PREPARATION, MODIFICATION AND CHARACTERIZATION OF ACTIVATED CARBONS FOR BATCH ADSORPTION STUDIES ON THE REMOVAL OF SELECTED METAL IONS

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This thesis is dedicated to the memories of my beloved late father

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ABSTRACT

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, various activated carbons have been prepared by phosphoric acid activation from oil palm and coconut shells to study the effect of preparation variables and metal removal capacity. Characterizations were done for the observation of surface area, pore development, textural structure, surface functional groups and its acidity. Thus preparation was customized for carbon with high surface area and wider micro- and mesopores, suitable for removing metal ions. Modification was conducted by dispersing hydrated iron-oxide onto carbon for selective removal of arsenic. Application was tested through batch adsorption in single, binary and ternary 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, copper(II) (25 $mg.g^{-1}$), nickel(II) (20 $mg.g^{-1}$), zinc(II) (10 $mg.g^{-1}$), and lead(II) (75 $mg.g^{-1}$), compared to that of commercial ones. Adsorption in binary solution shows that hard cation, calcium(II) is not at all competent to borderline cations while the mechanism is assessed as inner-sphere complexation. For low concentration range, ternary-solute adsorption shows the following selectivity order, Ni(II) $\leq$ Pb(II) $\leq$ Cu(II). Adsorption capacity of prepared activated carbon for Cr(VI) is saturated at 46 $mg.g^{-1}$. Although the adsorption capacity of commercial activated carbon dramatically decreases with the lowering of initial solute concentration, it shows a higher monolayer adsorption capacity (71 $mg.g^{-1}$). The modification significantly enhances the adsorption capacity for As(III) (1.5 $mg.g^{-1}$) and As(V) (1.0 $mg.g^{-1}$) than that of parent carbon. The developed activated carbons and modified adsorbents are 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.

ABSTRAK

Di antara pelbagai jenis bahan pencemar yang terdapat di dalam air sisa dan air minuman, spesies-spesies tak organik adalah pencemar utama dan sukar untuk disingkirkan disebabkan oleh saiznya yang lebih kecil, kepekatan yang rendah dan persaingan dengan spesies-spesies yang tidak toksik. Dalam kajian ini, pelbagai jenis karbon teraktif telah disediakan daripada tempurung kelapa sawit dan kelapa melalui pengaktifan asid fosforik untuk mengkaji kesan bagi pelbagai pembolehubah dalam penyediaan serta kapasiti penyingkiran logam. Pencirian telah dijalankan dengan memerhatikan luas permukaan, pembangunan keliangan, struktur tekstur, kumpulan berfungsi pada permukaan dan keasidannya. Justeru, penyediaan karbon dengan luas permukaan yang tinggi dan keliangan mikro serta meso yang lebih besar, adalah sesuai untuk penyingkiran ion-ion logam yang telah dikenalpasti. Pengubahsuaian dilakukan dengan penyebaran ferum oksida terhidrat ke atas karbon bagi kepilihan penyingkiran arsenik. Penggunaannya telah dikaji melalui penjerapan berkelompok di dalam larutan yang mepunyai zat terlarut tunggal, dedua atau tetiga dan data-data keseimbangan disuaikan terhadap pelbagai model keseimbangan dan kinetik. Karbon-karbon yang disediakan menunjukkan kapasiti penjerapan yang tinggi terhadap ion-ion perbatasan dan ion-ion lembut, kuprum(II) (25 mg.g^{-1}), nikel(II) (20 mg.g^{-1}), zink(II) (10 mg.g^{-1}), dan plumbum(II) (75 mg.g^{-1}), apabila dibandingkan dengan karbon komersial. Penjerapan dalam larutan dedua menunjukkan penjerapan kation-kation keras, kalsium (II) adalah lebih lemah daripada kation-kation perbatasan sementara mekanismanya didapati sebagai pengkompleksan sfera-dalaman. Bagi lingkungan kepekatan rendah, penjerapan zat terlarut tetiga menunjukkan susunan kepilihan berikut, Ni(II) $\leq$ Pb(II) $\leq$ Cu(II). Kapasiti penjerapan Cr(IV) bagi karbon teraktif yang disediakan mencapai ketepuan pada 46 mg.g^{-1}. Walaupun kapasiti penjerapan bagi karbon komersial merosot secara dramatik ketika kepekatan zat terlarut awal dikurangkan, namun ia menunjukkan kapasiti penjerapan lapisan tunggal yang lebih tinggi (71 mg.g^{-1}). Pengubahsuaian secara jelas meningkatkan kapasiti penjerapan bagi As(III) (1.5 mg.g^{-1}) dan As(V) (1.0 mg.g^{-1}) berbanding dengan karbon induk. Karbon teraktif yang dibangunkan dan penjerap yang terubahsuai diharapkan berupaya untuk menyingkirkan ion-ion logam perbatasan dan lembut serta ligan ionik dan bukan ionik bagi metaloid yang terdapat dalam air-air sisa dan air minuman.

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LIST OF SYMBOLS

°C - Degree Celsius
C_0 - Initial concentration
C_e - Equilibrium concentration
cm - Centi meter
dm - Deci meter
g - Gram
L - Liter
m - Meter
M - Molar
mA - Mili ampere
meq - Mili equivalent
mg - Mili gram
min - Minute
mL - Mili Liter
mm - Mili meter
mM - Mili Molar
nm - Nano meter
q or q_t - Metal uptake at any time, t
q_e - Metal uptake at equilibrium
t - Tonne
y - year
Å - Angstrom
µg - Micro gram
µm - Micro meter
µmol - Micro mole

LIST OF ABBREVIATIONS

AAS - Atomic absorption spectrophotometer
Av - Average
B.C. - Before Christ
BET - Brunauer, Emmett and Teller
CAC - Commercial activated carbon
DDW - Distilled deionized water
Dia - Diameter
DPC - 1,5-Diphenylcarbazide
EDL - Electric double layer
EDX - Energy dispersive X-ray analysis
EFB - Empty fruit bunches
EPA - Environment Protection Agency
Et - Ethyl
FAAS - Flame atomic absorption spectroscopy
FTIR - Fourier transform infrared spectrophotometer
GAC - Granular activated carbon
h - hour
HFO - Hydrated iron oxide
HSAB - Hard and Soft Acids and Bases
ICP-MS - Inducedly coupled plasma mass spectrophotometer
IUPAC - International Union of Pure and Applied Chemistry
Max - Maximum
MOX - Malaysian Oxygen
NOM - Naturally occurring organic matter
PAC - Powered activated carbon

QC	-	Quality control
rpm	-	Revolution per minute
RSD	-	Relative standard deviation
SCF	-	Surface complex formation
SD	-	Standard deviation
SEM	-	Scanning electron microscope
SOC	-	Synthetic organic chemicals
SOCs	-	Synthetic organic compounds
TGA	-	Thermogravimetric analysis
USA	-	United States of America
USEPA	-	United States Environment Protection Agency
UV	-	Ultra violet
VOCs	-	Volatile organic compounds
WHO	-	World Health Organization

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Ancient people were concerned about the quality of water. This awareness made the history of water treatment as old as humans. Historically, the scarcity of aesthetic quality drinking water was mitigated in most places either by digging wells or by filtering the surface water through sands. Once it was realized that clear and tasty water due to bad contaminations can cause diseases outbreak. The industrial revolution of nineteenth century added some other synthetic chemicals and heavy metals contaminants in the aquatic system. The presence of a wide range of synthetic organic chemicals (SOC) was confirmed by the Environmental Protection Agency (EPA) of USA in finished drinking water, in many locations, even those are from ground water supply (Cotruvo, Hanson and Thornton, 1983). This survey breaks the historical concept of viewing ground water as a relatively uncontaminated resource, unspoiled by the human activities that affect surface waters. The presence of even trace quantities of SOC in finished drinking water should be encountered as a major future threat to the supply water for the existing mechanism of contamination of the source by man-made pollution. It was soon realized that other than human activities, nature itself can contaminate natural waters. The natural contamination of highly toxic arsenic species in groundwater is spreading arsenic-poisoning in some part of the world and those are not affected, still in risk. As the contamination was manifested, without going through a detailed analysis and monitoring around the year, it is very hard to say whether the quality of drinking water is safe for health.

This is why regulations are imposed on permissible levels of contaminants in drinking water from the potential health risks exposure to these. To minimize human contributing pollution to a lower level, laws are also enforced to treat wastewater before discharge. Among various pollutants in drinking and wastewaters, inorganic species of metals and metalloids are major, and difficult to remove because of their smaller size, very low concentration and competition with non-toxic inorganic species. The present concern over the presence of inorganic species necessitates a cost effective, eco-friendly treatment process to remediate these contaminants from drinking water and wastewater. Therefore, it is not surprising that current research trend is focusing on the utilization of local raw materials such as agricultural wastes, as low cost eco-friendly materials, in treating drinking and wastewaters preferentially to remove inorganic toxic species. As Malaysia is moving rapidly towards the concept of healthy drinking water, her huge wastes from agricultural sector, such as oil palm kernel and coconut shells, are needed to be selected as a promising precursor in the removal of ionic- and non-ionic inorganic toxic species.

1.1.1 Water Purification

Long before the development of civilization, people noticed differences in water quality. Waters of various sources have characteristic taste whether sweet, salty, bitter, or, sour. Hippocrates suggested his colleagues to filter and boil water before drinking it. The ancient people of Egypt, Greece, Assyria, Persia and India used wells for drinking water (Ellms, 1928). Probably, wells furnished a safer drinking water than other water sources such as rivers and lakes. The treatment of waters by solid adsorbents such as sand is probably as ancient as civilization itself. The ancient people also learnt the technique of utilization of sandstone and unglazed earthen ware as domestic filtering media for purifying drinking waters. In some of the ancient water purification systems, muddy waters were settled in tanks or settling basins.

These early methods of water treatment, no doubt, were crude and imperfect, but these can be regarded as the beginnings of water purification on which modern art of water treatment technology is built. The necessity of treatment of public supply water was overlooked until the end of the nineteenth century, when cholera epidemics in England showed that infected water supplies were responsible for public disease. Over 53, 000 people died during this cholera epidemic in London in between 1848-1849 (Stevens, 1974). It was soon realized that drinking water should be free from disease causing organisms or toxic substances.

The impurities in water can be classified into three major groups such as i) suspended and colloidal matters, ii) dissolved substances and iii) biological contaminants. Suspended matters and colloidal particulates are responsible for making the water turbid. Coagulation, sedimentation and filtration are the processes usually employed to decrease the turbidity of water. Dissolved substances and some time odour and colour are resulted from the presence of inorganic and organic constituents. Dissolved impurities especially inorganic ones are difficult to remove. In the early days, lime and soda were used in the reduction of dissolved hard ions those causes the hardness of water. Activated carbon was used in controlling taste and odour. Oxidizing agents followed by filters were used to reduce iron and manganese. Recent technology, in addition to chemical precipitation and adsorption, uses ion exchange sorption, membrane separation technique, desalination, electrodialysis etc. for the purification of dissolved contaminants in water.

The presence of minerals and organic constituents as well as the presence of sunlight and temperature make a luxuriant growth of algae and micro-organisms in almost all natural waters. A few causes disease, some impact taste, odour, colour or turbidity to the water, others are beneficial, and the rest are of little interest (Lehr *et al.*, 1980). Depending on the water source, disinfection may be a simple or complex matter. Chlorine, a widely accepted oxidizer to the membrane of micro-organisms, is used extensively in the disinfection of supply water. Ground water from deep may not need disinfection.

Although the ion exchange phenomenon in clay and soil was reported in the beginning of the nineteenth century, its use for large scale water softening had begun only in the beginning of the twentieth century. At the beginning, natural and synthetic aluminium silicates were used for softening waters. The limitations of siliceous ion exchangers became more and more evident as commercial exploitation of these substances was attempted. Substitution was made by sulphonated coal as cation exchangers. Attachment of sulphonic acid groups on the surface of coal, lignite and peat by sulphonation reaction was a distinct contribution to the development of ion exchange resins. In 1935, Adams and Holmes (cited by Kunin, 1958) observed the ion exchange properties in the synthetic resins of phenol-formaldehyde. Further studies resulted in the synthesis of cation exchange resins containing strongly acidic sulphonic acid groups while condensing phenols and formaldehyde in the presence of sodium sulphite. Anion exchange resins were prepared in an analogous manner by the condensation polymerization of amines with formaldehyde. Since 1940, the synthesis of ion exchange resins has made spectacular advances having high cation and anion exchange capacity over the entire pH range and durable physical properties.

Today's municipal water treatment plant still uses conventional processes including screening, coagulation, sedimentation, and chlorination. Although modern water conditioning technology can solve almost all water quality problems, still the technology is not reachable to the majority of the world population because of high treatment cost. The modern water treatment plants are economically feasible in large scale operation and such big plants are usually installed in highly populated urban areas. As a consequence, majority of people residing in rural areas not only develop tolerances for drinking water of poor taste, odour or appearance but also belief that their water supply requires no treatment. On the other hand, tap water may be contaminated either from the corrosion of the pipelines or from the sources whether ground or surface. This is why, not only the rural and small community people, sometime urban people using supply water are still in scarcity of quality drinking water. In such cases, it is strictly advised to treat the water before drinking it.

Therefore, the present problem is to utilize the existing knowledge of water conditioning for developing a small scale low cost treatment process so that major individuals of the world population can benefit using this process in home water conditioning unit. The successful solution to this challenge largely depends upon the manufacturing of proper adsorbents followed by subsequent utilization in house hold filtering unit. The later work consists of three steps of investigations: i) bench-scale adsorption studies in a batch or column in laboratory using synthetic solution of mg.L^{-1} level, ii) medium-scale adsorption studies in a pilot plant using actual drinking water, iii) full-scale treatment evaluation in a modular unit.

1.2 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 along with metalloids, arsenic and selenium, that has been associated with contamination and potential toxicity or eco-toxicity (SenGupta, 2002; IUPAC, 2002). 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.

1.2.1 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 (Kadirvelu *et al.*, 2004). Since then, World Health Organization (WHO) set up various permissible limits on the discharge of heavy metals into the environment. According to WHO (cited by Rivera-Utrilla and Sanchez-Polo, 2003), 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. 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, agro-chemicals, 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.

Our bodies have become virtual dumping grounds for hundreds and hundreds of these toxic metals and chemicals. Studies indicate that we have between 400 and 800 toxic metal and chemical residues stored in our fat cells, and our tissues and organs. The Environmental Protection Agency of USA has estimated that we cannot metabolize most of these chemicals and metals. That means they accumulate in our fat cells, in our organs such as the liver, kidneys and brain, in our glands such as the thyroid and adrenals, and in the central nervous system. These chemicals and metals together result in a chronic toxic overload condition in our bodies. As these toxins build up, they block the receptor sites for essential minerals, so that minerals such as iron, calcium and magnesium cannot be utilized and absorbed. This causes enzyme dysfunction, nutritional deficiencies, hormonal imbalances, neurological disorders, damages brain chemistry, and can even lead to auto-immune disorders, cancer, and other debilitating chronic conditions. As early as 1974 in Florence, Italy, at the Congress of the World Health Organization, attention was drawn to the fact that 60-80% of the environmental toxins, which includes heavy metals, contribute to many diseases like neuro-dermitis, autoimmune disorders, allergies etc.

For short- and long-term toxic effects, the maximum permissible concentrations of heavy metals in drinking water as well as in municipal and industrial discharges are closely regulated in most of the countries through legislation. Drinking water quality standards for some species of metals/metalloids, according to the National Drinking Water Quality Standards, 2000 of Malaysia, are presented in Appendix A. Ultimately, as heavy metal regulations for both drinking water and wastewater are becoming stricter, the conventional means of water treatment becomes either costly or inefficient.

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.

Iron coprecipitation/adsorption is another well accepted process for the removal of heavy metal ions from water and wastewater. In this process, ferric salt, such as $FeCl_3$ or $Fe_2(SO_4)_3$, is added to water to form an amorphous precipitate of iron oxyhydroxide, ($Fe_2O_3.H_2O$). The dissolved and suspended trace elements/species are adsorbed onto the floc of iron oxyhydroxide and trapped within.

Flocs grow until they get heavy enough to settle down. The settled precipitate is then separated out from water, leaving a purified effluent. The process depends on reaction pH, adsorbate and adsorbent concentrations as well as the presence of competing cations and anions. Depending on pH, this process is also capable of removing oxyanions of arsenic, chromium and selenium from water and wastewater. The proposed mechanism of coprecipitation/adsorption of heavy metal ions on hydrous iron oxide surface can be presented by the following reactions (Benjamin, Hayes and Leckie, 1982), where oxide surface of iron, depicted by $\equiv SO^-$, acts as weak acid or base while gain or lose a proton.

Protonation of surface oxide:

$$\equiv SO^- + H^+ = \equiv SOH \tag{1.1}$$

$$\equiv SOH + H^+ = \equiv SOH_2^+ \tag{1.2}$$

Cation adsorption on protonated surface oxide:

$$M^{n+} + mH_2O = M(OH)_m^{n-m} + mH^+ \tag{1.3a}$$

$$\equiv SOH + M(OH)_m^{n-m} = \equiv SO.M(OH)_m^{n-m-1} + H^+ \tag{1.3b}$$

(The system pH decreases as the reactions go forward)

Anion adsorption on hydro-oxylated surface:

$$\equiv SOH + mH^+ = \equiv SOH_{m+1}^{m+} \tag{1.4a}$$

$$\equiv SOH_{m+1}^{m+} + A^{n-} = \equiv SOH_{m+1}A^{m-n} \tag{1.4b}$$

(The system pH increases as the above reactions go forward)

Here, M and A represent cationic and anionic adsorbate, respectively. The above equations, (1.3a) and (1.3b), reveal that protons are released into the system when an uncomplexed hydrated metal cation is adsorbed and equations (1.4a) and (1.4b) depict that protons are removed from the system during the adsorption of anions. These equations thus describe that increasing the concentration of deprotonated, SOH/SO^- and protonated, SOH_2^+ surface oxide sites, increases the adsorption capacity of cations and anions respectively. As the pH increases the adsorption of cation increases, while anion adsorption increases with the decrease of pH. But the limitation of the process of precipitation and coagulation/flocculation is that these are effective in removing some metal ions in drinking water to mg.L^{-1} levels but not always to µg.L^{-1} levels. This process also generates huge sludge. All of above, the removal of dissolved trace toxic substances or heavy metal ions is targeted at the point of use. Because it is considered a monetary burden, especially in the developing countries, to treat water at an early stage, when only 1% of water supplied to households is consumed by humans. Therefore, it is rational that adsorption processes are substituting precipitation methods.

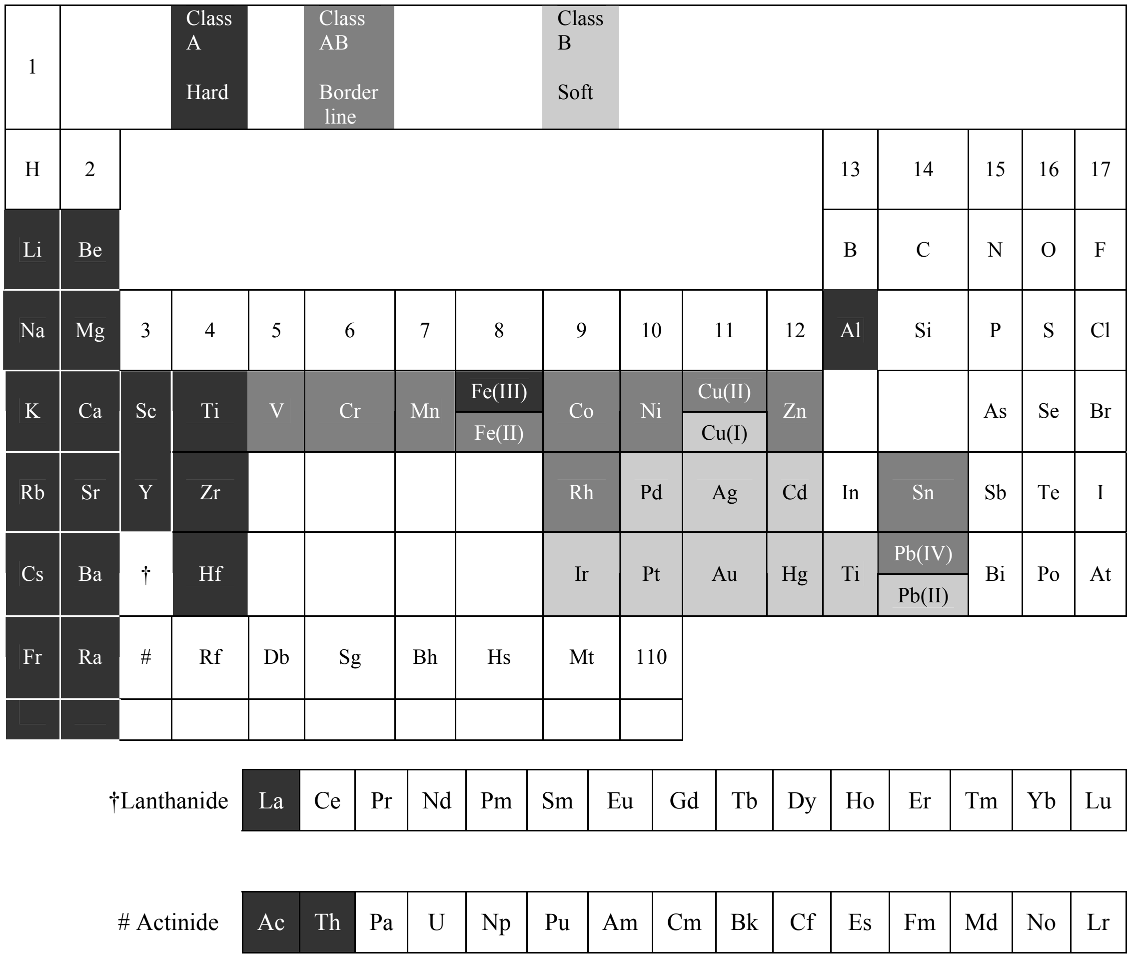
Ion exchange sorption and membrane processes such as reverse osmosis are capable of reducing metal concentrations to very low levels. But these are expensive and subject to operation problems such as fouling (Reed, Vaughan and Jiang, 2000). Thus, to mitigate the present problem of lowering the heavy 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+} (Sengupta and SenGupta, 2002). 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 (Shriver, Atkins and Langford, 1991). 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. 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' (Ahrland, Chatt and Davies 1958). 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 1.1 shows the periodical table classifying metals as Class A- hard, Class B- soft and Class AB- borderline metals (IUPAC, 2002).



1			Class A Hard		Class AB Border line			Class B Soft								
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 1.1: 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).

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.

Hard cations prefer hard (oxygen) donor ligands and form mainly ionically bound complexes. As the bonding of hard cation and hard ligand is mostly ionic in nature, metal ions are displaceable and mobile. Soft cations generally exhibit higher affinity toward nitrogenous and sulphurous species having donor lone-pair electrons. Thus soft cations are able to form strong inner-sphere complexes with these donor atoms. The higher atomic number *p*-block metals show strong affinity for soft ligands such as sulphide or sulphur donor and form highly covalent complexes from which they are difficult to displace. Thus they are relatively immobile in the environment. In living organisms, they are not readily excreted and tend to accumulate with resultant toxicity in protein molecule containing thiol group (-SH). The borderline metals generally form relatively stable complexes with both hard and soft donor ligands, but the exact order of stability is not easily determined. First row *d*-block transition metal ions fall mainly into this group and show widely variable coordination chemistry.

The basis of this principle has widely been used in the synthesis of chelating ion exchangers with various types of covalently attached functional groups for separating hard and soft cations. It is thus possible to utilize the Lewis acid-base interaction for the high selective uptake of heavy metal cations by the sorption process on chelating cation exchangers. As the composition of the functional groups of simple cation exchange resins changes from hard oxygen donor atoms, carboxylate groups, to relatively soft nitrogen donor atoms, such as bispicolylamine: $-CH_2-N.(CH_2-C_5H_9N)_2$, the affinity of soft cations is greatly enhanced over the hard cations. Chelating exchangers with sulphur containing thiol functional groups offer significantly higher selectivity for soft Hg(II) over Cu(II) and Zn(II). The composition of the functional groups in chelating exchangers can be judiciously tailored to improve specific affinities toward target metal ions.

The synthesis of polymeric chelating cation exchange resins involves a major step of covalent attachment of organic functional groups onto the parent polymer beads which makes the preparation difficult and costly. Moreover, sorption of metal ions onto chelating ion exchangers is kinetically slow due to the slower intraparticle diffusion of metal ions through the rigid structure and tortuous pathways within exchangers (SenGupta, 2002). Hence the present problem demands the replacement of the chelating/polymeric cation exchangers with renewable naturally occurring low-cost materials those contain carboxylate, carbonyl, phenolic groups and those exhibit moderate to high affinity toward heavy metal ions.

1.3 Activated Carbon

Activated carbon is a processed carbon material. Due to highly developed internal surface area and porosity, porous carbon materials or activated carbons have been used for thousands of years and have now become extremely versatile adsorbents. The adsorptive properties of carbon were well known long before the terms active and activated had been developed or doped.

The major applications of activated carbon are the removal of species by adsorption from liquid or gas phase, to effect the purification or recovery of chemicals (Girgis *et al.*, 2002), storage of natural gas of vehicles, catalysis supporter and electric double-layer capacitors (Yang *et al.*, 2004). Although activated carbon is an inexpensive and widely used adsorbent, its commercial application in water treatment, till now, is limited to remove taste and odour. Granular activated carbon (GAC) or powered activated carbon (PAC) is used in water treatment especially in the developed countries. It is also used in high-tech application for the removal of synthetic organic compounds (SOCs), volatile organic compounds (VOCs), and naturally occurring organic matter (NOM).

It is expected that through controlled oxidation/activation, concentration of carboxylate and phenolic groups in activated carbon particles can greatly be enhanced, resulting in a higher metal ion removal capacity (SenGupta, 2002). It has been shown by many researchers (Dastgheib and Rockstraw, 2001; Toles *et al.*, 1999; Johns *et al.*, 1998; Toles *et al.*, 1998; Toles *et al.*, 1997) that lignocellulosic agricultural wastes, particularly nutshells, are very good precursors for the production of granular activated carbons having suitable surface active sites for the removal of heavy metal ions from aqueous solutions. Since the ions of heavy metals, Class B and Class AB, have the stronger affinity toward donor sulphur and nitrogen atoms, simultaneous/stepwise activation and functionalization of the precursor or the surface of activated carbons by these donor atoms can improve largely the removal capacity of these metal ions (Gomez-Serrano *et al.*, 1998; Krishnan and Anirudhan, 2002; Krishnan and Anirudhan, 2003; Yantasee *et al.*, 2004). The utilization of such modified activated carbons would be very promising for the removal of particular, especially Class B, metal/metalloid species.

1.3.1 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. (Hassler, 1974). 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. In 1915 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.

1.3.2 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 micro-crystal 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 neighbouring 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 (Hassler, 1974).

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 (Cini, Pantani and Sorace, 1980).

1.3.2.1 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.

Wheeler (cited by Faust and Aly, 1987) 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

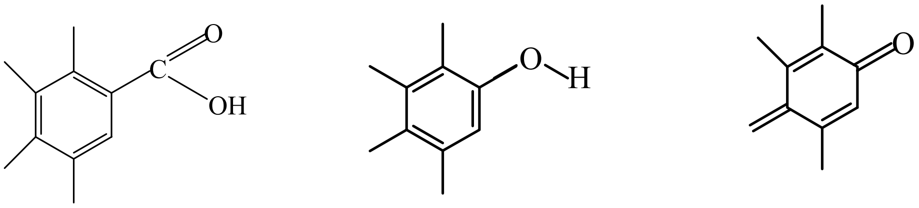
900°C in air, steam, or carbon dioxide. Amphoteric properties are found in carbons prepared between 500 to 800°C. The activated carbons prepared at low activation temperature, below 500-600°C, adsorb OH^- ions primarily are called L-carbons. Those activated carbons are prepared at above 500-600°C and 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 1.2) 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 1.3). On the other hand, proposed basic surface 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:

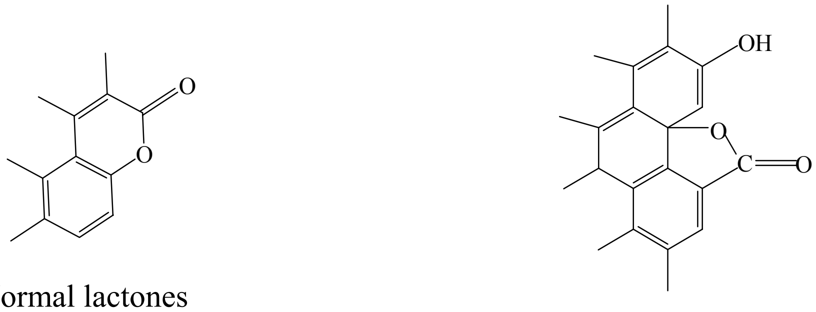
1) a strongly acidic carboxyl group which is neutralized by $NaHCO_3$, Na_2CO_3, NaOH, and $NaOC_2H_5$,
2) a more weakly acidic carbonyl group which is neutralized by Na_2CO_3 or stronger bases such as NaOH and $NaOC_2H_5$; but not by $NaHCO_3$,
3) a phenolic hydroxyl group which is neutralized by NaOH 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 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.



Carboxyl groups Phenolic hydroxyl groups Quinones

Figure 1.2 Structures of carboxyl, phenolic hydroxyl and quinone type carbonyl groups.



Normal lactones

Fluorescein type lactones

Carboxylic acid anhydrides

Cyclic peroxide

Figure 1.3 Structures of lactones, acid anhydrides and cyclic peroxide.

Chemically bound oxygen on the edges localizes electrons in surface states and withdraws them from the π electron system of the basal planes. Depletion of electrons by oxygen creates an increase in the population of positive holes in the conduction band of the π electron system and thus reduces the non-polar nature with an ultimate reduction in adsorption capacity of aromatic compounds. This is consistent with the concept of dispersion forces.

The motion of electrons in an atom or molecule would lead to a rapidly oscillating dipole moment while at any instant experiences the lack of symmetry of the electron distribution about the nuclei. When this atom or molecule approaches in close proximity to a non-polar solid surface, each instantaneous dipole induces an appropriately oriented (so that attraction could occur) dipole moment in a molecule on the surface. The interaction of these instantaneous dipoles with their counter induced ones produces an instantaneous attraction between adsorbate and adsorbent. The dispersion forces between the phenol's π electron system and the π band of the graphitic planes of the carbon are responsible for adsorption. Removal of electrons from the π band of the carbon by chemisorbed oxygen may interfere with and weaken the adsorptive forces resulted from the permanent polarity in the surface.

Since the polarity of carbon arises with the introduction of surface oxygen, the adsorption of metal ions on carbon surface seems to be favoured accordingly. The acid-base and metal removal behaviour of several commercial activated carbons have been modelled successfully by the Surface Complex Formation (SCF) model (Corapcioglu and Huang, 1987; Reed and Matsumoto, 1991). This model basically uses the law of mass action to describe ion interactions with hydrous solid surface.

According to this model (SCF), the surface of the hydrous solid acquires a surface charge due to various surface groups or sites and thus develops an electric double layer (EDL) around the charged particle. It has been assumed that all surface sites are capable of binding and releasing protons equally for which the solid can be modeled as a single, weak diprotic acid. Using this assumption, the surface functional groups can be described by the following surface reactions:

$$\equiv \mathrm{SOH_2^+} \longleftrightarrow \equiv \mathrm{SOH} + \mathrm{H_s^+} \tag{1.5}$$

$$\equiv \mathrm{SOH} \longleftrightarrow \equiv \mathrm{SO^-} + \mathrm{H_s^+} \tag{1.6}$$

where, the symbol ($\equiv \mathrm{SO^-}$) represents the active surface site attached on interface.

The amphoteric behaviour of activated carbon surface as shown by the above equations (equations 1.5 and 1.6) was interpreted by Snoeyink and Weber (cited by Reed, 2002) assuming phenol and lactone functional groups may be amphoteric while Mattson and Mark (1971) suggested carboxyl and quinone groups. Later on, the carbon surface, regardless of the specific functional groups, was assumed as a number of weak monoprotic acids rather than a single diprotic acid by many researchers. There are two types of monoprotic acid sites to consider:

A positively charged site,

$$\equiv P^{i}\,OH_2^{+} \longleftrightarrow \equiv P^{i}\,OH^{0} + H_s^{+} \tag{1.7}$$

And a negatively charged site,

$$\equiv N^{i}\,OH^{0} \longleftrightarrow \equiv N^{i}\,O^{-} + H_s^{+} \tag{1.8}$$

where, ‘i’ is an index to differentiate between sites and H_s^+ is the activity of proton at the solid surface.

This model enables to measure the acidity constants for the above two types of equations (equations 1.7 and 1.8). It is assumed that the sites that release and bind protons are also responsible for removing metal cations. We have seen that the surface acidity of activated carbons play an important role in adsorbing positively charged species. In addition, many researchers established the ability of activated carbons in removing heavy metal ions. Therefore, it is hoped that the use of granular activated carbon in removing heavy metal ions (class AB and class B) will become more common in near future.

1.3.3 Preparation

Almost any carbonaceous material can be converted into activated carbon (Hsisheng and Sheng-Chi, 2000; Girgis *et al.*, 2002), 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.

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.

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 (Wigmans, 1989). 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 (Smisek and Cerny 1970).

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 density suitable 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 (Molina-Sabio *et al.*, 1995). Then, in the next step, thermal treatment of the impregnated feedstock modifies the morphology and dimensions of the cellular units existing before impregnation. There is first an expansion of the cellular structure at impregnation state, then a subsequent contraction during carbonization at a temperature above 450°C (Caturla *et al.*, 1991).

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 (Jagtoyen *et al.*, 1992).

The use of chemical activation of wood, sawdust, with phosphoric acid has been known for many decades (Jankowska *et al.*, 1991) and has been applied to different cellulosic and lignocellulosic materials to prepare high surface area activated carbons. 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.

1.3.3.1 Processing of Lignocellulosic Materials

A summary of the processing of lignocellulosic precursors to obtain activated carbons, reported in recent literatures, is presented in Table 1.1.

Table 1.1 : A survey of recent literatures on the production of activated carbons from various lignocellulosic precursors.

Precursor	**Carbonization and activation process**	**Surface area, m^2/g**	**Reference**
Coconut shells	H_3PO_4 impregnation; carbonization under air at 300-550°C.	BET: 1360	Laine *et al.* 1989
Peach stones	$ZnCl_2$ impregnation: heat treated; carbonized in N_2 at 500-800°C, in CO_2 at 825 or 875°C.	BET: 1000-2000, 2700-3000	Caturla, *et al.,* 1991

Table 1.1 : Continued.

Precursor	**Carbonization and activation process**	**Surface area, m^2/g**	**Reference**
Coconut shell	Physical activation: CO_2, CO_2 + K-phosphate catalyst; carbonization at 800°C.	BET: 696-1341	Laine and Yunes, 1992
Oil palm shell	Activated using steam, CO_2, H_3PO_4.	BET: 1000	Asiah, 1993
Olive stones	Physical activation: CO_2 and water vapour; carbonization at 750-825°C.	-	Rodríguez-Reinoso, *et al.*, 1995
Peach stones	H_3PO_4 impregnation, sink 2 h at 85°C; carbonization under N_2 at 450°C, hold time 4 h.	BET: 338-1323	Molina-Sabio *et al.,* 1995
Oil palm shell	Impregnated with varying amounts of $ZnCl_2$ and carbonized at 500°C.	BET: 1500	Hussein *et al.*, 1996
Rice straw, sugarcane bagasse, soybean hull, peanut, pecan and walnut shells	Carbonized at 750°C in N_2 for 1 h; activated with CO_2/steam at 850/800°C for 5-15 h followed by oxidative treatment using air + N_2 at 300°C or chemical oxidation at 23°C.	85-721	Johns, Marshall and Toles, 1998
Almond, pecan, English walnut, black walnut and macadamia nut shells	H_3PO_4 impregnation, pre-heat treatment at 170°C, carbonization at 450°C in N_2 or air for 1-2 h followed by oxidation in air at 300°C those prepared in N_2.	991-1693	Toles, Marshall and Johns, 1998

Table 1.1 : Continued.

Precursor	**Carbonization and activation process**	**Surface area, m^2/g**	**Reference**
Pecan shell	Char preparation followed by activation using steam, CO_2 or H_3PO_4. Physical activation was carried out at 850°C in N_2 followed by oxidation at 370-410°C. Chemical activation was carried out by impregnating for 24 h in air and then pre-heat treated and carbonized at 170 and 450°C respectively.	618-1561	Johns, Marshall and Toles, 1999
Almond shells	Pyrolysis at 700-800°C; activation with steam/CO_2 at 800°C, hold time 2/4 h.	425-673 and 197-560	Toles *et al.*, 2000
Pecan shell	Air and H_3PO_4, pre-heat treatment 160-215°C, carbonization temperature: 160, 300-500°C.	27-1017	Dastgheib and Rockstraw, 2001
Coconut shells and palm seeds	Combining $ZnCl_2$ and CO_2 activation; carbonized at 800°C, hold time 2-3 h.	937-2450	Hu and Srinivasan, 2001
Oil palm stone	Impregnation with $ZnCl_2$, H_3PO_4 or KOH for 24 h followed by carbonization in N_2 for 2 h at temperature up to 600°C; after cooling activated with CO_2 at 700-900°C for 1 h.	$ZnCl_2$: 1837 H_3PO_4: 1563 KOH: 1408 Physical activation: 892	Guo and Lua, 2000
Oil palm stone	Activation using CO_2 at 650-950°C for 0.3-3 h.	942-1410	Lua and Guo, 2000

Table 1.1 : Continued.

Precursor	Carbonization and activation process	Surface area, m^2/g	Reference
Oil palm shell	Char obtained at 500-900°C; activated at 820°C for 20-250 minutes under a mixture of steam and N_2.	(High temperature char results higher micro-porosity)	Daud, Ali and Sulaiman, 2000
Corn cob	Chemically activated with potassium salts or physically activated with CO_2. KOH and K_2CO_3 were found effective catalysts for corn cob.	BET: 437 (un-impregnated) 490-903 (KCl, K_3PO_4, KNO_3, CO_2) 1266/1682 (K_2CO_3/KOH, CO_2) 369/506 (KOH, K_2CO_3, N_2)	Tsai *et al.*, 2001
Peanut hulls	Powdered precursor was activated chemically by H_3PO_4, $ZnCl_2$, KOH and physically by steam. Carbonized at various temperatures, 300-900°C. The ratio of H_3PO_4 and precursor was varied from 0.5-1.6.	BET: 97-253 (steam pyrolysis) 228-420 ($ZnCl_2$ and KOH activation) 240-1177 (H_3PO_4 activation)	Girgis *et al.*, 2002
Rice straw	Carbonized at 700°C and activated at 900°C.	BET: 2410	Oh and Park, 2002.
Candlenut	CO_2 activation at temperature 800°C while hold times were varied from 0.5-6 h, and at 700-900°C with 1 h hold time	990-1050	Turmuzi *et al.* 2004

Table 1.1 : Continued.

Precursor	Carbonization and activation process	Surface area, m^2/g	Reference
Palm shells	Precursor was impregnated with 5-40 % H_2SO_4 at 25°C for 24 h, and then evaporated at 110°C. Carbonized in N_2 atmosphere at 300-700°C. For comparison, char was prepared at 300-700°C for 2 h and then activated using CO_2 500-900°C for 2 h.	1014-1062	Guo *et al.*, 2005
Apricot	Soaked by impregnating agent (72 h) and then dried at 70°C. H_3PO_4 (25-75 %) activation at 400 and 600°C; $ZnCl_2$ activation at 600 and 700°C varying the ratio of $ZnCl_2$ and precursor. Also activated using steam at 900°C.	211-728	Youssef *et al.*, 2005

1.3.3.2 Utilization of Oil Palm and Coconut Shells as Carbon Precursor

Although coals are being used as principal precursor, the renewable agricultural solid wastes have potential prospects over conventional materials because of high carbon but low ash contents (Guo and Lua, 2002). Malaysia is the largest producer of palm oil product. Figure 1.4 shows the cross section of masocarp of oil palm fruit bunch. This country produces 8.5 million tonnes of oil per annum. Since the oil is extracted from fresh fruit bunches it generates large amounts of wastes such as fibre $(5.4\times10^6 \text{ t y}^{-1})$ from the masocarp, shell $(2.3\times10^6 \text{ t y}^{-1})$ from around the kernel and the empty fruit bunches (EFB) as residues (Husain, Zainac and Abdullah, 2002).

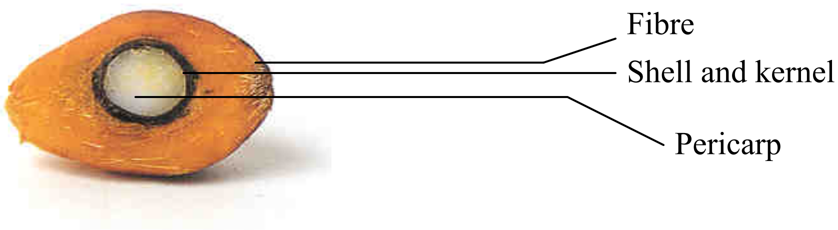


Figure 1.4 A cross section of masocarp of oil palm fruit bunch showing fibre, shell, kernel and pericarp.

Figure 1.5 presents process flow diagram of palm oil extraction to show the generation of solid wastages such as shells and fibres. Palm oil mills use the fibre and shell, in a ratio of 60:40, as fuel to generate steam and electricity (Husain, Zainac and Abdullah, 2002). The proximate analysis of solid oil palm residues are shown in Table 1.2 and the ultimate analysis of those are given in Table 1.3. Lignocellulosic contents in oil palm shell are as follows: cellulose 29.7, hemicelluloses 47.7 and lignin 53.54 % respectively (Daud and Ali, 2004). The fibres of oil palm are short and thin. While the majority of fibres are used as fuel, the huge amount of palm shells are creating environmental problem. As oil palm shells can be obtained abundantly, the utilization of these shells as carbon precursor is very promising.

Although this country produces huge amounts of coconut shells as agricultural wastages, no statistical data are available on the quantity. The proximate and ultimate analyses of coconut shells are given in Table 1.4. The proximate analyses of oil palm and coconut shells are not very different except in ash content. Ultimate analysis shows higher carbon, nitrogen and sulphur contents in oil palm shell. The higher nitrogen and sulphur contents in oil palm shell may be converted into functional groups containing donor nitrogen and sulphur atoms during activation and thus may be functioned more effectively in removing borderline and soft metal ions. Both precursors contain higher amounts of volatile matter and oxygen suitable to develop porosity and surface acidic groups containing oxygen depending on activation process. Identical carbon content in the proximate analyses of oil palm and coconut shells grouped them in a similar type of lignocellulosic precursor. Thus the utilization of coconut shells as supplementary precursor in the oil palm shell based carbon manufacturing industry allows more flexibility on the consumption of raw material. This is why, oil palm and coconut shells are chosen as carbon precursors in this study.

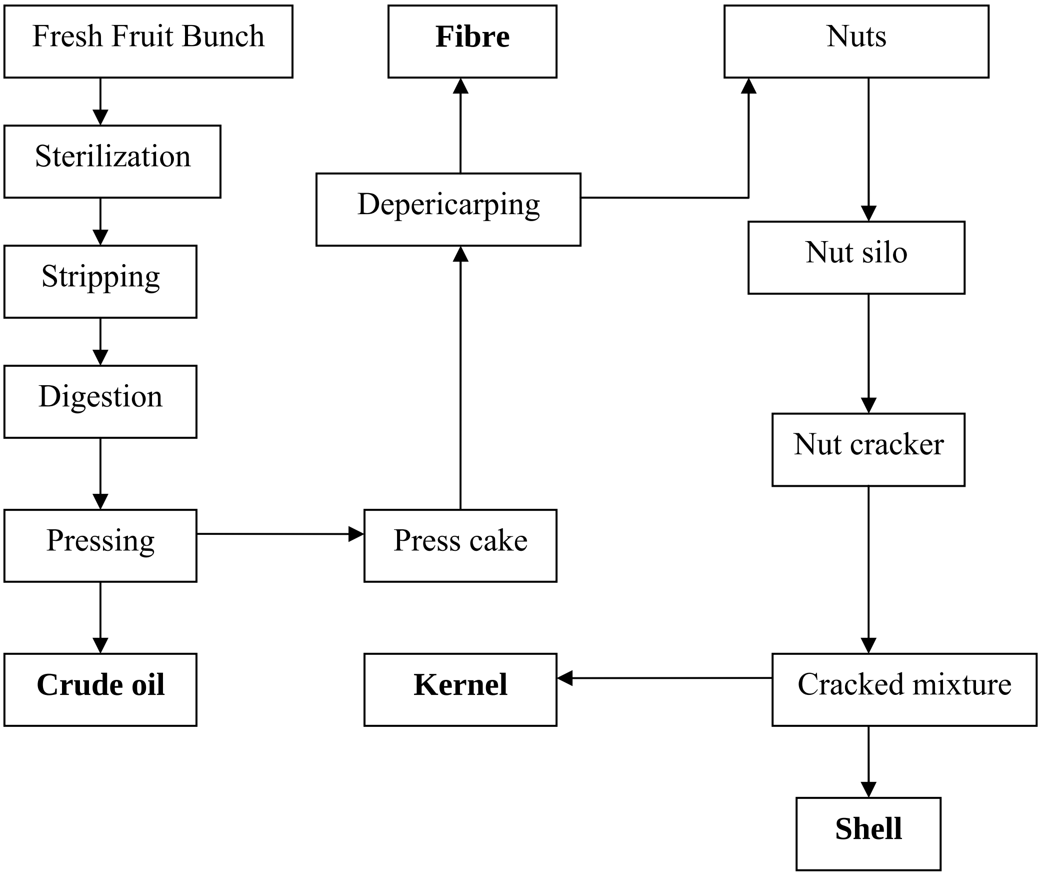


Figure 1.5 Process flow diagram of palm oil extraction showing the production of crude oil and wastages such as shells, kernel and fibres.

Table 1.2 : Proximate analysis of solid oil palm residues (Husain, Zainac and Abdullah, 2002).

Composition	**Fibre**	**Shell**	**EFB**
Volatile matter, wt.%	72.8	76.3	75.7
Fixed carbon, wt.%	18.8	20.5	17
Ash, wt.%	8.4	3.2	7.3

Table 1.3 : Ultimate analysis of solid oil palm residues (Mahila *et al.*, 2001).

Element	Fibre	Shell	EFB
Hydrogen, wt.%	6	6.3	6.3
Carbon, wt.%	47.2	52.4	48.8
Sulphur, wt.%	0.3	0.2	0.2
Nitrogen, wt.%	1.4	0.6	0.7
Oxygen, wt.%	36.7	37.3	36.7
Ash, wt.%	8.4	3.2	7.3

Table 1.4 : Proximate and ultimate analyses of coconut shell (Banerjee, *et al.*,1976).

Composition	Proximate analysis	Ultimate analysis
Moisture, wt.%	8.4	-
Volatile matter, wt.%	72.8	-
Fixed carbon, wt.%	18.7	-
Ash, wt.%	0.1	-
Carbon, wt.%	-	48.4
Hydrogen, wt.%	-	6.3
Oxygen, wt.%	-	44.3
Sulphur, wt.%	-	0.03-0.09
Nitrogen, wt.%	-	0.1-0.15

1.4 Adsorption of Metal Ions onto Activated Carbon

In the last two decades, the adsorptions of metal ions from the single- and a few binary- and multi-solute solutions onto mostly commercial and some non-commercial, laboratory prepared activated carbons were investigated. These studies were reviewed in the following paragraphs.

Corapcioglu and Huang (1987) studied the adsorption characteristics of some heavy metals, namely Cu(II), Pb(II), Ni(II) and Zn(II) onto the hydrous surface of 14 different activated carbons obtained from various commercial brands. The adsorption characteristics were determined for carbon type, pH and surface loading. They observed that adsorption is the major phenomenon in the removal of metal ions at least in the pH less than neutral region. The adsorption equilibrium data were obtained at varying pH, from 2.5 to 10.5, in a single-solute solution. The initial concentrations of Cu(II), Pb(II), Ni(II) and Zn(II) were kept constant at 6.4, 20.7, 29.3 and 32.7 $mg.L^{-1}$ respectively. The concentration of adsorbent was kept constant at 10 $g.L^{-1}$. The highest adsorption capacity for the above mentioned metal ions in the acidic region were observed by the activated carbons having acidic properties (Nuchar SA and Nuchar SN brands). Since the ashes of these acidic carbons contain higher level of phosphorus, they speculated that heavy metals were removed through the formation of organometallic complexes with phosphoryl group rather than hydroxo complexes. Within the pH range from 3 to 5, the acid activated carbon had removed above 90% of the metal ions of Cu(II) and Pb(II). But the removal of Ni(II) and Zn(II) by the acid activated carbon was observed only below 70% at pH 3 which increased gradually to above 90% at pH 5. In the alkaline region, the metal ions removal capacities of all activated carbons were indistinguishable. The effect of surface loading was studied varying initial concentrations over the pH range, 2.5-10.5. The results showed that the percentage of heavy metal removal by acid activated carbon decreases with increasing surface loading. The adsorption edges for Cu(II) and Pb(II) were found in the pH range from 3 to 5 and 3 to 6 respectively.

Examining various models to describe adsorption reaction, they selected the surface complex formation model with some variations. To develop the present version of this model, they include all the hydroxo species, $M(OH)_y^{2-y}$, along with the free metal ions, M^{2+} as adsorbate. Although their evaluation indicated that covalent or hydrogen bonding is responsible for the adsorption, they concluded their opinion in favour of hydrogen bonding. Thus they suspected that electrostatic interaction (outer-sphere complexation) plays a significant role rather than chemical interaction (inner-sphere complexation) in the adsorption reaction. This speculation seems to be questionable since hydrogen bonding results in a very weak bonding and non-selectivity among the cations having similar charge. This assumption is contradictory to the findings of Strelko and Malik (2002) that activated carbon adsorbs metal ions selectively.

Tan and Teo (1987) studied the adsorption of Pb(II) and chromium on activated carbon. They showed that adsorption depended significantly on the pH, carbon dosage and initial adsorbate concentration. They proposed empirical modifications of the expressions of Langmuir and Freundlich equations in terms of mass ratio of carbon to initial amount of adsorbate in the solution to correlate the experimental isotherms for the combined influence of initial adsorbate concentration and carbon dosage.

Johns, Marshall and Toles (1998) studied the single and competitive adsorption of Cu(II) and of Cd(II), Cu(II), Pb(II), Ni(II) and Zn(II) in single and multi-solute solutions respectively onto various granular activated carbons. The adsorbent and initial Cu(II) concentrations were 10 g.L^{-1} and 635 mg.L^{-1} respectively and the solution was buffered at pH 5. For competitive adsorption, unbuffered (pH 5) solution of concentration of each cation as 2.5 mM was used. Some of the activated carbons used were derived from various lignocellulosic precursors while others were obtained from commercial sources. They found that physically activated and controlled air oxidized activated carbons have higher Cu(II) adsorption capacities as 41-51 mg.g^{-1}. But the limitation of this study is that they determined the equilibrium adsorption data for the single point concentration which is not enough to understand the adsorption characteristics. The highest adsorption of the total solutes by one of the prepared activated carbon was observed as 510 μmol.g^{-1} and the selectivity order was reported as Pb > Cu > Cd > Zn >Ni. All granular activated carbons adsorbed Pb(II) and Cu(II) in much higher amounts than other cations such as Cd, Zn and Ni.

Toles, Marshall and Johns (1998) in another experiment prepared some activated carbons using phosphoric acid and controlled air from different nut shell precursors. They observed that various acid activated/oxidized carbons regardless of precursor type scavenged 13-19 mg-Cu.g^{-1}-adsorbent. The adsorbent and initial Cu(II) concentrations were 10 g.L^{-1} and 190 mg.L^{-1}. Since acid activated carbons altered the equilibrated pH to a value out of the range of optimum metal adsorption, they buffered the solution pH at 4.8. They also studied the adsorption from the initial concentration of 635 mg.L^{-1} and observed the highest adsorption capacity by one of the acid activated carbon derived from almond shell as 59 mg.g^{-1}. The adsorption behaviour was not well documented by fitting the data to equilibrium and kinetic models. They successfully studied the feasibility of the reuse of phosphoric acid used in precursor activation. Activated carbon prepared from 85% concentrated recycled acid produces lower surface area. They recycled the acid up to 50% concentration and mixed with fresh acid in a 1:1 ratio. As the activated carbon prepared from mixed acid has a much higher surface area, this technique brought success to them.

Seco and co-workers (1999) investigated the single adsorption of Cd(II) and Cu(II) on commercial activated carbon as a function of pH, metal ion and carbon concentrations. Their results showed that activated carbon has the potential to remove Cd(II) and Cu(II) from aqueous solution. They also observed that the adsorption increased with the increase of pH and carbon concentration. They found that an increase of initial metal concentration reduced the metal removal percentage. They successfully interpreted the stronger affinity of Cu(II) than Cd(II) towards carbon from their electronegativities, as 2.00 and 1.69 and first hydrolysis equilibrium constants (pK values), as 8.00 and 10.08 respectively. They applied mechanistic model, such as Triple Layer SCF model, to predict the adsorption behaviour of Cd(II) and Cu(II) on carbon. They also tested Langmuir and Freundlich models while Langmuir model failed to fit the data indicating multi-layer adsorption. They also found that while Triple Layer SCF model has the advantage to use in a wide range of pH and carbon concentration, Freundlich model is applicable only in one pH, that is, for the whole pH range Freundlich model requires the conjunctive use of one equation for each pH.

Chen and Wang (2000) studied the adsorption of Cu(II), Zn(II) and Pb(II) in their single-, binary- and ternary-solutes solution conducting the experiment in a fixed-bed column. They observed that the breakthrough capacity increases with the increase of influent pH and the lowering of flow rate. The ionic strength has small increasing effect only on the removal of Cu(II). The selectivity order for the adsorption of metal ions in single solution was showed as: Cu > Pb > Zn. The multi-solute adsorption indicated that activated carbon has higher affinity towards Cu(II) and least affinity towards Zn(II). The adsorption capacity for Cu(II) was slightly suppressed by the presence of competing ions Zn(II) or Pb(II) in binary- and by Pb(II) and Zn(II) in ternary-solute solution. Adsorption of Pb(II) was found similar to that of Cu(II) and the competitive effect by Cu(II), and by Cu(II) and Zn(II) was slightly higher than that for Cu(II). The competing effect of Cu(II), and of Cu(II) and Pb(II) on the suppression of adsorption of Zn(II) was quite significant. They also observed that addition of Cu(II) reduces the amount of Zn(II) removal and that was why, they directly assumed that only one functional group affecting the adsorption of various metal ions. Since it seemed correct, they uphold their opinion by adding that if several groups are present to bind different metal ions, there would be no competition. Actually here they failed to generalize their observation and thus they went against the very well known concept of the presence of various surface functional groups on activated carbon. However, utilizing the concept of HSAB (Pearson, 1968) the various active sites on carbon as well as the types of metal ions can be categorized to hard and soft sites or ions and can be derived to a more realistic interpretation.

Alfarra, Frackowiak and Francois (2004) applied successfully the HSAB concept to interpret the adsorption behaviour of metal ions on activated carbon by considering surface groups of activated carbon as their hard sites and the surface of basal planes as soft sites. In a recent report of IUPAC (2002) Pb(II) is shown as soft cation whereas Ahrland, Chatt and Davies (1958) classified Pb(II), Cu(II) and Zn(II) as borderline cations. Therefore, Chen and Wang’s (2000) assumption that Pb(II), Cu(II) and Zn(II) were adsorbed on a same functional group may not be correct. However, Pb(II) might be suspected as to be adsorbed onto both harder and softer active sites on carbon while Cu(II) and Zn(II) only onto the harder active sites. Thus the differences in Lewis acidity of Pb(II) and Cu(II) directed them to bind differently which explains more correctly the less effect of competing ions in the adsorption of Cu(II) and Pb(II) on carbon. Chen and Wang (2000) did not explain the cause of higher affinity towards Cu(II) which can be showed from the stability of complexes of transition metal as a function of electronegativity in Irving-Williams series (cited by Shriver, Atkins and Langford, 1991).

Uzun and Güzel (2000) studied the adsorption of heavy metal ions, Mn(II), Fe(II), Ni(II) and Cu(II) on commercial activated carbon, chitosan and agar. They described the adsorption data as percent removal which is inadequate to evaluate the adsorption behaviour. However, they obtained the order of adsorption of metal ions on activated carbon in the series: Cu > Ni > Fe > Mn which was consistent with the stability of complexes of transition metal in Irving-Williams series.

Chen and Lin (2000) investigated the adsorption of metal ions, Cu(II), Zn(II) and Co(II), on an H-type (basic) commercial activated carbon. They used adsorbent and initial solution concentration as 10 $g.L^{-1}$ and <10 $mg.L^{-1}$. In these experiments equilibrated solution pH was found to increase from 5 to 7. The removal order of cations in single-solute solution was observed as follows: Cu > Zn ≈ Co. They also observed that the competitive effect of Zn(II) and Co(II) on Cu(II) is less prominent whereas the adsorption of Zn(II) and Co(II) was reduced dramatically with the addition of Cu(II). The kinetic study showed that most Cu(II) removal occurred in the first hour and was completed within four hours. They also observed that Cu(II) adsorption is much faster than that of Zn(II).

Dastgheib and Rockstraw (2001) prepared activated carbon with a high adsorption capacity for Cu(II) from pecan shell using air and H_3PO_4. They proposed that the acidic groups as detected using Boehm titration not only be considered as oxygen-containing acidic groups, but also as oxygen/phosphorous groups. They used buffered (pH 4.8) solution of Cu(II) and found the adsorption capacities by prepared activated carbons to be varied from 33 to about 40 $mg.g^{-1}$ depending on the extent of oxidation. They proposed the mechanism as ion-exchange in very low concentrations and accounted the pH shift by acid activated carbon as the release of H^+ by the equivalent (eq) Cu^{2+}. Since the release of H^+ ion by acid activated carbon depends on pH at zero point charge (pH_{ZPC}) one can relate the released H^+ ion concentration to the adsorbed metal ion density on the adsorbent only to a certain level of adsorption. That was why, while correlating the meq H^+ released per gram carbon by the meq Cu^{2+} adsorbed per gram carbon, they failed to establish any relation for higher concentration. Thus they proposed another mechanism for high concentration as some other forms of ion-exchange and surface complexation of metal ions with oxygen- and phosphorous-containing functional groups. They did not show any evidence or interpretation of this assumption.

Toles and Marshall (2002) investigated the utility of phosphoric acid-activated/oxidized, steam-activated and steam-activated/oxidized activated carbons in removing Cu(II) from solution in batch and column. The equilibrium data were obtained varying initial Cu(II) concentrations from 31 to 1906 mg.L^{-1} while adsorbent concentration was maintained 10 g.L^{-1}. The obtained equilibrium data were compared with commercial activated carbons by fitting to Freundlich model. The acid activated carbons were found most effective in both, batch and column mode, for the removal of Cu(II).

Strelko and Malik (2002) investigated the effect of chemical (HNO_3) oxidation on a commercial activated carbon to modify it to a cation-exchanger. They tested the adsorption behaviour of some transition metal ions such as Cu(II), Ni(II), Co(II), Zn(II) and Mn(II), on unoxidized and oxidized activated carbons. Their results showed that Cu(II) uptake was 4 fold enhanced by the oxidized carbon. They also observed that Cu(II) was the most preferred cation and its non-linear Langmuir isotherm was considerably steeper at low concentration than that for other metal ions. Metal ions uptake capacity by the unoxidized activated carbon was significantly lower than that of oxidized activated carbon while uptake pattern/sequence by both carbons was detected similar. They also depicted the affinity series as: $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ from the respective selectivity coefficients as: 2.66×10^{-3}, 6.38×10^{-3}, 9.45×10^{-3}, 1.95×10^{-1} and 5.61×10^{-3}. They proposed distorted and more stable octahedral complexation of Cu(II) with activated carbon to understand its stronger affinity towards carbon.

Mohan and Singh (2002) investigated single and multi-component adsorption of Cd(II) and Zn(II) on H_2SO_4 impregnated activated carbon derived from bagasse precursor. They observed that equilibrium time was reached within 10-12 h and the kinetic data followed Lagergren pseudo-first order model with rate constants of Cd(II) and Zn(II) as 0.006 and 0.008 min^{-1} respectively. They fitted their data to the Langmuir and Freundlich models and evaluated the adsorption behaviour. They found that the prepared activated carbon had a very high capacity to remove Cd(II) and Zn(II) in single-solute-solution as 38.03 and 31.11 mg.g^{-1} respectively. They also showed that the competitive effect of Cu(II) and Zn(II) on Cd(II) and that of Cu(II) and Cd(II) on Zn(II) in binary and ternary solutions was not much as the ratio of maximum monolayer adsorption capacities in multi-solute to single-solute solutions were within 0.78-0.87 for Cd(II) and 0.61-0.84 for Zn(II).

Krishnan and Anirudhan (2002) studied the adsorption of Pb(II), Hg(II), Cd(II) and Co(II) on the prepared sulphurized steam activated carbon as a function of time, concentration, pH, and temperature. Their results showed that while adsorbent and initial metal ion concentrations were kept at 2 g.L^{-1} and 100 mg.L^{-1} respectively and the pH at 6, the maximum sorption had occurred (Pb 49.60, Hg 48.61, Cd 46.55, Co 40.95 mg.g^{-1}) within four hours. The following adsorption sequence was observed: Pb(II) > Hg(II) > Cd(II) > Co (II). Their obtained kinetic data were fitted to pseudo-second order kinetic model. They analysed the adsorption data by Langmuir and Freundlich isotherms. The maximum adsorption capacities for Pb(II), Hg(II), Cd(II) and Co(II) were as follows: 200, 188.68, 153.85 and 128.70 mg.g^{-1}. The effect of competing ions on the single adsorption capacities for all metal ions was found suppressive. An acidic solution of 0.2 M HCl was found as regenerating agent for the spent activated carbon.

Macías-García and co-workers (2004) investigated the adsorption of Pb(II) on SO_2-treated as well as on untreated activated carbon from the kinetic and equilibrium standpoints. The kinetic result showed that adsorption on untreated carbon was much faster (equilibration time 20 h) than that on treated ones (equilibration time 80 h). Therefore, they proposed that untreated carbon adsorbs Pb(II) physically whereas the adsorption on SO_2-treated activated carbon might be due to chemisorption which was resulted from the interaction of metal ions with the sulphur bearing functional groups. They derived the pseudo-first order rate constant applying Lagergren kinetic model and assumed that chemisorption is the rate limiting step. The values of rate constants by one untreated and three various treated activated carbons at pH 5.4 and at temperature 25°C were respectively as follows: 0.903, 0.065, 0.042 and 0.034 h^{-1}.

Aggarwal, Goyal and Bansal (1999) studied the adsorption of Cr(III) and Cr(VI) on various as received and oxidized activated carbon. They constructed the adsorption isotherms and found that activated carbon fibres having higher portion of very small micropores adsorbed least Cr(III) due to inaccessible pores than others as received activated carbons. The adsorption of Cr(III) increased on oxidation and decreased on degassing of adsorbent. They found that surface acidic groups were well developed by treatment with HNO_3 acid than that by H_2O_2, air and $(NH_4)_2S_2O_8$. It was also observed that the amount of Cr(VI) adsorption was much higher than Cr(III) on as received activated carbons and carbon-fibers. The larger adsorption was interpreted by the smaller size of Cr(VI). In the adsorption of Cr(VI) they noticed a reverse behaviour that the removal capacity decreased with the oxidation while increased with degassing. That is, acidic surface groups exposing more negative active sites repulsed anions of Cr(VI) with an ultimate suppressive effect.

Selomulya, Meeyoo and Amal (1999) studied the removal mechanism of Cr(VI) using different types of activated carbons. In their experiment, one of the commercial activated carbons was derived from wood and was of L-type while the other two were of H-type and obtained from coconut shell (prepared in laboratory) and dust coal (commercial). They observed that the removal capacity of Cr(VI) ions always decreased with the increase in pH for all types of carbons used in their study. They proposed the mechanism of total chromium removal by activated carbon as the direct adsorption of Cr(VI) that could be followed by the reduction of some Cr(VI) to Cr(III). They also observed that the mechanism was highly dependent on the type of activated carbon they used, the pH values and the amount of Cr present in the solution while the optimum pH for the removal was largely depended on the surface properties and the reduction capacity of carbons. H-type coconut shell based carbon was found to be excellent in removing Cr in a wide range of concentration and in a low level of pH while L-type carbon was found good only at low concentration and at low pH.

Ho and Mckay (1999) studied the kinetics of adsorption of divalent metal ions such as Cu(II), Pb(II), and Ni(II) onto sphagnum moss peat. They followed batch- adsorption technique to obtain the equilibrium adsorption and the extent of metal ion removal. Since their kinetic data did not fit to Lagergren pseudo-first order model, they developed a pseudo-second order rate equation and calculated the rate constants and the initial adsorption rates. They claimed that chemisorption, which involves valency forces through sharing or the exchange of electrons between adsorbent and adsorbate, was the rate-limiting step. They also showed that the parameter which had the influence on the kinetics of the adsorption reaction was the adsorption equilibrium capacity which was a function of initial metal ion concentration, peat dose and the nature of solute ion.

Rivera-Utrilla and Sánchez-Polo (2003) investigated the potential of a series of ozonised activated carbons to remove Cr(III) from aqueous solution and the mechanism of adsorption. They studied their data by applying Langmuir model and observed that maximum monolayer adsorption capacity of unoxidized basic carbon (H-type) could be increased from 7.33 to 19.23 $mg.g^{-1}$ by oxidation with ozone. In that experiment, they altered the nature of a hydrophobic carbon ($pH_{ZPC} = 8.82$) to a hydrophilic one ($pH_{ZPC} = 1.82$). Thus they showed that the ionized surface groups of oxidized carbon attracted Cr(III) species by electrostatic interaction. They also established a linear relationship between the amount of metal adsorbed and the concentration of acid groups on the carbon surface. While they observed that basic carbon even with positive surface charge density could remove the Cr(III) species, they proposed a mechanism of Cл (*л*-electron clouds of basal plane of activated carbon) and cations interactions. They also analysed the effect of pH and reported the result as follows: the maximum adsorption occurred when the charge sign of the carbon surface dominated as the opposite to that of the Cr(III) species present at the pH of that experiment.

Demirbas and co-workers (2004) prepared three activated carbons from cornelian cherry (CC), apricot stone (AS) and almond shell (ACS) using H_2SO_4 activation to remove aqueous Cr(VI). They determined the optimum pH for the removal of Cr(VI) as 1 when all activated carbons showed identical capacity as 20-21 $mg.g^{-1}$. But they observed different adsorption capacities at pH 4, as 4.21, 11.44 and 14 $mg.g^{-1}$ by CC, AS and ACS carbons respectively. They determined the equilibration time as 72 hours and fitted the kinetic data to the pseudo-second order equation. They found that the values of pseudo-second order rate constant decreased with the increase of initial concentration. The rate constants by three activated carbons, CC, AS, and ACS were determined as 0.058, 0.040 and 0.053 mg.g^{-1}.h^{-1} respectively while they were adsorbed in the initial concentrations of 53, 58 and 21 mg.L^{-1}.

Yantasee and co-workers (2004) developed an adsorbent material by the functionalization of amine (-NH_2) onto fine-grained activated carbon to remove transition metal ions such as Cu(II) effectively and selectively. The equilibration time was reached within 1 min., while the maximum monolayer adsorption capacity was determined as 54.6 mg.g^{-1} by the developed adsorbent. They also determined the effect of competing ions such as Cd(II), Ni(II), and Pb(II) on Cu(II) in the series as follows Cu(II) >> Pb(II) > Ni(II) > Cd(II).

Reed, Vaughan and Jiang (2000) obtained Fe(III)-oxide impregnated activated carbon (FeAC) and its non-impregnated counterpart from Norit Americas, Atlanta, Georgia to study the removal of As(III), As(V), Hg(II), and Pb(II). The detail of impregnating the virgin carbon, which was derived from lignite precursor, is trade confidential. They conducted adsorption experiments using adsorbate concentration 1 mg.L^{-1} while pH were varied from 3 to 11 and adsorbent concentrations were varied between 0.015 and 0.3 g.L^{-1} for virgin carbon and between 0.2 and 1.2 g.L^{-1} for FeAC. They observed that the removal of oxyanions of As(V) decreased with increasing pH, while reverse phenomenon was observed for cations, Pb(II) and Hg(II). The removal behaviour of As(III) was observed different from As(V). The adsorption of As(III) was maximized at pH $\approx$ 7; whereas adsorption was independent of pH at pH below 5 and was decreased at pH above 7. From a single point of concentration at pH 7, they showed that the adsorption capacities of virgin and FeAC activated carbons for As(III), As(V), Hg(II) and Pb(II) were as follows: 0.73 and 4.67, 0.09 and 4.50, 2.1 and 4.57, 3.0 and 4.35 mg.g^{-1} respectively. A substantial increase in the removal of As(III) and As(V) by the Fe-oxide impregnated carbon was occurred due to the empty *d*-orbitals which allowed the rooms for the complexation of heavy metal anions through oxolation/replacement of the hydroxyl group. Thus they showed that instead of carbon-oxygen functional groups' interaction with anions, the effective removal of heavy metal anions has occurred by the Fe(III)-oxide impregnated carbon.

Peräniemi and Ahlgrén (1995) studied the preconcentration of As(V), Se(IV), Se(VI) and Hg(II) in aqueous solution using zirconium-loaded activated charcoal (ZrC^*) to develop a rapid and accurate determination technique using dispersive X-ray fluorescence as well as to provide an effective recovery for these species. They used slurry of activated charcoal (25 g) in an aqueous solution (250 mL) of zirconyl nitrate (10.0 g $Zr.L^{-1}$, pH 1.6) to load Zr onto charcoal. Their results showed that their developed method was very suitable to be used for industrial wastewaters. Since the analyte contents in environmental waters are usually too low they concluded that this method was not directly suitable for the samples from environment.

Peng and co-workers (2005) developed carbon nanotubes-iron oxides magnetic composites as effective adsorbent for the removal of Pb(II) and Cu(II). They studied the effect of pH on the removal percentage as well as on the constructed isotherms. They obtained the adsorption capacities for Pb(II) and Cu(II) at pH 5 as 103 and 45 $mg.g^{-1}$ respectively.

1.5 Adsorption Equilibrium Models

Adsorption equilibrium models (Weber, McGinley and Katz, 1991) are classified in two major groups, mechanistic and phenomenological models. Mechanistic models include hydrophobic, ion-exchange, and surface complex formation (SCF) models. In ion-exchange and SCF models the calculations are based on the stability constants of the adsorbent surface. These constants can be obtained from the potentiometric titrations and other experiments. At equilibrium, the relationship between the concentrations of solute in the liquid or gas phase with that of solid phase at a constant temperature is expressed by adsorption isotherm equations. The phenomenological models are based on these adsorption isotherms. Many phenomenological models are developed for the gas phase adsorption in single and multi-component systems. Although these equations were developed for gas phase adsorption, they also have been successfully applied to dilute liquid phase adsorption. Among them, Langmuir and Freundlich adsorption isotherms are most common models in the adsorption of gas or liquid on a solid phase (Faust and Aly, 1987).

1.5.1 Langmuir Adsorption Model

The term ‘adsorption’ deals with the process in which molecules accumulate in the interfacial layer, but desorption denotes the converse process. Adsorption can result either from the universal van der Waals interactions (physical adsorption, physisorption) or it can have the character of a chemical process (chemical adsorption or chemisorption). Since the adsorption isotherm is the equilibrium relation between the quantity of the adsorbed material and the pressure or concentration in the bulk fluid phase at constant temperature, it provides the primary source of information on the adsorption process.

The Langmuir equation initially derived from kinetic studies was based on the assumption that on the adsorbent surface there is a definite and energetically equivalent number of adsorption sites, at each of which one molecule of a perfect gas may be adsorbed. The bonding to the adsorption sites can be either chemical or physical, but it must be sufficiently strong to prevent displacement of adsorbed molecules along the surface. Therefore, adsorption occurs only in monolayer and thus Langmuir isotherm notices the uniformness or homogeneity of a surface.

Langmuir, for the first time, introduced a clear concept of the monomolecular adsorption on energetically homogeneous surfaces. The statement proposed by Langmuir was applied to chemisorption and with some restrictions to physical adsorption. The constant parameters of the Langmuir equation have a strictly defined physical meaning, in contrast to the parameters of the empirical Freundlich equation. For adsorption from solution by solid adsorbents, the Langmuir adsorption isotherm is expressed as:

$$\mathrm{q_e} = \frac{q_{\max} bC_e}{1 + bC_e} \tag{1.9}$$

where, q_e = amount of metal ion adsorbed at equilibrium per unit mass activated carbon ($mg.g^{-1}$); C_e = equilibrium concentration of metal ion in solution ($mg.L^{-1}$); q_{max} = the maximum monolayer adsorption capacity ($mg.g^{-1}$); b = affinity or adsorption constant, related to the heat of adsorption, ($dm^3.g^{-1}$).

The linear form of equation (1.9) is derived as equation (1.10) to determine the Langmuir parameters. Plotting C_e/q_e against C_e gives a straight line with a slope $1/q_{max}$ and an intercept $1/bq_{max}$.

$$\frac{C_{\mathrm{e}}}{q_{\mathrm{e}}} = \frac{1}{q_{\mathrm{max}}} C_{\mathrm{e}} + \frac{1}{bq_{\mathrm{max}}} \tag{1.10}$$

The monolayer capacity, q_{max}, determined from the Langmuir isotherm, defines the total capacity of the adsorbent for a specific adsorbate. Reliable q_{max} values can be obtained only for systems exhibiting Type-1 isotherms of the Brunauer's classification. The monolayer capacity may be used to determine the specific surface area of the adsorbent by utilizing a solute of known molecular area.

1.5.2 Freundlich Adsorption Model

At the end of the 1940s and at the beginning of the 1950s, work on physical adsorption of gases on energetically heterogeneous solid surfaces became an object of interest with an ultimate derivation of an adsorption isotherm in the form of the so-called generalised Freundlich equation. The main source of heterogeneity for microporous solids is their complex porous structure which contains micropores of different dimension and shape. The mathematical forms of the overall adsorption isotherms depend only on the shape of the energy distribution functions, that characterise the global heterogeneity of the adsorbent surface.

The Freundlich adsorption equation is perhaps the most widely used mathematical description of adsorption in aqueous systems. Generally, the Freundlich isotherm describes adsorption of organic compounds on activated carbon better than the Langmuir-like isotherms. Freundlich isotherm can be obtained from the Langmuir isotherm using the following assumptions:

i) The adsorbent surface is heterogeneous.
ii) The site energies are distributed exponentially.
iii) For all sites with the same energy, a Langmuir isotherm is applicable.

The Freundlich equation is expressed as:

$$q_e = K_F C_e^{1/n} \tag{1.11}$$

where, q_e and C_e have the same meanings as in equation (1.9), K_F (mg.g^{-1}) and “n” (g.dm^{-3}) are the Freundlich empirical constants reveal the characteristic of adsorbent related to adsorption capacity and intensity respectively.

The Freundlich constant, K_F unlike Langmuir constant, q_{max} does not predict the saturation of the solid surface by the monolayer coverage of the adsorbate (Mohan and Singh, 2002). But it gives a relative measure in adsorption capacity. The value K_F is thus equivalent to q_{max} in Langmuir equation. Moreover it estimates the bond strength (Toles and Marshall, 2002).

The value of “n” discloses the adsorption pattern. The favourable adsorption is understood from the values of $1 < n < 10$ while irreversible adsorption is noticed from $n > 10$ and unfavourable from $n < 1$ (Do, 1998). Thus, one can see that the Freundlich equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies.

The simplified linear logarithm form of equation (1.11) is presented in equation (1.12). Plotting log q_e against log C_e gives a straight line with a slope 1/n and an intercept log K_F.

$$\log q_{\mathrm{e}} = \log K_{\mathrm{F}} + \frac{1}{n} \log C_{\mathrm{e}} \tag{1.12}$$

1.6 Aims and Objectives

Present research trends showed that many lignocellulosic materials are good precursors especially for scavenging borderline and soft metal ions. Since Malaysia is rapidly moving towards the concept of safe drinking water, her huge amounts of agricultural wastages namely, oil palm kernel and coconut shells are needed to be testified as metal ions scavenger. In the literature review, it is also observed that H_3PO_4 activation and low temperature carbonization produces activated carbon with enhanced metal ions removal capacity. Since the anions of metals/metalloids are expected to be adsorbed more effectively on the surface of Fe(III)-oxide, prepared activated carbons are also needed to modify through dispersing hydrated Fe(III)-oxide onto its surface.

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 (Cech, 2005). 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. Nickel and lead are the highly toxic (toxic to all life forms even in low concentrations) metals among all borderline and marginal soft metals. USEPA Safe Drinking Water Act Amendments of 1996 selected the contamination level of copper as 1.3 $mg.L^{-1}$ because of its toxicity to liver and kidney (Cech, 2005).

Thus, the divalent cations of lead, copper, nickel and zinc 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 arsenic(V), and the non-ionic species of arsenic(III) are taken into adsorption experiment to observe the suitability of the prepared activated carbon and modified carbon-HFO composites in the removal of highly toxic anionic and non-ionic species. Among various adsorption experiments bench scale batch technique, which uses synthetic solution of $mg.L^{-1}$, is considered an effective method especially for the preliminary stage of investigation.

1.6.1 Objectives

Particularly the development of the activated carbon preparation method is based on the trial and error approach guided by the background reading of the previous processes and reviewed articles. The following objectives have been addressed to testify the hypothesis:

1. To prepare and characterize activated carbon from oil palm kernel and coconut shells as local raw materials.

2. To study the effect of preparation variables and to modify the prepared activated carbon with subsequent characterization.

3. To conduct the batch adsorption of some metal ions on the prepared activated carbon and on modified carbon-hydrated iron(III)-oxide composite adsorbent as to study the adsorption equilibria and kinetics using established models.

1.7 Scope and Limitations

The prepared acid activated carbons are expected to have the potential in removing borderline and soft metal ions in single as well as in multi solutes solutions over a wide range of concentrations and pH. The removal of As(III) and As(V) is attempted to be feasible through the modification of activated carbon using hydrated Fe(III) oxide. Thus to suit the adsorbent as filtering media in a fixed bed to be used especially in water treatment, selective adsorption of target metal ion as well as its desorption studies are designed to conduct. The main limitation in the preparation of activated carbon is that the atmosphere of muffled furnace cannot be defined. The leakage of air through the door controls the furnace atmosphere by design default.

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