the pH study, the pH of MB solution was adjusted in the range of 2-9 by adding 0.1N hydrochloric acid or 0.1 Nsodium hydroxide. About 0.20 g adsorbent was then added to the solution and shaken at predetermined time.

The effect of contact time was used to determine equilibrium time for the adsorption at optimized pH 7. For the effect of contact time study, 50 ml of MB solution was added into a screw cap conical flask containing 0.20 g activated carbon and shaken constantly. Samples solutions were withdrawn at predetermined time intervals for the colour removal analysis.

In the experiment to investigate the effect of adsorbent dosage on MB adsorption, various amounts of adsorbent in the range of 0.1 g to 0.1 g were added to 100 ppm MB with optimized pH 7. After shaking the flasks for predetermined time intervals, all samples were withdrawn -
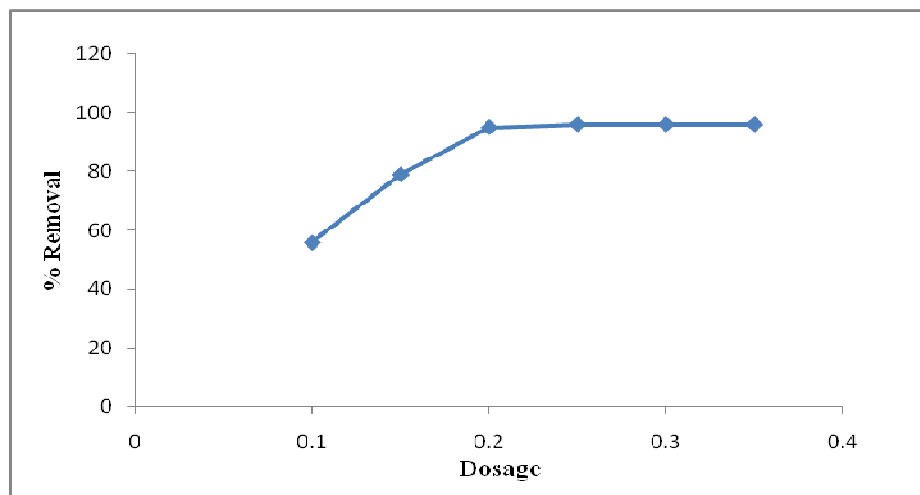
Figure 3.6 Effect of adsorbent dosage(gm) on the adsorption(%) of methylene blue 100ppm using activated carbon Conditions: initial pH of MB solution = 6.5; contact time = 120 minutes

-from the conical flasks and the MB solutions were separated from the adsorbent by filtration then followed by centrifugation. Dye concentrations in the solutions were estimated by measuring absorbance at maximum wavelengths of dye with Ultraviolet--visible spectrophotometer (UV-1800, Shimadzu, Japan); and computing from the calibration curves.

The effect of adsorbent dosage on the removal of MB has been presented in Fig. 4. The amount of carbon required for quantitative removal of MB from 50 mL (50 mg/L) of solution was 150 mg. The percentage of removal increased to 99% with an adsorbent dose of 150 mg/50 ml. It is apparent that by increasing the adsorbent dose, the removal efficiency increased but adsorption density, the amount adsorbed per unit mass, decreased. It is readily understood that the number of available adsorption sites increased by increasing the adsorption dose. The decrease in adsorption density with increase in the adsorbent dose is mainly due to unsaturation of adsorption sites through the adsorption reaction. Another reason may be due to the particle interactions, such as aggregation, resulting from high sorbent concentration. Such aggregation would lead to a decrease in the total surface area of the sorbent.

Chapter 4

Results and Discussions

4.1 Adsorption Studies

All adsorption experiments were carried out in batch. A preliminary adsorption was conducted using a solution of Pb(II), Cr(VI), Cd(II), As(V).

4.1.1 Test and Standard Metal Ion Solutions

Stock solution of concentration of about 1000 mg.L^{-1} of each of the Pb(II), Cr(VI), Cd(II), As(V) by using lead nitrate (1.598g), potassium dichromate (2.83g), Cadmium nitrate (2.10g), sodium arsenate (4.163g) respectively, followed by dilution to 1000 mL using DDW. Various concentrations of test solutions of single Pb(II) [40,41,53], Cr(VI) [43,44,45,46,47,48,49,50], Cd(II) [42,52], As(V) [47,51]were prepared by subsequent dilution of the respective stock solution using DDW. The initial pH of test solutions were adjusted to selected values using 0.01N HCl and 0.01N NaOH.

4.1.2 Adsorption Equilibrium Studies: Metal Cations

All batch adsorption experiments were carried out at room temperature using 0.15 g dried GBC (CT+TT), which is 1.5 N KOH activated having 50 mL metal ion solution in a screw cap conical flask. That is, adsorbent concentration was kept constant at 3g.L^{-1}. At the end of adsorption experiment, solutions were separated by filtration then followed by centrifugation.

4.2 Adsorption Equilibrium Studies: Pb(II)

The adsorption equilibrium data were obtained by varying pH from 2 to 9 while the initial metal ion concentrations; mass of activated carbon, contact time, shaking rate were kept constant. The pH of the aqueous solution is an important controlling parameter in the -
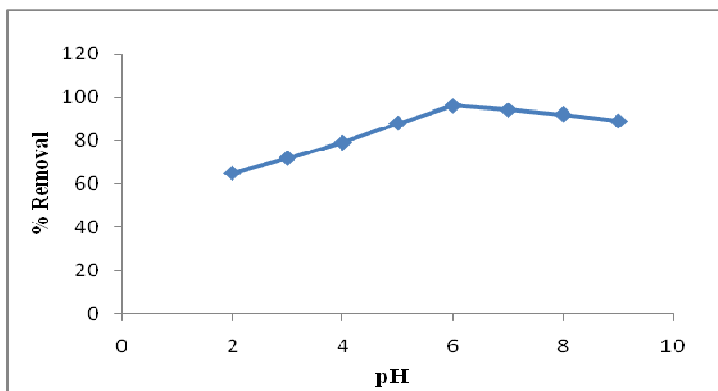

Figure 4.1 Effect of initial pH on the % Removal 50 ppm of Pb(II) metal ions using GBC (CT+TT)

-adsorption process. The binding of metal ions by surface functional groups is strongly pH dependent. To observe the effect of pH, adsorption was conducted within the pH range of 2 to 9 for the GBC (CT+TT). The effect of pH on removal of lead is shown in Fig 4.1. The analysis of the results shows that adsorption of Pb is maximum at equilibrium pH 6. At this pH, time was varied from 0 to 2 hr and samples were kept overnight and analysed, which shows that 70 to 90 min is the time, when equilibrium was almost achieved.
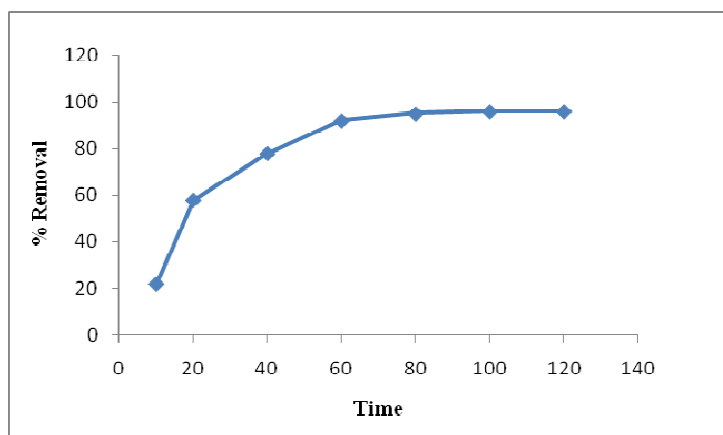

Figure 4.2 Effect of time on the % Removal of 50 ppm Pb(II) metal ions using GBC (CT+TT)

The equilibration time is one of the parameters for economical wastewater treatment plant applications. Fig. 4.2 shows the effect of contact time on removal of lead; the adsorption of lead increased as a function of time up to 50 min initial concentration of 50 mg/L and remained almost constant. The rate of sorption of lead on activated carbon was rapid, with 60–70% of lead adsorption occurring within the first 30-40 min and attaining equilibrium was at 70-90 min.
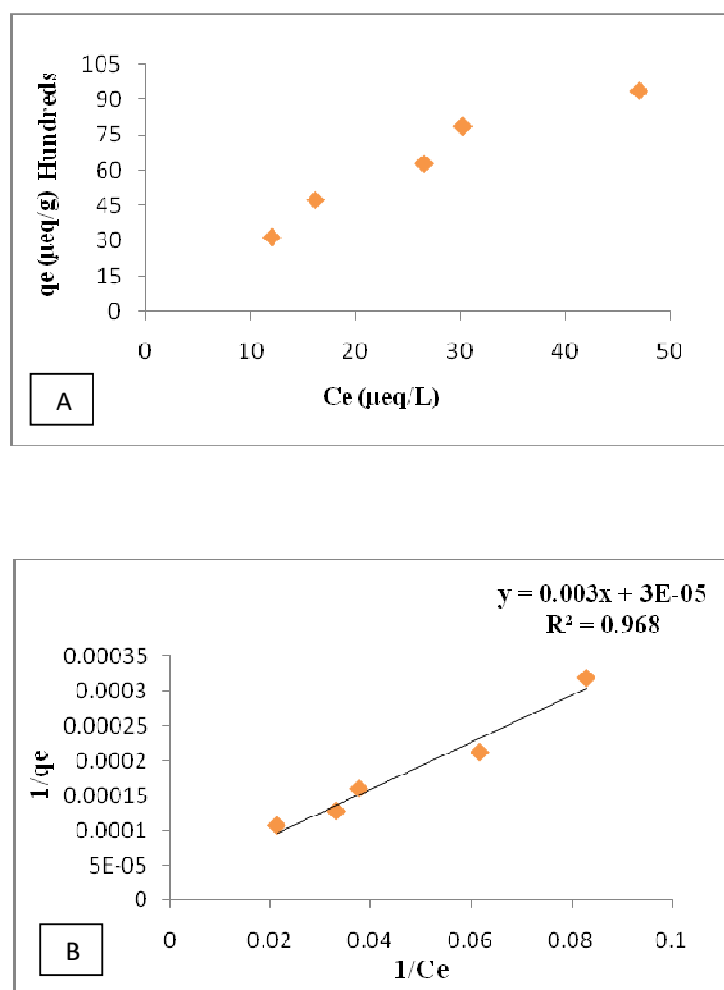

Figure 4.3 Langmuir non-linear (A) and linear (B) adsorption isotherm of Pb(II) at initial pH 6 by using GBC (CT+TT) while initial concentrations were Varied from 50 to 150 mg.L^{-1}.

This behavior suggests that at the initial stage, sorption takes place rapidly on the external surface of the sorbent followed by a slower internal diffusion process, which may be the rate determining step. The trend in adsorption Pb suggests that the binding may be through interactions with functional groups located on the surface of the activated carbon. According to these results, the agitation time was fixed as 2 h for the rest of the batch experiments to make sure that equilibrium was attained.

Effect of initial solution concentrations: Figures 4.3 (A) and 4.3(B) show the Langmuir and Freundlich adsorption isotherms of Pb(II), for an initial pH 6, using GBC(CT+TT). The physical parameters for the adsorption of Pb(II) are determined from the linear Langmuir (Figures 4.3(B)) and Freundlich (Figure 4.3(C)) isotherms and are tabulated in Table 4.1.

The values of correlation coefficients (see Table 4.1) of all Langmuir adsorption isotherms indicate that this model fits all the adsorption equilibrium data very well throughout the experimental range of study. GBC(CT+TT) shows higher adsorption capacity as well as stronger affinity towards Pb(II) which is also evident from the H-type isotherms (Figure 4.3(A)).
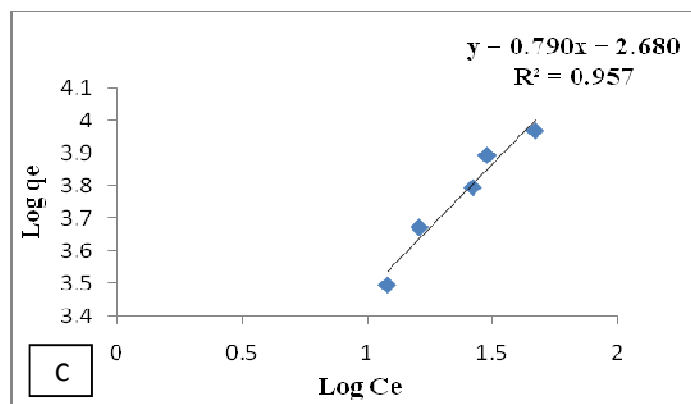

Figure 4.3: Freundlich adsorption isotherm (C) of Pb(II) at initial pH 6 by using GBC (CT+TT) while initial concentrations were varied from 50 to 150 mg.L^{-1}.

The adsorption data by all activated carbons are also fitted to Freundlich model, but the better fitting is observed with the Langmuir model.

Table 4.1 : Langmuir and Freundlich model parameters for the adsorption of Pb(II) at initial pH 6 and at varying concentrations from 50 to 150 mg.L^{-1}.

Langmuir			
Slope	Intercept	Qa	b
0.003	0.00003	33333.33	0.01

freundlich			
Slope	Intercept	kf	n
0.79	2.68	478.6301	0.79

The comparatively higher values of kf and "n" (see Table 4.1) by GBAC indicate that Pb(II) is more strongly bound onto the surface of GBAC. The contradiction to the values of qmax and kf may arise from the different mechanism of adsorption of Pb(II) as soft cation.

Table 4.2 : The initial and equilibrium concentrations, and fractions removal of Pb(II) by GBC (CT+TT) in the low concentration range at pH 6.(contact time = 120 minutes, adsorbent dose=0.15gm/50ml)

Sr. no.	Co ppm	Co meq	Co microeq	Ce ppm	Ce meq	Ce microeq
1	50.00	0.48	482.63	1.25	0.01	12.07
2	75.00	0.72	723.94	1.68	0.02	16.22
3	100.00	0.97	965.25	2.75	0.03	26.54
4	125.00	1.21	1206.56	3.13	0.03	30.21
5	150.00	1.45	1447.88	4.87	0.05	47.01

Sr. no.	Do	qe= (Co-Ce)/Do	1/Ce	1/qe	Log Ce	Log qe
1	0.15	3137.07	0.08	0.00	1.08	3.50
2	0.15	4718.15	0.06	0.00	1.21	3.67
3	0.15	6258.04	0.04	0.00	1.42	3.80
4	0.15	7842.34	0.03	0.00	1.48	3.89
5	0.15	9339.12	0.02	0.00	1.67	3.97

Table 4.3 : Langmuir and Freundlich model parameters, developed from experimental results for the adsorption of Pb(II) at initial pH 6 and at varying concentrations from 50 to 850 mg/L

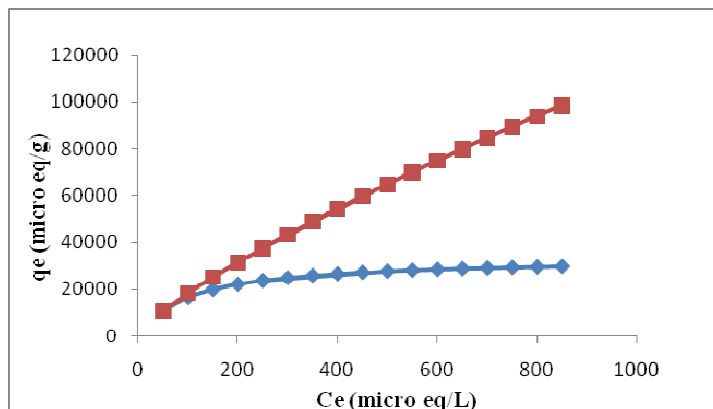| Langmuir		Freundlich	
Ce	qe	Ce	qe
50	11111.11	50	10524.13
100	16666.67	100	18197.01
150	20000	150	25067.56
200	22222.22	200	31463.98
250	23809.52	250	37529.49
300	25000	300	43343.68
350	25925.93	350	48956.88
400	26666.67	400	54403.57
450	27272.73	450	59708.74
250	23809.52	250	37529.49
500	27777.78	500	64891.27
550	28205.13	550	69965.92
600	28571.43	600	74944.45
650	28888.89	650	79836.51
700	29166.67	700	84650.1
750	29411.76	750	89391.95
800	29629.63	800	94067.82
850	29824.56	850	98682.68

Fig. 4.4: Langmuir and Freundlich model Response, developed from experimental results for the adsorption of Pb(II) at initial pH 6 and at varying concentrations from 50 to 850 mg/L

The results reveal the suitability of base activated carbons in the removal of Pb(II) (above 96%) and thus it is expected to be useful for the removal of Pb(II) in wastewater purification.

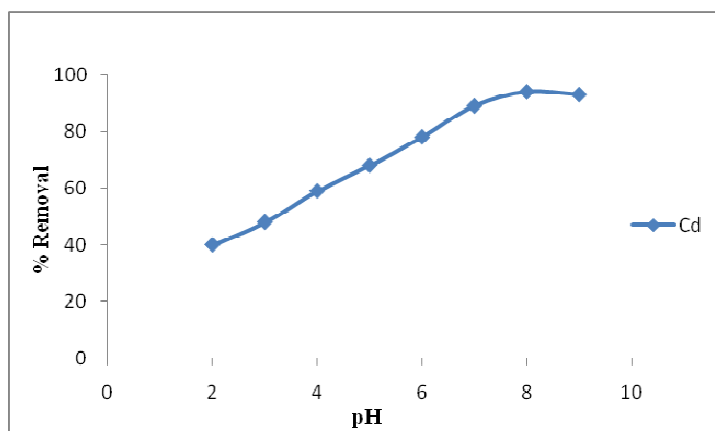## 4.3 Adsorption Equilibrium Studies: Cd(II)

Figure 4.5 : Effect of initial pH on the % Removal of Cd(II) metal ions using GBC (CT+TT)

The pH of the aqueous solution is an important controlling parameter in the adsorption process. The binding of metal ions by surface functional groups is strongly pH dependent. The effect of pH on removal of Cadmium is shown in Fig 4.5. The analysis of the results shows that adsorption of Cd is maximum at equilibrium pH 8. At this pH 8 time was varied from 0 to 2 hr and samples were kept overnight and analyzed, which shows that 80 to 100 min is the time, when equilibrium was almost achieved.
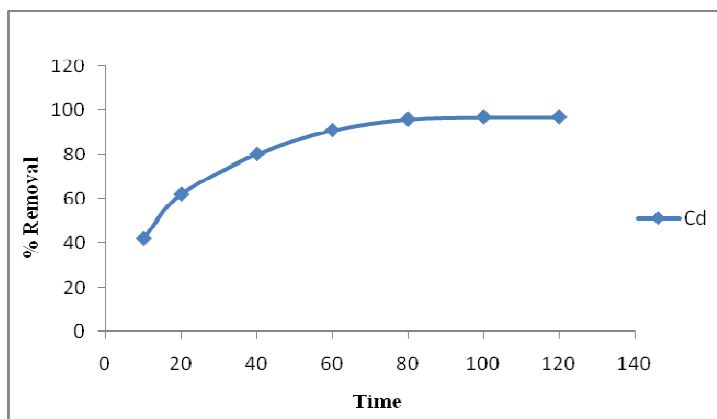

Figure 4.6 **:** Effect of time on the % Removal of 50 ppm Cd(II) metal ions using GBC (CT+TT)

The equilibration time is one of the parameters for economical wastewater treatment plant applications. Fig. shows the effect of contact time on removal of cadmium; the adsorption of cadmium increased as a function of time up to 70 min at an initial concentration of 50 mg/L and remained almost constant. The rate of sorption of cadmium on activated carbon was rapid, with 60–70% of lead adsorption occurring within the first 20-30 min and attaining equilibrium was at 70-90 min.
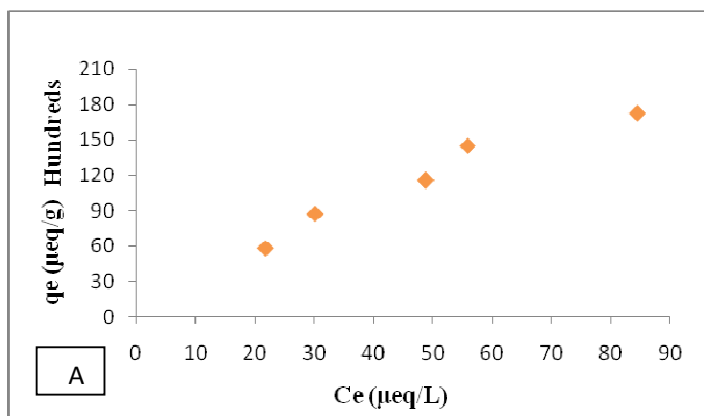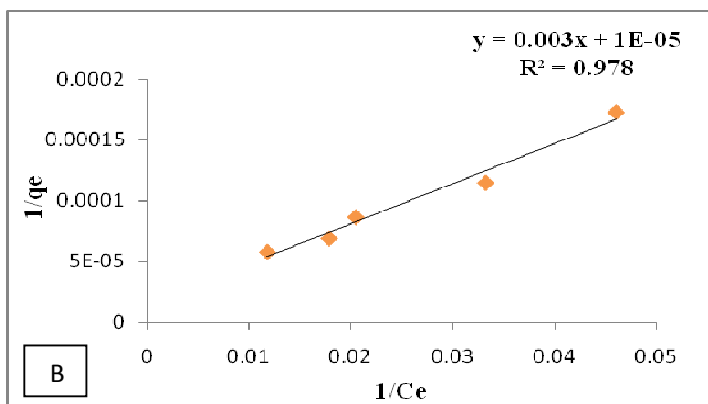
Figure 4.7 Langmuir non-linear (A) and linear (B) adsorption isotherm of Cd(II) at initial pH 8 by GBC (CT+TT) while initial concentrations were Varied from 50 to 150 mg.L^{-1}.

This behavior suggests that at the initial stage, sorption takes place rapidly on the external surface of the sorbent followed by a slower internal diffusion process, which may be the rate determining step. The trend in adsorption Cd suggests that the binding may be through interactions with functional groups located on the surface of the activated carbon. According to these results, the agitation time was fixed as 2 h for the rest of the batch experiments to make sure that equilibrium was attained.

Effect of initial solution concentrations: Figures 4.7(b) and 4.7(c) show the Langmuir and Freundlich adsorption isotherms of Cd(II), for an initial pH 8, by GBC (CT+TT). The physical parameters for the adsorption of Cd(II) are determined from the linear Langmuir (Figures 4.7(B)) and Freundlich (Figure 4.7(C)) isotherms and are tabulated in Table 4.5.
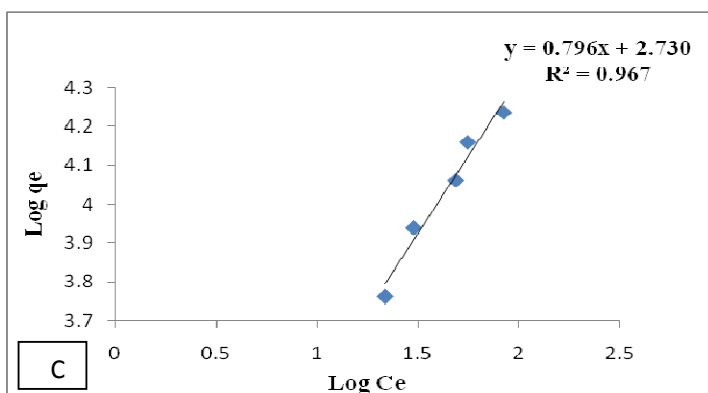

Figure 4.7 Freundlich adsorption isotherm(C) of Cd(II) at initial pH 8 by GBC (CT+TT) while initial concentrations were varied from 50 to 150 mg.L^{-1}.

The values of correlation coefficients (see Table 4.4) of all Langmuir adsorption isotherms indicate that this model fits all the adsorption equilibrium data very well throughout the experimental range of study. GBC (CT+TT) shows higher adsorption capacity as well as stronger affinity towards Cd(II) which is also evident from the H-type isotherms (Figure 4.7(A)).The adsorption data by all activated carbons are also fitted to Freundlich model, but the better fitting is observed with the Langmuir model.

Table 4.4 : Langmuir and Freundlich model parameters for the adsorption of Cd(II) at initial pH 8 and at varying concentrations from 50 to 150 mg.L^{-1}.

Langmuir			
Slope	Intercept	Qa	b
0.003	0.00001	100000	0.0033

Freundlich			
Slope	Intercept	kf	n
0.796	2.73	537.0318	0.796

The comparatively higher values of kf and "n" (see Table 4.4) by GBC (CT+TT) indicate that Cd(II) is more strongly bound onto the surface of GBC (CT+TT). The contradiction to the values of qmax and kf   may arise from the different mechanism of adsorption of Cd(II) as soft cation.

Table 4.5: The initial and equilibrium concentrations, and fractions removal of Pb(II) by GBAC in the low concentration range at pH 8.(contact time = 120 minutes, adsorbent dose=0.15gm/50ml)

Sr. no.	Co ppm	Co meq	Co microeq	Ce ppm	Ce meq	Ce microeq
1	50.00	0.89	889.59	1.22	0.02	21.71
2	75.00	1.33	1334.39	1.69	0.03	30.07
3	100.00	1.78	1779.19	2.74	0.05	48.75
4	125.00	2.22	2223.98	3.14	0.06	55.87
5	150.00	2.67	2668.78	4.75	0.08	84.51

Sr. no.	Do	qe= (Co-Ce)/Do	1/Ce	1/qe	Log Ce	Log qe
1	0.15	5785.91	0.05	0.00	1.34	3.76
2	0.15	8695.47	0.03	0.00	1.48	3.94
3	0.15	11536.24	0.02	0.00	1.69	4.06
4	0.15	14454.10	0.02	0.00	1.75	4.16
5	0.15	17228.44	0.01	0.00	1.93	4.24

Table 4.6: Langmuir and Freundlich model parameters, developed from experimental results for the adsorption of Cd(II) at initial pH 8 and at varying concentrations from 50 to 850 mg/L

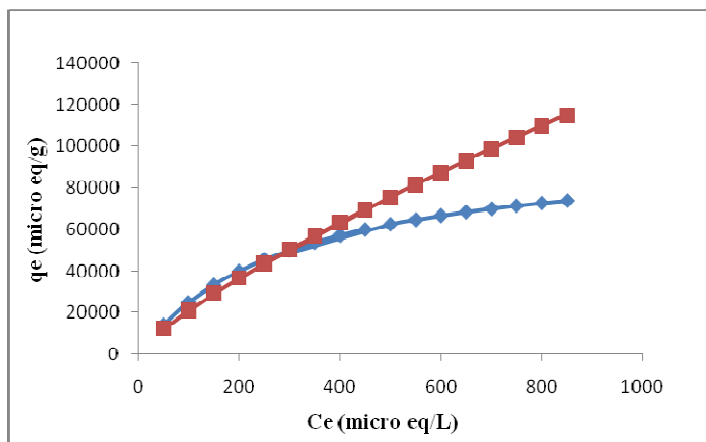| Langmuir		Freundlich	
Ce	qe	Ce	qe
50	14285.71	50	12088.71
100	25000	100	20989.4
150	33333.33	150	28984.69
200	40000	200	36443.48
250	45454.55	250	43527.15
300	50000	300	50325.55
350	53846.15	350	56895.53
400	57142.86	400	63276.11
450	60000	450	69495.58
250	45454.55	250	43527.15
500	62500	500	75575.34
550	64705.88	550	81532.11
600	66666.67	600	87379.27
650	68421.05	650	93127.73
700	70000	700	98786.6
750	71428.57	750	104363.5
800	72727.27	800	109865.1
850	73913.04	850	115296.9

Fig. 4.8: Langmuir and Freundlich model Response, developed from experimental results for the adsorption of Cd(II) at initial pH 8 and at varying concentrations from 50 to 850 mg/L

The results reveal the suitability of base activated carbons in the removal of Cd(II) (above 94%) and thus it is expected to be useful for the removal of Cd(II) in wastewater purification.

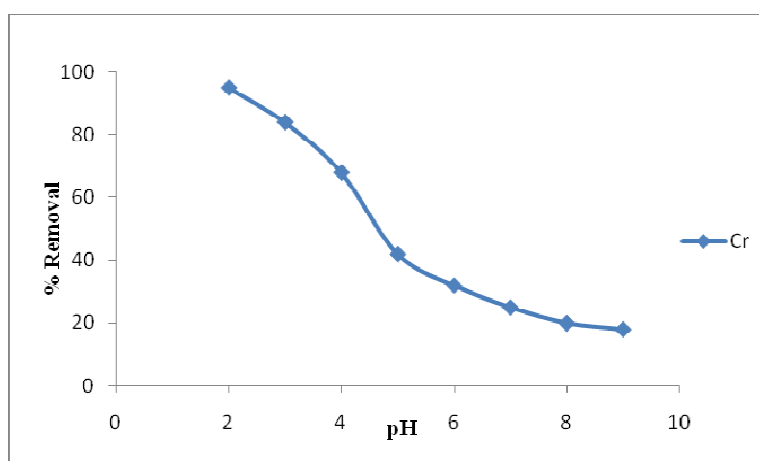## 4.4 Adsorption Equilibrium Studies: Cr(VI)

Figure 4.9 Effect of initial pH on the % Removal of 50 ppm Cr(VI) metal ions using GBC (CT+TT)

The pH of the aqueous solution is an important controlling parameter in the adsorption process. The binding of metal ions by surface functional groups is strongly pH dependent. The effect of pH on removal of chromium is shown in Fig 4.9. The analysis of the results shows that adsorption of Cr is maximum at equilibrium pH 2, at pH 2 time was varied from 0 to 2 hr and samples were kept overnight and analysed, which shows that 80 to 100 min is the time, when equilibrium was almost achieved.

Hexavalent chromium exists in different forms in aqueous solution such as $HCrO^{4\,-}$, $Cr_2O_7^{\,2-}$, CrO^{4-} and the stability of these forms is mainly dependent on the pH of the system [43]. The behavior for better adsorption at low pH by activated carbon may be attributed to the large number of H+ ions present at low pH values which in turn neutralize the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion of chromate ions [44,45]. It is well known that the dominant form of Cr(VI) between pH 1.0 and 4.0 is $HCrO^{4-}$ [48,50]. So that $HCrO^{4-}$ is adsorbed preferentially on carbon. The decrease in removal at higher pH may be due to abundance of OH^- ions causing increased hindrance to diffusion of dichromate ions. Increasing the pH will shift the concentration of $HCrO^{4-}$ to other forms.
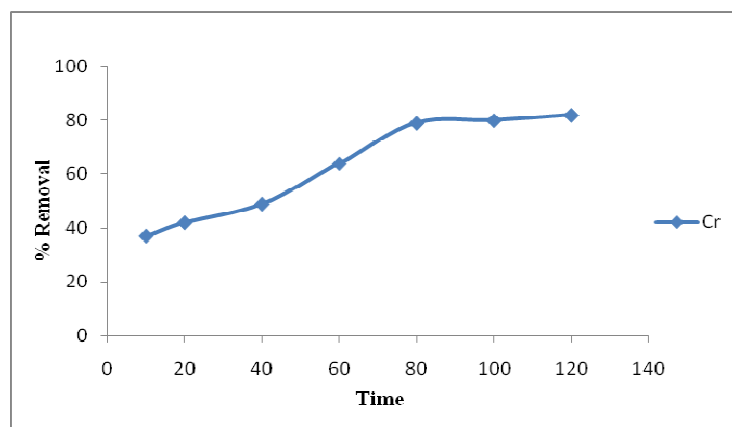

Figure 4.10 Effect of time on the % Removal of 50 ppm Cr(VI) metal ions using GBC (CT+TT)

The equilibration time is one of the parameters for economical wastewater treatment plant applications. Fig 4.9 shows the effect of contact time on removal of Chromium; the adsorption of lead increased as a function of time up to 80 min at an initial concentration of

50 mg/L and remained almost constant. The rate of sorption of Chromium on activated carbon was slowly increased as compared to Pb and Cd, with only 40–60% of chromium adsorption occurring within the first 40-60 min and attaining equilibrium was at 90-100 min. According to these results, the agitation time was fixed as 2 h for the rest of the batch experiments to make sure that equilibrium was attained.
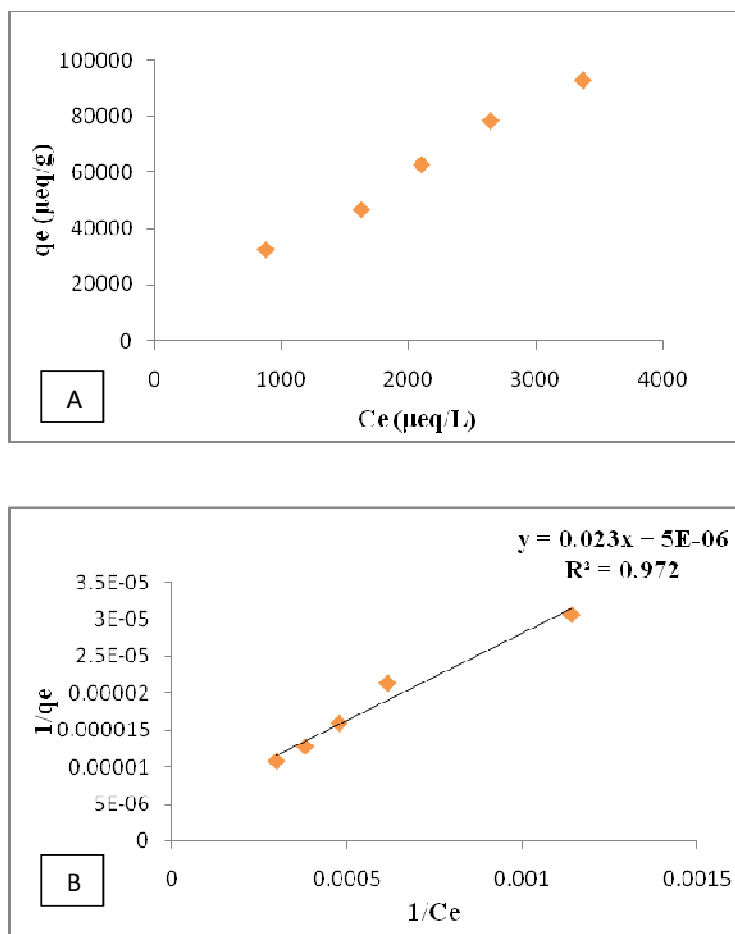

Figure 4.11 : Langmuir non-linear (A) and linear (B) adsorption isotherm of Cr(VI) at initial pH 2 by GBAC while initial concentrations were Varied from 50 to 150 mg.L^{-1}.

Effect of initial solution concentrations: Figures 4.10(B) and 4.10(C) show the Langmuir and Freundlich adsorption isotherms of Cr(VI),for an initial pH 2, by GBC (CT+TT). The-physical parameters for the adsorption of Cr(VI) are determined from the linear Langmuir (Figures 4.10(B)) and Freundlich (Figure 4.10(C)) isotherms and are tabulated in Table 4.7.

The values of correlation coefficients (see Table 4.7) of all Langmuir adsorption isotherms indicate that this model fits all the adsorption equilibrium data very well throughout the experimental range of study. GBC (CT+TT) shows higher adsorption capacity as well as stronger affinity towards Cr(VI) which is also evident from the H-type isotherms (Figure 4.1(a)).
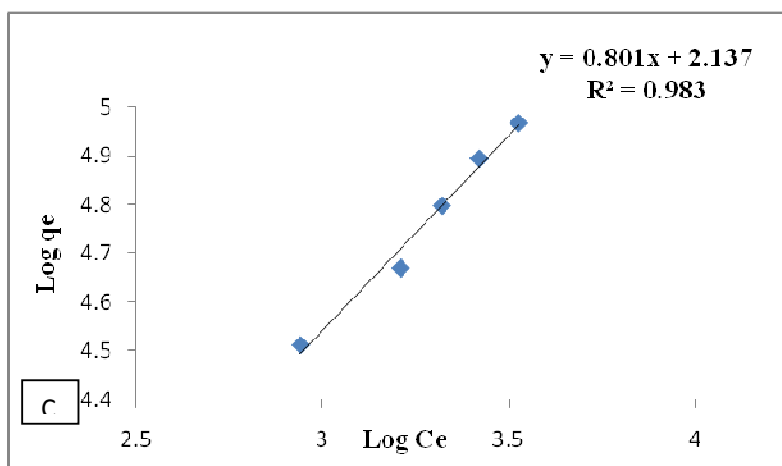

Figure 4.11 Freundlich adsorption isotherm (C) of Cr(VI) at initial pH 3 by GBC (CT+TT) while initial concentrations were varied from 50 to 150 mg.L^{-1}.

The adsorption data by all activated carbons are also fitted to Langmuir model, but the better fitting is observed with the Freundlich model.

The comparatively higher values of k_f and "n" (see Table 4.7) by GBAC indicate that Cr(VI) is more strongly bound onto the surface of GBC (CT+TT).

Table 4.7 : Langmuir and Freundlich model parameters for the adsorption of Cr(VI) at initial pH 2 and at varying concentrations from 50 to 150 mg.L^{-1}.

Langmuir	Slope	Intercept	Qa	b
	0.023	0.000005	200000	0.000217391
Freundlich	Slope	Intercept	kf	n
	0.801	2.137	137.0882	0.801

Table 4.8 : The initial and equilibrium concentrations, and fractions removal of Cr(VI) by GBC (CT+TT) in the low concentration range at pH 2.(contact time = 120 minutes, adsorbent dose=0.15gm/50ml)

Sr. no.	Co ppm	Co meq	Co microeq	Ce ppm	Ce meq	Ce microeq
1	50.00	5.77	5769.67	7.60	0.88	876.99
2	75.00	8.65	8654.51	14.10	1.63	1627.05
3	100.00	11.54	11539.35	18.20	2.10	2100.16
4	125.00	14.42	14424.19	22.90	2.64	2642.51
5	150.00	17.31	17309.02	29.20	3.37	3369.49

Sr. no.	Do	qe= (Co-Ce)/Do	1/Ce	1/qe	Log Ce	Log qe
1	0.15	32617.89	0.0011	0.00003	2.94	4.51
2	0.15	46849.76	0.0006	0.00002	3.21	4.67
3	0.15	62927.92	0.0005	0.00002	3.32	4.80
4	0.15	78544.50	0.0004	0.00001	3.42	4.90
5	0.15	92930.23	0.0003	0.00001	3.53	4.97

The equilibrium concentrations and fractions removal of Cr(VI), in the low concentration, are shown in Table 4.8. The results reveal the suitability of base activated carbons in the removal of Cr(VI) (above 94%) and thus it is expected to be useful for the removal of Cr(VI) in wastewater purification
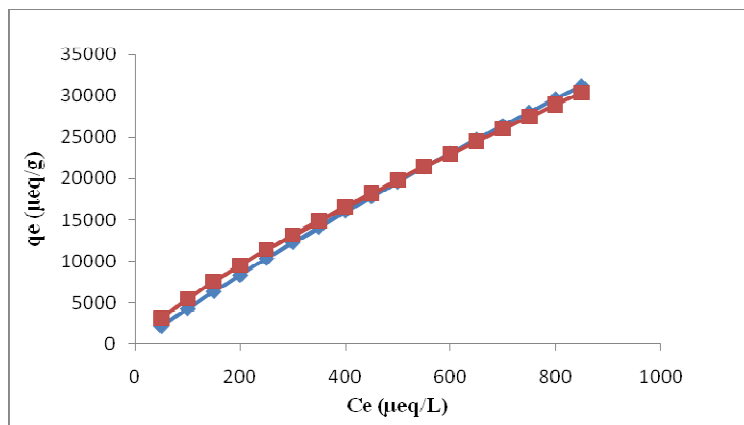
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Fig. 4.12: Langmuir and Freundlich model Response, developed from experimental results for the adsorption of Cr(VI) at initial pH 2 and at varying concentrations from 50 to 850 mg/L

Table 4.9 : Langmuir and Freundlich model parameters, developed from experimental results for the adsorption of Cr(VI) at initial pH 2 and at varying concentrations from 50 to 850 mg/L

Langmuir		Freundlich	
Ce	qe	Ce	qe
50	2150.538	50	3146.842
100	4255.319	100	5482.77
150	6315.789	150	7586.633
200	8333.333	200	9552.676
250	10309.28	250	11422.2
300	12244.9	300	13218.25
350	14141.41	350	14955.42
400	16000	400	16643.71
450	17821.78	450	18290.4
250	10309.28	250	11422.2
500	19607.84	500	19901
550	21359.22	550	21479.81
600	23076.92	600	23030.28
650	24761.9	650	24555.21
700	26415.09	700	26056.95
750	28037.38	750	27537.47
800	29629.63	800	28998.47
850	31192.66	850	30441.4

4.5 Adsorption Equilibrium Studies: As(V)

Adsorption of Arsenic(V) on activated carbon was carried out using a bath experiments method in a mechanical shaker. The effect of solution pH, contact time was investigated by using Arsenic kit supplied by Transchem Agritech Limited, Gujarat. The adsorption process-
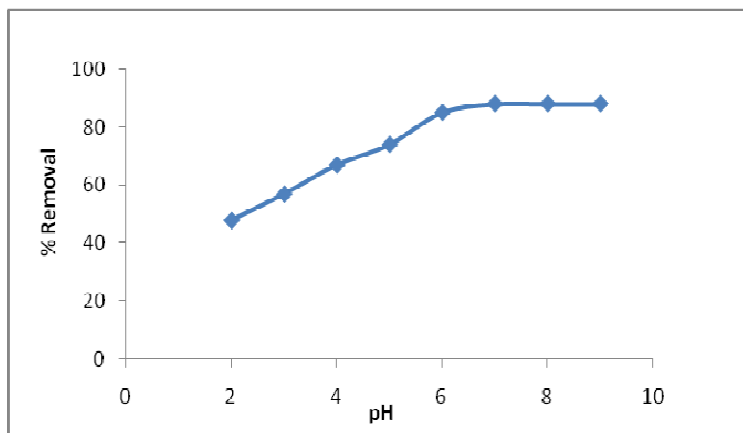

Figure 4.13 Effect of pH on the adsorption(%) of As(V) 50 ppm using GBC (CT+TT)
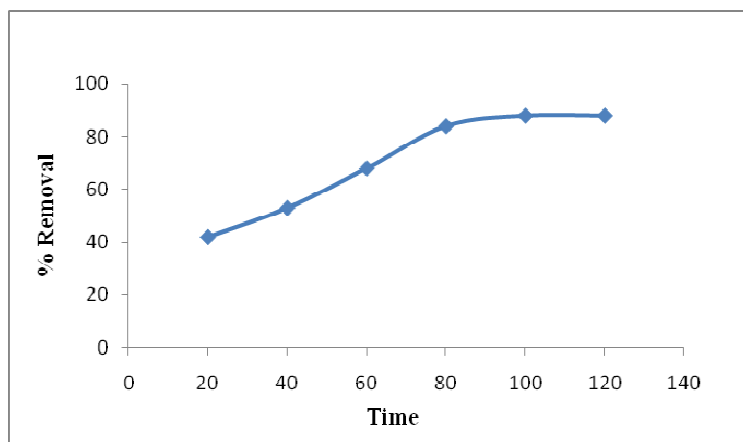Condition: contact time = 120 minutes, adsorbent dose=0.15gm/50ml

Figure 4.14 Effect of time on the adsorption(%) of methylene blue 100 ppm using GBC (CT+TT) Conditions: initial pH of As(V) solution =7; adsorbent dose=0.15gm/50ml

-was carried out with initial concentrations at 50 ppm. In the pH study, the pH of As(V) solution was adjusted in the range of 2-9 by adding 0.1N hydrochloric acid or 0.1 N sodium hydroxide. About 0.15 g adsorbent was then added to the solution and shaken at predetermined time.

The effect of contact time was used to determine equilibrium time for the adsorption at optimized pH 8. For the effect of contact time study, 50 ml of As(V) solution was added into a screw cap conical flask containing 0.15 g activated carbon and shaken constantly. All samples were withdrawn from the conical flasks and the As(V) solutions were separated from the adsorbent by filtration then followed by centrifugation. Metal concentrations in the solutions were estimated using Arsenic kit by following its standard method.

4.6 Results summary

The prepared activated carbons show the potential in removing borderline and soft metal ions from the solutions over a wide range of concentrations and pH. The adsorption of anions of-
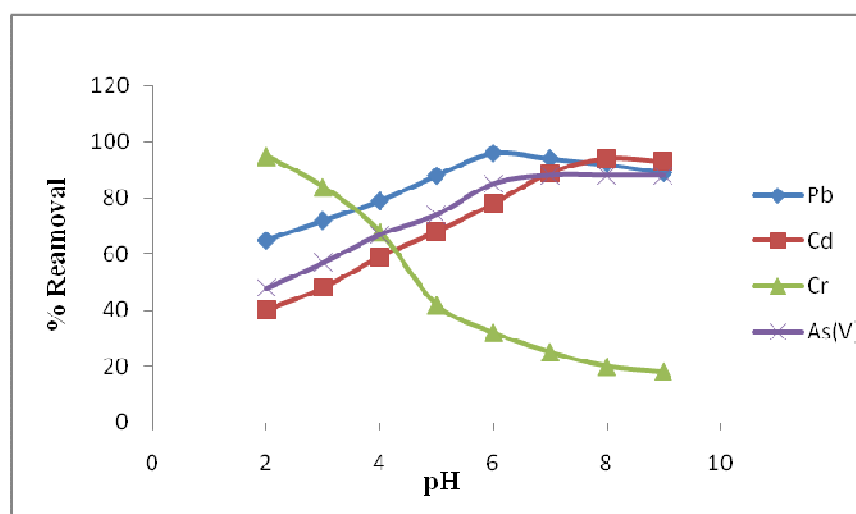

Fig 4.15: Effect of pH on the adsorption(%) of Pb(II), Cr(VI), Cd(II), As(V) : 50 ppm using GBC (CT+TT), Condition: contact time = 120 minutes, adsorbent dose=0.15gm/50ml

Table 4.10: Effect of pH on the adsorption(%) of Pb(II), Cr(VI), Cd(II), As(V) : 50 ppm using GBC (CT+TT), Condition: contact time = 120 minutes, adsorbent dose=0.15gm/50ml

pH	Pb	Cd	Cr	As(V)
2	65	40	93	48
3	72	48	84	57
4	79	59	68	67
5	88	68	42	74
6	96	78	32	85
7	94	89	25	88
8	92	94	20	88
9	89	93	18	88

-Cr(VI) is highly pH dependable, that optimizes at pH 2 with an decreasing trend with the increase of pH. For another metal ions like -Pb(II), Cd(II), As(V) were adsorbed optimum at pH 6,8,7 Respectively.
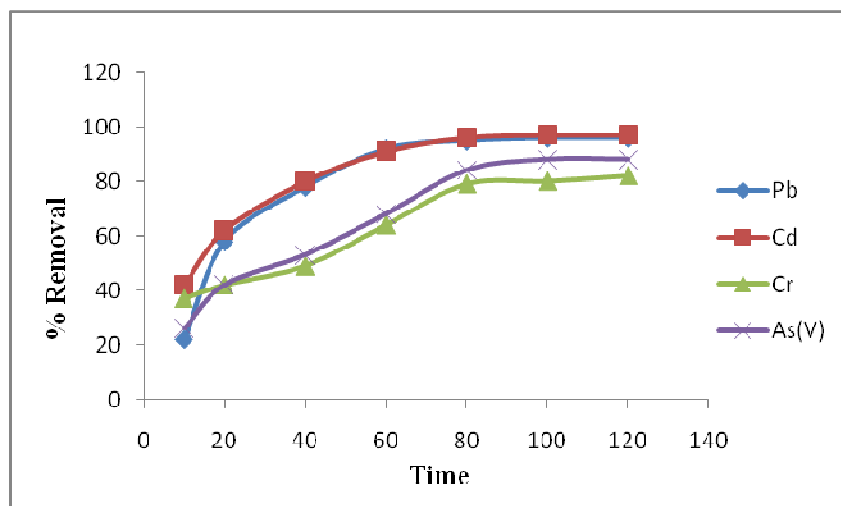

Fig. 4.16: Effect of time on the adsorption(%) of Pb(II), Cr(VI), Cd(II), As(V) : 50 ppm using GBC (CT+TT), Condition: optimum pH for all metal ions, adsorbent dose=0.15gm/50ml

Table 4.11: Effect of time on the adsorption(%) of Pb(II), Cr(VI), Cd(II), As(V) : 50 ppm using GBC (CT+TT), Condition: optimum pH for all metal ions, adsorbent dose=0.15gm/50ml

Time	Pb	Cd	Cr	As(V)
10	22	42	37	26
20	58	62	42	42
40	78	80	49	53
60	92	91	64	68
80	95	96	79	84
100	96	97	80	88
120	96	97	82	88

Almost all metal ions adsorption uptake rate was increase with time. Samples were collected at 10, 20, 40, 60, 80, 100, 120 min time span. In case of lead and arsenic almost 40% metal ions were adsorbed and it was almost 60% for that of cadmium and chromium for their optimized pH.

Chapter 5

Conclusions and Future Scope

5.1 Conclusions

The present study shows that gasifier based waste can be effectively used as precursor material for the preparation of activated carbon. As the raw material for preparing the activated carbon is a discarded or sell having lowest economic value by the industries, which are using gasifiers. Due to an adequate chemical and thermal activation this waste yielded a porous adsorbent that displays an interesting and promising adsorbent possessing a relatively high surface area (715 m2 g^{-1}), while activated with KOH, in the remediation of toxic species of metals. It is observed that acid chemical treatment controls volatile evolution. Chemical treatment of raw material with KOH extends the impregnation step of KOH activation resulting in the good BET surface area.

The prepared activated carbons show the potential in removing borderline and soft metal ions from the solutions over a wide range of concentrations and pH. The adsorption of anions ofCr(VI) is highly pH dependable, that optimizes at pH 2 with an decreasing trend with the increase of pH. For another metal ions like -Pb(II), Cd(II), As(V) were adsorbed optimum at pH 6,8,7 Respectively.

Almost all metal ions adsorption uptake rate was increase with time. Samples were collected at 10, 20, 40, 60, 80, 100, 120 min time span. In case of lead and arsenic almost 40% metal ions were adsorbed and it was almost 60% for that of cadmium and chromium for their optimized pH.

Max.% Removal efficiency achieved at optimized pH and single solute solution: lead (96%), cadmium (94%), chromiumVI (93%), arsenicV (88%)

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The main limitation in the preparation of activated carbon in this study is that the atmosphere of muffled furnace was not defined. The leakage of air through the door controls the furnace atmosphere by design default.

5.2 Future Scope

- Since preliminary investigations show the feasibility of H_3PO_4 activated carbon as metal ion scavenger, further studies are needed with actual water in a pilot plant and in a modular unit column to evaluate full-scale drinking or wastewater treatment.

- The adsorption studies are also needed to be extended for the remediation of some other metal ions, namely Fe(II), Mn(II), Hg(II) and Cd(II) etc. as well as for some organic compounds, namely benzene, toluene, dioxane, acetonitrile, acetone and methanol.

- The removal capacities for As(V) were determined by Arsenic Removal kit not by sophisticated instrument like AAS . Further studies are needed to predict the adsorption behavior as well as to scrutinize the best composite adsorbent. Studies are also needed to optimize the initial solution pH for As(V) adsorption and to observe the competitive effect of competing ions such as, Cl-, SO_4^{2-} and PO_4^{3-}

- Therefore, still some works have to do to develop a modular filtering unit to be used in a home water condition unit or in a fixed bed in water treatment plant for a complete

solution to the contaminated, minor to trace level, drinking water supply or source or to the wastewater stream.

- The most difficult and important part of the whole process is washing of the produced activated carbon from acids. A special technique should be used facilitate this process. The produced activated carbon should be tested against different contaminants from either industrial wastewater.

- A similar study should be conducted using chlorinated secondary effluent.

- The produced activated carbon should be tested for the possibility of regeneration.

- Standard stock solutions should be used for the calibration curve set up in the AAS and UV visible photospectrometer.

- Further investigation should be done over a wide concentration range of solutions and development of kinetics and adsorption model to get the full picture on the performance of the produced activated carbon.

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