SORPTION OF CADMIUM AND LEAD ON ACTIVATED CARBONS PRODUCED FROM RESINS AND AGRICULTURAL WASTES

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

AYDIN MERT AKGÜN

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMICAL ENGINEERING

NOVEMBER 2005

Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Nurcan Baç
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis and for the degree of Master of Science.

Dr. Cevdet Öztin
Co-Supervisor

Prof. Dr. Hayrettin Yücel
Supervisor

Examining Committee Members

Prof. Dr. Nurcan Baç (METU, CHE)

Prof. Dr. Hayrettin Yücel (METU, CHE)

Dr. Cevdet Öztin (METU, CHE)

Prof. Dr. Suzan Kıncal (METU, CHE)

Prof. Dr. Ülkü Yetiş (METU, ENVE)

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

AYDIN MERT AKGÜN

ABSTRACT

SORPTION OF CADMIUM AND LEAD ON ACTIVATED CARBONS PRODUCED FROM RESINS AND AGRICULTURAL WASTES

AKGÜN, Aydın Mert
M.Sc. Department of Chemical Engineering

Supervisor: Prof. Dr. Hayrettin YÜCEL
Co-Supervisor: Dr. Cevdet ÖZTİN

November 2005, 112 pages

In this work, adsorption of cadmium and lead from waste solutions by activated carbon was investigated. The activated carbons were produced from ion exchange resins and agricultural wastes in previous thesis studies under different conditions.

BET surface areas of the activated carbons were given in previous studies. They were further characterized in this study. Slurry pH was measured by change in pH of water in which activated carbon was added. Methylene blue numbers were determined by adsorption of methylene blue onto activated carbons. Isoelectric points were determined by measuring zeta potential of activated carbons at different equilibrium pH.

Results of the first part of sorption experiments showed a strong dependency of adsorption on pH since adsorption mechanism was exchange of heavy metal ions with H^+ ions on the surface. Activated carbon produced from hazelnut shell had the highest removal efficiency with 95% Pb removal and 50% Cd removal at pH 6. However, activated carbon produced from apricot stone removed only 25% and 80% of Cd and Pb, respectively at the same pH.

Initial concentration had positive effect on percent removal as shown by the second part of sorption experiments. This can be explained with saturation of available active sites as initial concentration increased. Activated carbon produced from hazelnut shell could remove 42% of Cd and 85% of Pb, but the one produced from synthetic resin couldn’t remove Cd and Pb more than 20% and 35%, respectively at initial concentration of 100 mg/l.

Langmuir and Freundlich isotherms were plotted and both isotherms were in good agreement with experimental data.

Keywords: Activated Carbon, Adsorption, Heavy Metal, Isoelectric Point

ÖZ

REÇİNE VE TARIMSAL ATIKLARDAN ÜRETİLEN AKTİF KARBONLAR ÜZERİNDE KADMİYUM VE KURŞUNUN TUTULMASI

AKGÜN, Aydın Mert
Yüksek Lisans, Kimya Mühendisliği Bölümü

Tez Yöneticisi: Prof. Dr. Hayrettin YÜCEL
Ortak Tez Yöneticisi: Dr. Cevdet ÖZTİN

Kasım 2005, 112 sayfa

Bu çalışmada atık çözeltilerindeki kadmiyum ve kurşunun aktif karbon tarafından tutulması incelenmiştir. Aktif karbonlar, önceki çalışmalarda ve değişik şartlar altında iyon değiştirici reçinelerden ve tarımsal atıklardan üretilmiştir.

BET yüzey alanları önceki tez çalışmalarında verilmiştir. Bu çalışmada aktif karbonlar uygun yöntemler ile karakterize edilmişlerdir. Bulamaç pH'sı, aktif karbonun eklendiği suyun pH'sındaki değişim ile ölçülmüştür. Metilen mavisi sayıları, metilen mavisinin aktif karbon üzerinde tutulması ile belirlenmiştir.

İzoelektrik nokta aktif karbonların değişik denge pH’larındaki zeta potansiyelleri ile tespit edilmiştir.

Tutulma deneylerinin ilk kısmının sonuçları, ağır metal tutulmasının çözelti pH’sına güçlü bir şekilde bağlı olduğunu göstermiştir çünkü tutulma mekanizması ağır metal iyonları ile yüzeydeki H^+ iyonları arasındaki değişimdir. Fındık kabuğundan üretilen aktif karbon, pH 6’da %95 kurşun ve %50 kadmiyum uzaklaştırması ile en yüksek etkinliğe sahiptir. Ancak aynı pH’da, kayısı çekirdeğinden üretilen aktif karbon, kadmiyum ve kurşunun sırasıyla %25 ve %80’ini uzaklaştırabilmiştir.

Ayrıca, tutulma deneylerinin ikinci kısmının gösterdiği üzere başlangıç konsantrasyonunun yüzde uzaklaştırılma üzerinde olumsuz bir etkisi vardır. Bu durum, başlangıç konsantrasyonu arttıkça uygun aktif bölgelerin doygunluğa ulaşması ile açıklanabilir. Fındık kabuğundan üretilen aktif karbon, başlangıç konsantrasyonu 100 mg/l iken kadmiyumun %42’sini ve kurşunun %85’ini tutabilmişken sentetik reçineden üretilmiş aktif karbon kadmiyum ve kurşunun sırasıyla %20 ve %35’inden fazlasını tutamamıştır.

Langmuir ve Freundlich izotermleri çizilmiş ve her iki izotermin de deneysel sonuçlar ile uyum içinde olduğu görülmüştür.

Anahtar Kelimeler: Aktif Karbon, Ağır Metal, İzoelektrik Nokta, Yüze Tutunma

ACKNOWLEDGEMENTS

I am very grateful to my thesis supervisors Prof. Dr. Hayrettin Yücel and Dr. Cevdet Öztin for all their continuous support, helpful suggestions and guidance during my research work and for their interest in its progress.

I should mention my laboratory mates Yurdaer Babuçcuoğlu, Kerem Bayraktaroğlu and Sedat Aşiroğlu for their help and suggestions. I especially would like to express my gratitude to Wisam Abdallah and Çiğdem Çuhadar for their support and guidance.

I would like to thank Ms. Kerime Güney and Dr. Necati Özkan for their help in the chemical and physical analysis during experimental work. Besides, I would also like to thank all the members of Chemical Engineering Department of Middle East Technical University.

It is great honor for me to express my sincere appreciation to my mother Kamelya Akgün and my father Razi Akgün who encouraged me to begin my master study. Finally, I cannot forget my dear beauty for her existence in my life and for her infinite moral support.

TABLE OF CONTENTS

CHAPTER

APPENDICES

LIST OF TABLES

Table

LIST OF FIGURES

Figure

LIST OF SYMBOLS

b : Langmuir isotherm constant, l/mg

C_0 : Initial concentration of solution, mg/l

C_{blank} : Final concentration of blank experiment, mg/l

C_e : Equilibrium concentration of solution, mg/l

C_{final} : Final concentration of solution, mg/l

d : Pore diameter, nm

K : Freundlich constant, $(=q_e/C_e^{1/n})$

m_{AC} : Mass of activated carbon, g

n : Freundlich exponent, dimensionless

pH_{IEP} : Isoelectric point

pH_{ZPC} : Point of zero charge

q_e : Adsorption quantity, mg/g

Q : Langmuir monolayer capacity, mg/g

S_{MB} : Surface area determined by methylene blue method, m^2/g

S_{BET} : Surface area determined by BET method, m^2/g

V_{sol} : Volume of solution, l

ΔH : Enthalpy of adsorption, kcal/mol

Abbreviations

AAC : Activated carbon produced by Abdallah

YAC : Activated carbon produced by Yağşi

CAC : Activated carbon produced by Çuhadar

CHAPTER I

INTRODUCTION

Wastewater is the spent water after homes, commercial establishments, industries, public institutions and similar entities have used their waters for various purposes. It is synonymous with sewage, although sewage is a more general term that refers to any polluted water including wastewater. The keyword in the definition of wastewater is “used” or “spent”. That is, the water has been used or spent and now it has become a wastewater. On the other hand, to become sewage, it is enough that water becomes polluted whether or not it had been used (Sincero and Sincero, 2002).

Wastewater may contain organic and inorganic substances, industrial wastes, groundwater that happens to infiltrate and to mix with the contaminated water, storm runoff and other similar liquids. Many different types of organisms living in wastewater; many disease-causing viruses, parasites, and bacteria; many organics such as proteins, carbohydrates, or fats; oil and grease; inorganic minerals, metals, and compounds such as sodium, potassium, calcium, magnesium, cadmium, copper, lead, nickel, and zinc or gases such as ammonia, methane or hydrogen sulphide are common in wastewater from both residential and non-residential sources.

There are 4 main sources of contaminants and these are:

1. **Municipal Sources:** Municipal wastes such as human waste or food scraps from these sources are transferred to receiving water by wastewater collection systems or by uncontrolled ways such as rainwater.

2. **Agricultural Sources:** Chemical fertilizers, weeds or insecticides are important sources which pollute water. These contaminants are easily mixed with groundwater or transferred with erosion to rivers.

3. **Industrial Sources:** Heavy metals or organic pollutants are widely used in industry. Industrial facilities drain these pollutants directly to the water sources or soil. But these sources can easily be prevented by effective control techniques.

4. **Natural Sources:** Water can also be polluted by natural sources such as swamp or waste of natural life in the water. In addition, wastes of animals or plants can be mixed with water sources by erosion.

Wastewater can harm public health and the environment unless it is properly treated.

Heavy metals are introduced into water from various industrial sources. They are used to make all sorts of products and very little quantities of various heavy metals are essential for various physiological processes taking place in our bodies. However, in larger amounts, they become toxic. They may build up in biological systems and become a significant health hazard.

Cadmium (Cd) is an extremely toxic heavy metal commonly found in industrial workplaces, particularly where any ore is being processed or smelted. Several deaths from acute exposure have occurred among welders who have welded on cadmium-containing alloys or working with silver solders. Occupational exposure to lead (Pb) is one of the most prevalent overexposures found throughout industry. Industries with high potential exposures include construction work, most smelter operations, radiator repair shops, and firing ranges.

Precipitation is widely used to remove heavy metals from wastewater in the form of metal hydroxides. This method is extremely effective in high concentrations of heavy metals. But at low concentrations, adsorption which involves the interphase accumulation of concentration of substances at a surface or interface is a more effective technique.

The aim of this study is to investigate the adsorption of heavy metals (Pb, Cd) onto activated carbon produced from strongly acidic cation exchange resins and natural wastes (apricot stones and hazelnut shells) under different conditions in previous thesis studies (Abdallah, 2004, Yağşi, 2004 and Çuhadar, 2005).

The main objectives of this work are to investigate the characteristics of activated carbons used in this study by BET surface area, methylene blue number, slurry pH and isoelectric point, to perform adsorption experiments with activated carbons at different initial pH and initial metal concentrations for cadmium and lead and to determine the effects of these parameters on adsorption of heavy metals.

CHAPTER II

THEORETICAL BACKGROUND

2.1. Adsorption

Adsorption, first observed by C. W. Scheele in 1773 for gases and subsequently for solutions by Lowitz in 1785, is recognized as a significant phenomenon in most natural physical, biological and chemical processes. Adsorption involves the interphase accumulation or concentration of substances at a surface or interface. The process can occur at an interface between any two phases such as liquid-liquid, gas-liquid, gas-solid or liquid-solid interfaces. The material being concentrated or adsorbed is the adsorbate and the adsorbing phase is called the adsorbent. When those adsorbed molecules are released from the interphase, desorption takes place (Weber Jr., 1972).

In contrast, absorption is a process in which the molecules or atoms of one phase penetrate nearly uniformly among those of another phase to form a solution with the second phase. This means that adsorption is an interphase phenomenon but absorption is a bulk phenomenon.

The main area of applications of adsorption is in separation and purification processes. Many different ways of operating such processes have been devised and it is helpful to consider the various systems according to the mode of fluid-solid contact.

In batch-type contact operations a quantity of adsorbent is mixed continuously with a specific volume of water or waste until the pollutant in that solution has been decreased to a desired level. The adsorbent is then removed and either discarded or regenerated for use with another volume of solution. If finely powdered adsorbent is used in this type of system, separation of the spent adsorbent from the water is generally difficult. Conversely, the use of large particles of adsorbent, which may be removed more readily when exhausted, requires long periods of contact between solution and adsorbent, necessitating larger basins or tanks in which to retain the water or waste during treatment.

Column-type continuous-flow operations appear to have advantage over batch-type operations because rates of adsorption depend on the concentration of solute in the solution being treated. For column operation the concentration in the solution in contact with a given layer of adsorbent in a column is relatively constant. For batch treatment, the concentration of solute in contact with a specific quantity of adsorbent steadily decreases as adsorption proceeds, thereby decreasing the effectiveness of the adsorbent for removing the adsorbate.

2.1.1. Types of Adsorption

Adsorption takes place in two ways. These are physical adsorption and chemical adsorption or chemisorption depending on the nature of the surface forces.

2.1.1.1 Physical Adsorption

In the first way, the molecules are attached to the surface of the solid. The forces between the adsorbed molecule and the surface of the adsorbent are van der Waals type interaction. These forces are similar to those that cause vapor molecules to condense to liquid. The chemical nature of the adsorbed molecules does not change in this type of adsorption. This type of adsorption is called van der Waals or physical adsorption. It is predominant at low temperature, and is characterized by a relatively low energy of adsorption. It is highly reversible process. Adsorbed material can be easily desorbed if vacuum is applied or if the temperature is increased (Hassler, 1974).

Most applications of adsorption in separation and purification processes depend on physical adsorption. The adsorption of nitrogen on activated carbon at low temperatures can be given as example. The higher capacities achievable in physical adsorption result from multilayer formation and this is obviously critical in such applications as gas storage, but it is also an important consideration in most adsorption separation processes since the process cost is directly related to the adsorbent capacity.

2.1.1.2. Chemisorption

In chemisorption, the adsorbate undergoes chemical interaction with the adsorbent. Electrons are shared or exchanged between the adsorbate and adsorbent surface. Chemisorption is specific and it depends on the chemical nature of both the adsorbent and adsorbate. The forces between them are much stronger than those involved in physical adsorption since a chemical bond is formed. Adsorption of oxygen on activated carbon can be given as example. Oxygen can be removed from carbon surface by increasing temperature but it comes off not as oxygen but as carbon monoxide or carbon dioxide. This indicates that bonds between oxygen and carbon atoms are stronger than those between carbon atoms (Hassler, 1974). Chemisorption is favored by higher temperature and it exhibits high energy of adsorption.

Heterogeneous catalysis generally involves chemisorption of the reactants. In addition, chemical adsorption is sometimes used in trace impurity removal since very high selectivity can be achieved. However, in most situations the low capacity imposed by the monolayer limit and the difficulty of regenerating the spent adsorbent more than outweigh this advantage.

Adsorption may take place under static conditions where both adsorbent and adsorbate are at rest or under dynamic conditions where they move with respect to each other. Under static conditions, the distribution of the adsorbate molecules between two phases is determined by the adsorption isotherm. Under dynamic conditions, the distribution of adsorbate can not only be determined by adsorption isotherm, but it depends also on adsorption kinetics such as rate of transport of adsorbate molecules from the solution bulk to the surface of the adsorbent or rate of adsorption process.

2.1.2. Factors Affecting Adsorption

2.1.2.1. Agitation

The rate of adsorption is controlled by either film or pore diffusion - depending on the amount of agitation. Film diffusion is dominant since surface film around the adsorbent is thicker because of lower agitation rate (continuous system). Higher agitation rate will lead pore diffusion (batch type contacting system).

2.1.2.2. Nature of the Adsorbent

The amount of adsorption is proportional to specific surface area. Specific surface area can be defined as that portion of the total surface area that is available for adsorption. Thus the amount of adsorption accomplished per unit weight of a solid adsorbent is better if the solid is more finely divided and the more porous the solid (Weber Jr., 1972).

The adsorption capacity of a nonporous adsorbent should vary as the inverse of the particle diameter; that for a highly porous adsorbent should be relatively independent of particle diameter. However, for porous materials such as activated carbon, the breaking up of large particles to form smaller ones can in some instances serve to open some tiny, sealed channels in the carbon which might then become available for adsorption, thus possibly yielding dependence of equilibrium capacity on particle size.

2.1.2.3. Solubility of the Adsorbate

The solubility of the solute is one of the main controlling factors for adsorption equilibria. In general, an inverse relationship can be expected between the amount of adsorption of a solute and its solubility in the solvent from which adsorption occurs. For example, 1:2:4.5 ratios of uptake are observed for iodine adsorption on activated carbon from CCl_4, $CHCl_3$ and CS_2, respectively. These ratios are close to the inverse ratios for the solubility of iodine in the respective solvents. The greater the solubility, the stronger the solute-solvent bond and the smaller the amount of adsorption (Weber Jr., 1972).

2.1.2.4. Size of Adsorbate Molecules

Molecular size of an adsorbate is very important because, they have to enter into the micropores. Adsorption is strongest when the pores are just large enough to permit the molecules to enter. Most wastewater contains mixture of compounds of many different molecules. However, the irregular shape of molecules and pores and constant motion of the molecules prevent such blockage from occurring. In addition, smaller molecules allow a greater mobility and diffuse much faster into the pores than the large molecules.

2.1.2.5. pH

The pH of a solution from which adsorption occurs may influence the amount of adsorption for one or more of a number of reasons. Because hydrogen (H^+) and hydroxide (OH^-) ions are adsorbed quite strongly, the adsorption of other ions is influenced by the pH of the solution. Furthermore, to the extent to which the ionization of an acidic or basic compound affects its adsorption, pH affects adsorption in that it governs the degree of ionization (Weber Jr., 1972).

In general, adsorption of typical organic pollutants on activated carbon from wastewater is increased with decreasing pH. In many cases, this may result from neutralization of negative charges at the surface with increasing hydrogen ion concentration. This effect can be expected to vary in degree for different activated carbons because the charges at the surfaces of the activated carbon depend on the composition of the precursors and on the technique of activation.

2.1.2.6. Temperature

Adsorption reactions are normally exothermic, thus the amount of adsorption generally increases with decreasing temperature. The changes in enthalpy for adsorption are usually of the order of those for condensation or crystallization reactions. Small variations in temperature tend not to alter the adsorption process to a significant extent (Weber Jr., 1972).

The change in the energy content of a system in which adsorption occurs, i.e., the total amount of heat evolved in the adsorption of a definite quantity of solute on an adsorbent, is termed the enthalpy of adsorption, ΔH. Enthalpies of gas phase adsorption generally are several kcal per mole, but because water is desorbed from the surface when adsorption from aqueous solution occurs, heat effects for the latter process are somewhat smaller than those for gas phase adsorption.

2.1.3. Adsorptive Properties

2.1.3.1. Surface Area

Adsorption capacity of activated carbon is proportional with its surface area. This means that the greater the surface area, the higher the number of adsorptive sites available. Typical commercial products have specific surface areas in the range of 250 – 2500

m^2/g. But values as high as 5000 m^2/g have been reported (Kirk-Othmer, 2001).

Total surface area of activated carbon is usually determined by application of the Brunauer-Emmett-Teller (BET) model of physical adsorption using nitrogen as the adsorbate and it is expressed in square meters of surface area per gram of activated carbon. There is no guarantee that the entire surface is available for the adsorption of organic compounds since organic molecules are much larger than a nitrogen molecule. Thus, it is essential for an adsorptive carbon to have a large accessible surface area, which in turn is related to its pore size distribution.

2.1.3.2. Pore Size Distribution

Determination of the pore size distribution of an activated carbon is an extremely useful way to understand the performance characteristics of the material. IUPAC defines the pore size distribution as micropore ($d < 2$ nm), mesopore (2 nm $< d <$ 50 nm) and macropore ($d > 50$ nm). The macropores are used as the entrance to the activated carbon, the mesopores for transportation and the micropores for adsorption.

2.1.3.3. Adsorption Capacity

Adsorption capacity is characterized by the effectiveness of activated carbon in removing a given contaminant. For comparison, several standard compounds are used for these measurements.

For example, the iodine number, which is the milligrams of iodine adsorbed by one gram of carbon, is the most fundamental parameter used to characterize the adsorption performance of activated carbon. It describes capacity of activated carbon to adsorb substances which have low molecular weight and it gives information about micropore content of activated carbon. As similar, methylene blue number (MBN), which is the milligrams of methylene blue adsorbed by one gram of carbon in equilibrium, gives information about mesopore structure of activated carbon. The molasses number is the milligrams of molasses adsorbed by one gram of activated carbon and it characterizes activated carbon's capacity for more complex compounds.

2.1.3.4. Surface Chemistry

Commercial activated carbons can be prepared from a variety of precursors and generally these precursors are activated in an atmosphere of water vapor, air or other selected gases at very high temperatures. It is very difficult to characterize the surface chemistry because of the impure nature of the precursors used in the production and because of the concentration and temperature gradients that develop within the beds of carbon during activation.

Functional groups are formed during activation by interaction of free radicals on the carbon surface with atoms such as oxygen and nitrogen, both from within the precursor and from the atmosphere (Zawadski, 1989). The functional groups render the surface of activated carbon chemically reactive and influence its adsorptive properties (McEnaney and Mays, 1989). Surface oxidation is an inherent feature of activated carbon production. It results in hydroxyl (-OH), carbonyl (=CO), and carboxylic (-COOH) groups that impart an amphoteric character to the activated carbon. So it can be either acidic or basic.

Zero point of charge (ZPC) is one of the most important surface properties of adsorbents and it is where the total charge from anions and cations at the surface is equal to zero. The pH that corresponds to the ZPC is referred to as the pH_{ZPC}. When the pH is lower than pH_{ZPC} then, the net surface charge of the activated carbon is positive. That’s why, adsorption of cations gets harder as a result of repulsive electrostatic interaction. When the medium is basic, net surface charge becomes negative and then adsorption gets easier.

2.1.4. Adsorbents

An adsorbent must have a high specific area, which implies a highly porous structure with very small micropores to achieve a significant adsorption capacity. These production procedures generally yield a fairly wide distribution of pore size. The crystalline adsorbents are different in that the dimensions of the micropores are determined by the crystal structure and there is therefore virtually no distribution of micropore size. Although structurally very different from the crystalline adsorbents, molecular sieves also have a very narrow distribution of pore size (Kirk-Othmer, 2001).

The search for a suitable adsorbent is generally the first step in the development of an adsorption process. A practical adsorbent has four primary requirements: selectivity, capacity, mass-transfer rate, and long-term stability. The requirement for adequate adsorptive capacity restricts the choice of adsorbents to microporous solids with pore diameters ranging from a few tenths to a few tens of nanometers.

Traditional adsorbents such as silica, activated alumina and activated carbon exhibit large surface areas and micropore volumes. The surface chemical properties of these adsorbents make them potentially useful for separations by molecular class. However, the micropore size distribution is fairly broad for these materials. This characteristic makes them unsuitable for use in separations in which steric hindrance can potentially be exploited.

Typical polar adsorbents are silica gel and activated alumina. The order of affinity for various chemical species is saturated hydrocarbons < aromatic hydrocarbons = halogenated hydrocarbons < ethers = esters = ketones < amines = alcohols ≤ carboxylic acids. In general, the selectivities are parallel to those obtained by the use of selective polar solvents; in hydrocarbon systems, even the magnitudes are similar. Consequently, the commercial use of these adsorbents must compete with solvent-extraction techniques.

The principal nonpolar-type adsorbent is activated carbon. With some exceptions, the least polar component of a mixture is selectively adsorbed; eg, paraffins are adsorbed selectively relative to olefins of the same carbon number, but dicyclic aromatics are adsorbed selectively relative to monocyclic aromatics of the same carbon number.

Polymeric resins are widely used in the food and pharmaceutical industries as cation–anion exchangers for the removal of trace components and for some bulk separations, such as fructose from glucose. These resins are primarily attractive for aqueous-phase separations and offer a fairly wide potential range of surface chemistries to fit a number of separation needs. For example, polymeric resins are effective in partitioning by size and molecular weight and may also be effective in ion exclusion.

In contrast to these adsorbents, zeolites offer increased possibilities for exploiting molecular-level differences among adsorbates. Zeolites are crystalline aluminosilicates containing an assemblage of SiO_4 and AlO_4 tetrahedral joined together by oxygen atoms to form a microporous solid, which has a precise pore structure. The versatility of zeolites lies in the fact that widely different adsorptive properties may be realized by the appropriate control of the framework structure, the silica-to-alumina ratio (Si/Al), and the cation form. For example, zeolite A, has a three-dimensional (3D) isotropic channel structure constricted by an eight-membered oxygen ring. Its effective pore size can be controlled at ~ 3–4 Å. The potassium form, with 3-Å pores, is used for removing water from olefinic hydrocarbons. The sodium form can be used to efficiently remove water from nonreactive hydrocarbons, such as alkanes. The substitution of calcium can provide a pore size that will admit n-paraffins and exclude other hydrocarbons.

In addition to the fundamental parameters of selectivity, capacity, and mass-transfer rate, other more practical factors, namely, pressure drop characteristics and adsorbent life, play an important part in the commercial viability of a practical adsorbent (Kirk-Othmer, 2001).

2.1.5. Adsorption Isotherms

Adsorption in a solid-liquid system results in the removal of solutes from solution and a dynamic equilibrium is occurred between the concentration of the adsorbate at the surface of the solid and that remaining in the solution. At this position of equilibrium, there is a defined distribution of adsorbate between the liquid and solid phases. The distribution ratio is a measure of the position of equilibrium in the adsorption process. It may be a function of the concentration and the nature of the adsorbate or the nature of solution. The preferred form of this distribution is to express the quantity (q_e), which is the amount of adsorbate adsorbed per unit weight of solid adsorbent, as a function of C_e, which is the concentration of adsorbate remaining in solution at equilibrium, at fixed temperature. An expression of this type is called an adsorption isotherm. The adsorption isotherm is a functional expression for the variation of adsorption with concentration of adsorbate in bulk solution at constant temperature. Several types of isothermal adsorption relations may occur (Weber Jr., 1972).

2.1.5.1. Langmuir Isotherm

Langmuir isotherm is the simplest form of isotherm equations. It was originally developed to represent monolayer adsorption on an ideal surface. The Langmuir treatment is based on the assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, that the heat of adsorption is constant, and that there is no migration of adsorbate in the plane of the surface.

The Langmuir equation is:

$$q_e = \frac{QbC_e}{1+bC_e} \qquad \text{(Eq. 2.1)}$$

where b is the equilibrium constant related to the heat of adsorption and Q is the amount of adsorbate adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface. The equilibrium constant decreases with increasing temperature.

The linear form of this equation is:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \qquad \text{(Eq. 2.2)}$$

This means that if C_e/q_e vs. C_e graph is plotted, then the linear representation of adsorption process is occurred. The slope of the line gives Q and the intercept gives Qb.

Langmuir equation can be used for describing equilibrium conditions for sorption behavior in different sorbate-sorbent systems, or for varied conditions within any given system.

2.1.5.2. Freundlich Isotherm

Another equation for isothermal adsorption is Freundlich isotherm. This isotherm is a special case for heterogenous surface energies and it is used most often in real world examples. In this equation, relationship between metal uptake and equilibrium concentration is logarithmical and it is assumed that uptake capacity of adsorbent is infinite. Unlike Langmuir isotherm, Freundlich isotherm does not assume that all active sites are uniform. Different active sites have different characteristics from each other. General form of Freundlich equation is:

$$q_e = KC_e^{1/n} \qquad \text{(Eq. 2.3)}$$

where K and n are constants. K shows the ability of adsorbent and n shows the tendency of adsorbate to be adsorbed. If Eq. 2.3 is linearized:

$$\ln q_e = \ln K + \frac{1}{n}\ln C_e \qquad \text{(Eq. 2.4)}$$

The slope of the line gives n and the intercept gives K since $\ln q_e$ vs. $\ln C_e$ graph is plotted.

It is easier to use Freundlich isotherm to handle with more complex calculations.

2.2. Activated Carbon

2.2.1. Definition and Properties

Activated carbon is a microcrystalline, amorphous form of carbon and it has an extraordinarily large pore volume and internal surface area. These unique characteristics are responsible for its adsorptive properties, which are used in many different liquid- and gas-phase applications. Activated carbon is an exceptionally versatile adsorbent because the size and distribution of the pores within the carbon matrix can be controlled to meet the needs of current and emerging markets (Jüntgen, 1977). X-ray Difractometer (XRD) analysis of activated carbons shows a structure which is much more disordered than that of graphite, having crystallites only a few layers in thickness and less than 10 nm in width. The spaces between the crystallites of activated carbon constitute the microporous structure. Its chemical structure allows it to preferentially adsorb organic materials and other nonpolar compounds from the gas or liquid streams.

Pore structure of activated carbon using scanning electron microscopy (SEM) is shown in Figure 2.1 (Park et. al, 2002).

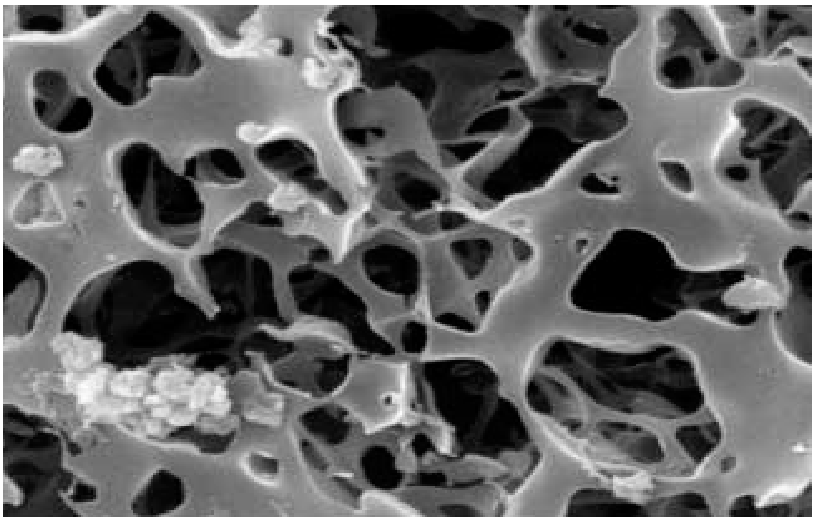

Figure 2.1: Pore Structure of Activated Carbon

Producing activated carbons in the form of powders, granules, and shaped products satisfies engineering requirements of specific applications. Through choice of precursor, method of activation, and control of processing conditions, the adsorptive properties of products are tailored since many decades for a wide variety of applications. These applications are such as the decolorization of sugar and sweeteners, purification of potable water, gold recovery, production of pharmaceuticals, catalytic processes, off gas treatment of waste incinerators, automotive vapor filters, color / odor correction in wines and fruit juices, etc (Smisek and Cerny, 1970; Hassler, 1974).

2.2.2. History

In 1900, two very significant processes in the development and manufacture of activated carbon products were patented. The first commercial products were produced in Europe under these patents: Eponite, from wood in 1909, and Norit, from peat in 1911. Westvaco Corp. first produced activated carbon in the United States in 1913 under the name Filtchar, using a by-product of the papermaking process (Hassler, 1958). Further milestones in development were reached as a result of World War I. In response to the need for protective gas masks, a hard, granular activated carbon was produced from coconut shell in 1915. Following the war, large-scale commercial use of activated carbon was extended to refining of beet sugar and corn syrup and to purification of municipal water supplies (Hassler, 1963). The termination of the supply of coconut char from the Philippines and India during World War II forced the development of granular activated carbon products from coal in 1940 (Carrubba et al., 1984). More recent innovations in the manufacture and use of activated carbon products have been driven by the need to recycle resources and to prevent environmental pollution.

2.2.3. Production of Activated Carbon

Activated carbon is the title of a family of substances and none of these substances can be characterized by a structural formula nor can be separately identified by chemical analysis. The way to differentiate between activated carbons is their adsorptive properties and catalytic properties. This important point should be taken into account when talking about production of activated carbon.

2.2.3.1. Precursors

The quality of the resulting activated carbon is considerably influenced by the starting material. Although the activation procedure employed mainly determines the chemical nature of the surface oxides and the surface area of the resulting product, the structure of the pores and the pore size distributions are largely predetermined by the nature of the starting material. Any cheap substance with a high carbon and low ash content can be used as a precursor. Activated carbon is mostly produced from organic materials that are rich in carbon such as lignite, coal, wood, coconut shell or bone. It also can be manufactured from various synthetic resins. The choice of precursor is largely dependent on its availability, cost, and purity.

2.2.3.2. Production Methods

Activated carbon can be produced by two methods:

1. By carbonizing material of vegetable origin with the addition of activating agents which influence the course of pyrolysis. The method is called "chemical activation".

2. By pyrolyzing the precursor, then activating with gaseous substances (generally steam or carbon dioxide). This procedure is called “physical activation".

2.2.3.2.1. Chemical Activation

In this method, the precursor is carbonized after the addition of substances, which restrict the formation of tar. The activating agent added to the precursor is recovered for reuse and to free the pores after carbonization. Activating agent is minimized the amount of aqueous phase in the distillate (acetic acid, methanol, etc.) and it increases the yield of carbon in the product. Potassium thiocyanate, potassium sulphide, zinc chloride, phosphoric and sulphuric acids are mostly used as activating agents.

2.2.3.2.2. Physical Activation

2.2.3.2.2.1. Carbonization

Carbonization is the thermal treatment of precursors in the absence of air. The main aim of carbonization is to reduce the volatile content of the source material in order to convert to a suitable form for activation. At the end of the process, carbon content of the product attains a value of about 80% (El-Gazar, 1996).

Most of the non-carbon elements, hydrogen and oxygen are removed in gaseous form by carbonization and the elementary carbon atoms that become free are grouped into organized crystallographic formation called elementary graphitic crystallites. The mutual arrangement of the crystallites is irregular, so that free interstices remain between them. As a result of deposition and decomposition of tarry substances, these become filled or at least blocked by disorganized (amorphous) carbon.

2.2.3.2.2.2. Activation with Gaseous Substances

Activated carbon with a large adsorption capacity can also be produced by activating the carbonized material under conditions that the activating agent reacts with the carbon. Steam, carbon dioxide and oxygen (air) are the most often used activating agents. Steam is preferable to carbon dioxide and better than air. Activation procedure takes place in two steps. In the initial step, when the burn off is not higher than 10%, disorganized carbon is burnt out preferentially and the closed and clogged pores between the crystallites are freed. In the final step, carbon of the elementary crystallites is burnt and larger size pores are formed.

2.2.4. Applications

Two distinct types of activated carbon are recognized commercially. Gas-phase activated carbons are hard granules or formed pellets. They are characterized by benzene or carbon tetrachloride tests. Liquid-phase activated carbons generally light, fluffy powders. These carbons are characterized by adsorption tests such as methylene blue number or iodine number (Kirk-Othmer, 2001).

2.2.4.1. Gas-phase Applications

2.2.4.1.1. Solvent Recovery

Most of the activated carbon used in gas-phase applications is used to prevent the release of volatile organic compounds into the atmosphere. Air containing vapor of the solvent is passed through a bed of activated carbon on which the solvent vapor is adsorbed. Activated carbon is desorbed (usually with steam) after saturation with the solvent and it is recovered by separating the condensed vapor. Much of this use has been in response to environmental regulations.

2.2.4.1.2. Control of Gasoline Emissions

A principal application of activated carbon is in the capture of gasoline vapors that escape from vents in automotive fuel systems (Clarke, et al., 1967). Fuel vapors vented when the fuel tank or carburetor are heated are captured in a canister containing 0.5 to 2 L of activated carbon. Regeneration of the carbon is then accomplished by using intake manifold vacuum to draw air through the canister. The air carries desorbed vapor into the engine where it is burned during normal operation. Activated carbon systems have also been proposed for capturing vapors emitted during vehicle refueling, and activated carbon is used at many gasoline terminals to capture vapor displaced when tank trucks are filled. The type of carbon pore structure required for these applications is substantially different from that used in solvent recovery.

2.2.4.1.3. Deodorization of Air

Staying in a place having a little offensive odor is unpleasant. Temperature and humidity of air in public places must be controlled and kept at some level to have a comfortable atmosphere in these places. The most efficient method is air filtration by activated carbon.

2.2.4.1.4. Protection Against Atmospheric Contaminants

Activated carbon is widely used to filter breathing air to protect against a variety of toxic or noxious vapors, such as war gases, industrial chemicals, solvents, and odorous compounds. Although activated carbon can give protection against most organic gases, it is especially effective against high molecular weight vapors. The activated carbon is employed in individual canisters or pads, as in gas masks, or in large filters in forced air ventilation systems.

2.2.4.2. Liquid-phase Applications

2.2.4.2.1. Water Treatment

Water treatment can be divided into three groups: drinking water, industrial and municipal wastewater, and groundwater.

Treatment of drinking water accounts for about 31% of the total activated carbon used in liquid-phase applications. In drinking water, activated carbon is used to remove unpleasant odors and tastes and reduce the concentration of compounds constituting a health hazard (pesticides, chlorinated hydrocarbons, etc.).

Wastewater may contain suspended solids, hazardous microorganisms, and toxic organic and inorganic contaminants that must be removed or destroyed before discharge to the environment. In tertiary treatment systems, powdered, granular, or shaped carbon can be used to remove residual toxic and other organic compounds after the primary filtration and secondary biological treatment.

There are two ways to apply carbon in groundwater cleanup. One of these ways is the conventional method of applying powdered, granular, or shaped carbon to adsorb contaminants directly from the water. The other method utilizes air stripping to transfer the volatile compounds from water to air. The compounds are then recovered by passing the contaminated air through a bed of activated carbon (Canter and Knox, 1985).

2.2.4.2.2. Decolorization of Sweetener

About 11% of the liquid-phase activated carbon is used for purification of sugar and corn syrup. White sucrose sugar is made from raw juice squeezed from sugar cane or sugar beets. The clarified liquor is decolorized using activated carbon, or ion-exchange resins (Hessler, 1974). High fructose corn sweeteners

(HFCS) are produced by hydrolysis of corn starch and are then treated with activated carbon to remove undesirable taste and odor compounds and to improve storage life.

2.2.4.2.3. Applications in Chemical Industry

Activated carbon removes impurities to achieve high quality. For example, organic contaminants are removed from solution in the production of alum, soda ash, and potassium hydroxide. Other applications include the manufacture of dyestuffs, glycols, amines, organic acids, urea, hydrochloric acid, and phosphoric acid. Oils, dyes, and other organics are adsorbed on activated carbon in dry cleaning recovery and recycling systems. Medical applications include removal of toxins from the blood of patients with artificial kidneys and oral ingestion into the stomach to recover poisons or toxic materials. Activated carbon also is used as a support for metal catalysts in low volume production of high value specialty products such as pharmaceuticals, fragrance chemicals, and pesticides (Kirk-Othmer, 2001).

2.3. Zeta Potential and Isoelectric Point

Colloidal particles generally have electrical charge affecting their behaviors. The development of a net charge at the particle surface affects the distribution of ions in the surrounding interfacial region, resulting in an increased concentration of counter ions (ions of opposite charge to that of the particle) close to the surface.

These charges on the surface form an electrical layer. These layers are formed by activation of reactive groups of molecules on the surface or by adsorption of some ions in the solution on colloidal particles (Koyuncu, 1999).

The liquid layer surrounding the particle has two parts; an inner region (Stern layer) where the ions are strongly bound and an outer region (Diffuse layer) where they are attached less firmly. When a particle moves, ions within the boundary move with it, but any ions beyond the boundary do not travel with the particle. This boundary is called the surface of hydrodynamic shear or slipping plane. The potential that exists at this boundary is known as the zeta potential.

The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If all the particles in suspension have a large negative or positive zeta potential then they will tend to repel each other and there is no tendency to flocculate. However, if the particles have low zeta potential values then there is no force to prevent the particles coming together and flocculating.

The most important factor affecting zeta potential is pH. A zeta potential value is a meaningless number without pH value. If base is added into the suspension in which particles have negative zeta potential then, ionization of basic groups on the surface are prevented and the net surface charge becomes more negative. If acid is then added to this suspension a point will be reached where the negative charge is neutralized. Any further addition of acid prevents the ionization of acidic groups on the surface and then net charge of the surface becomes positive. So, zeta potential vs. pH curve will be positive at low pH and lower or negative at high pH.

The point where the plot passes through zero zeta potential is called isoelectric point. It is the point where the colloidal system is least stable. A typical plot of zeta potential versus pH is shown in Figure 2.2.

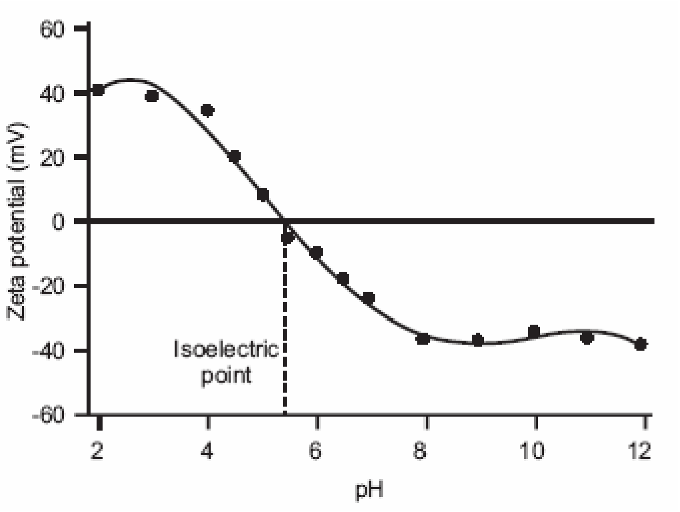

Figure 2.2: A Typical Plot of Zeta Potential vs. pH

Zeta potential measurements of solid-liquid interface can generally be used to study the nature of the solid surfaces and their charges in different electrolytes. Some of the more significant applications are studies of coagulation of mineral suspensions, flocculation, adsorption of metal cations at mineral-water interfaces, selective agglomeration processes and the study of flotation processes.

CHAPTER III

LITERATURE SURVEY

In today's world, heavy metals are used in wide range of industries. Wastewater containing heavy metals has low biological oxygen demand (BOD) and inorganic character; it is mostly acidic, highly poisonous and fatal for living organisms.

Main industries whose wastewater contains heavy metals are mining industry, metal and metal plating industry, electrical and electronics industry, paint industry, piping industry, automotive and white goods industries.

Many different methods are used to remove heavy metals from wastewaters such as precipitation, ion exchange or reverse osmosis. But adsorption of heavy metals onto activated carbon has gained importance very recently.

3.1. Heavy Metal Removal from Wastewater

Ouki and Neufeld (1997) investigated the use of activated carbon for recovery of chromium from wastewater. They used column packed with commercial activated carbon which had high surface area and synthetic wastewater was pumped through the system. The results showed that 99% of chromium removal efficiency could be achieved. The adsorption capacity of the activated carbon was increased with cycles of adsorption / regeneration. They deduced that adsorption and desorption of chromium on activated carbon depends on the pH conditions. Under acidic conditions, the reduction reaction was fast and it controlled the mechanism of chromium removal. Superior performance of regeneration with combination of caustic and acid was obtained as compared with only acid or caustic.

Seco et al. (1997) studied about adsorption of heavy metals from aqueous solutions on activated carbon in single (Cu, Ni) and binary (Cu-Ni, Cu-Cd, Cu-Zn) systems. They concluded that solution pH, initial metal concentration and temperature are the most important parameters affecting the removal of heavy metals from aqueous solutions on activated carbon. Increases in pH at acidic range and temperature yielded greater removal efficiency while increases of initial metal concentration reduce the metal removal percentages. In binary systems, Cu removal efficiencies were similar to those obtained in single Cu adsorption experiments. But the removal efficiencies of Ni, Cd and Zn decreased as the Cu concentration increased. Finally, predictions of triple layer model (TLM) developed in this study were quite close to the experimental data.

Teker and İmamoğlu (1999) investigated the removal of copper and cadmium on activated carbon produced from rice hulls by chemical activation. The adsorption parameters investigated in this study was pH, contact time, temperature, initial heavy metal concentration and adsorbent dosage. pH was highly effective on adsorption of both of heavy metals. Equilibrium was attained in a short time. Results indicated that the adsorption increased with increasing adsorbent dosage up to a certain value and then there was no further increase in adsorption. Adsorption of metal ions was decreased with increasing initial concentration. As a result, optimum conditions for removal of cadmium and copper were determined. Freundlich and Langmuir isotherms were plotted and constants for these isotherms and thermodynamic parameters were found.

Bello et al. (1999) produced activated carbon from peach stones and *Eucalyptus globulus* chips by physical activation in the presence of steam or carbon dioxide. The products were characterized with chemical structure, surface area and thermal decomposition. The products were used to remove mercury and chromium from aqueous solutions. Effects of initial metal concentration, temperature, particle size and pH on removal rate of heavy metals were studied. High initial concentration of heavy metals, small particle size and low temperature were favourable for both chromium and mercury adsorption on both types of adsorbents. On the other hand, high pH was favourable for mercury adsorption on both of activated carbons but influence of pH on chromium adsorption was different for different activated carbons. The highest removal rates of these ions were obtained by using activated carbon from *Eucalyptus globulus* due to their greater volume of meso- and macropores.

Mohan and Chandler (2001) studied the adsorption of ferrous, manganese, zinc and calcium from acid mine drainage in single, binary (Fe-Mn, Fe-Zn, Fe-Ca), ternary (Fe-Mn-Zn, Fe-Mn-Ca), and quaternary (Fe-Mn-Zn-Ca) systems. In their study, they used seven different commercial activated carbons. They performed batch studies to obtain equilibrium isotherms and column studies to demonstrate the effectiveness of adsorption. According their study, they deduced that data were better fitted by Langmuir isotherm in single component systems but Freundlich isotherm fitted the data better for adsorption from multi-component solutions. Another result of their study was that iron adsorption capacity of different carbons decreases more in ternary and quaternary systems as compared to binary systems. It was concluded from column studies that high adsorption capacities could be obtained in industrial size columns.

Rajeshwarisivaraj et al. (2001) prepared activated carbon from cassava peel by chemical activation in the presence of phosphoric acid and by physical activation in the presence of air and they used the products to remove different types of dyes (rhodamine-B, direct brown, procion orange, acid violet, malachite green, methylene blue) and heavy metals (Cr, Hg, Fe). They found that activated carbons were efficient to remove both of heavy metals and the dyes from aqueous solution. But carbon prepared by chemical activation was more efficient than that prepared by physical activation. In this study, they achieved very high removal efficiency (100%) in relatively short period of time (60-90 min).

Shekinah et al. (2002) used Eichhornia, an aquatic weed as precursor to produce activated carbon with physical activation in the presence of air and used it to remove lead from aqueous solution. Their parameters were agitation time, initial metal concentration, adsorbent dosage and pH. Adsorption parameters were obtained in this study with Langmuir and Freundlich isotherms. In their study, increase in agitation time and in carbon dosage increased the uptake of lead. Maximum adsorption was observed in the pH range of 2-5 and equilibrium was reached in a short time. The experiments were repeated for radiator-manufacturing industry wastewater and the results confirmed the validity of results obtained in batch studies.

Mohan and Singh (2002) studied production of activated carbon from bagasse, an agricultural waste, by sulphuric acid activation and adsorption of cadmium and zinc in single, binary (Cd-Cu, Cd-Zn, Zn-Cu) and ternary (Cd-Cu-Zn) systems. In single systems, removal of cadmium and zinc increased with increasing pH, temperature and amount of adsorbent. When the pH was higher than 8, precipitation became very effective. In ternary systems, adsorption capacity for cadmium and zinc decreased more than those in binary systems. The data were better fitted by the Freundlich isotherm as compared to Langmuir in both the single and multi-component systems. Activation energy and entropy of activation, mass transfer coefficient and effective diffusion coefficient were obtained to establish the mechanism. These parameters showed that adsorption occurred through the film diffusion mechanism.

Basso et al. (2002) used activated carbon produced from *Arundo donax*, a rapid growing plant, by phosphoric acid activation to remove cadmium and nickel from aqueous solutions. Surface area and surface functional groups were determined. Effects of pH of metal solution, activated carbon dosage and initial metal concentration on adsorption were investigated. Metal uptake was increased with decreasing initial concentration, increasing carbon dosage and increasing pH. Equilibrium isotherms were plotted. The results were satisfactorily described by Langmuir adsorption. Pseudo second order model was used to describe adsorption kinetics. Parameters obtained from the model and obtained from experimental results were in good agreement. Results were compared by commercial activated carbon. As a result, *Arundo donax* is a suitable precursor for activated carbon production.

Kadirvelu et al. (2003) produced activated carbons form several agricultural wastes such as silk cotton hull, coconut tree sawdust, sago waste, maize cob or banana pith and they used these carbons to remove heavy metals (Ni, Hg) and dyes (rhodamine-B, congo red, methylene blue, methyl violet, malachite green) from aqueous solutions. Activated carbons were produced by chemical activation with sulphuric acid. In their study, adsorption of all dyes and metal ions required a very short time and gave quantitative removal. They claimed that activated carbon prepared from agricultural wastes can be used effectively in the treatment of dyes and metal ions.

Dabek (2003) investigated the adsorption of zinc ions from aqueous solutions on regenerated activated carbon. The parameters were initial zinc concentration and pH. Activated carbon was recovered from spent catalyst generated by vinyl acetate synthesis by using supercritical extraction with carbon dioxide or by leaching with hydrochloric acid or a solution of nitric acid assisted by microwave energy. Activated carbon which had high surface area (1000 m^2/g) could be obtained in this study. Activated carbon recovered in this study had high adsorption capacity for zinc ions that was comparable to that of fresh commercial activated carbon.

Moon and Lee (2005) used composition of curdlan, a type of biopolymer and commercial activated carbon in different ratio to remove heavy metals (Pb, Cd, Cu, Mn). The strength of the particles was increased with pre-treatment of curdlan using acidic and basic solutions. The pore size of the particles decreased with increasing fraction of activated carbon. In addition, the heavy metal adsorption capacity increased with increasing activated carbon quantity for all four heavy metals. This indicated that activated carbon was the main adsorbent and that the curdlan was used as an activated carbon binder. Although the surface area was significantly low (82.3 m^2/g), the removal capacity for heavy metals was sufficiently high. In their study, equilibrium was reached after 1 h. The adsorption amount was highest with Cu, followed in decreasing order by Mn, Pb and Cd.

3.2. Effects of Surface Properties on Heavy Metal Adsorption

Toles et al. (2000) produced activated carbon from almond shell at six different activation conditions with steam and carbon dioxide. The products characterized with surface area, yield, surface charge and attrition. The products had high surface area and low yield. Attrition was higher for produced activated carbons as compared with commercial carbons. Surface charge was negative for all products. The products were used to remove copper from aqueous solution. All activated carbons produced in this study adsorbed copper more than commercial carbons. Adsorption capacity was higher for steam activated carbons. Adsorption of organic compounds such as methanol, acetone or benzene was also studied and similar results were obtained. Cost of production with these methods was estimated and the results showed that steam activated carbons could have potential as compared with commercial products.

Shim et al. (2001) modified activated carbon produced from pitch by steam activation with nitric acid and sodium hydroxide. BET surface area and zero point of charge of the products were determined. Surface functional groups were also investigated with Fourier Transform Infrared Spectroscopy (FTIR). The products had very high surface area (about 1000-1400 m^2/g) but the modified activated carbons had lower surface areas. The zero point of charge was 6, 10 and 4 for untreated activated carbon, base-treated activated carbon and acid-treated activated carbon, respectively. FTIR spectra showed that chemical modification was very effective on chemical structure of activated carbon. The products were used for copper and nickel adsorption. Acid-treated activated carbon had the highest adsorption capacity followed by base-treated and untreated activated carbons. Adsorption capacity was influenced by lactone groups at $pH<pH_{ZPC}$ and acidic groups at $pH>pH_{ZPC}$.

Puziy et al. (2002) produced activated carbon from styrene-divinylbenzene by chemical activation with phosphoric acid and by physical activation with steam; they characterized the products and used them for copper adsorption from aqueous solution. Elemental composition, cation exchange capacity, chemical structure and proton binding of products were investigated. As a result of phosphoric acid activation, phosphorus content of the products was very high. IR spectra showed that the products of chemical activation had considerable amount of carboxyl groups and phosphorus-containing carbonaceous structure. Higher adsorption of copper on chemically activated carbons is due to strongly acidic phosphorus-containing groups on the surface.

Park et al. (2002) modified commercial activated carbon in two steps. In first step, virgin activated carbon (AC) was treated with nitric acid (1AC). In second step, 1AC was treated with alkaline solution (2AC). All three types of activated carbon were characterized with BET surface area, pore volume, pH_{ZPC} and electrophoretic mobility. BET area and total pore volume decreased during treatment (1500 to 1150 m^2/g and 0.74 to 0.65 cm^3/g). pH_{ZPC} of AC, 1AC and 2AC was determined as 7.5, 4.5 and 5.8, respectively. First step of modification increased the number of carboxylic groups on the surface sharply, but in second step it was decreased slightly. 2AC had some sodium carboxylate groups on the surface. These products were used for adsorption of lead, cadmium and chromium. Adsorption capacity for all heavy metals followed the order of 2AC>1AC>AC. Results fitted with Langmuir isotherm.

Xiao and Thomas (2004) treated commercial activated carbon with nitric acid and oxidized the carbon surface. Activated carbon was characterized with BET surface area, FTIR, temperature programmed desorption (TPD), acid-base titration, Raman spectra and zero point of charge. Acid treatment increased the total and micropore volume. TPD showed that acid-treated carbon surface had anhydride, carbonyl, carboxylic and phenol groups. Acid-base titrations showed that acid-treated carbon was highly oxidized but untreated carbon had basic surface. pH_{ZPC} of untreated and acid-treated activated carbons were 8.1 and 2.5, respectively. Adsorption of cadmium, mercury, calcium and lead were investigated in single and binary systems. Adsorption isotherms were plotted and Langmuir isotherm was in good agreement. Maximum adsorbed amounts were in order of Hg>Pb>Cd>Ca. A mathematical model was prepared for binary systems and the results of model were validated with experimental results.

Chen and Wu (2004) modified commercial activated carbon with hydrochloric and phosphoric acid followed by sodium hydroxide. The modified activated carbons were characterized by surface area, pH, and total acidity capacity with SEM, XRD and FTIR. All products had very close surface areas. pH of the carbons varied from 3.7 to 10.7 and total acidity capacity varied from 0.15 mmol/g to 0.51 mmol/g. Acid-treated activated carbons had more porous surface than untreated activated carbon. FTIR showed that sodium hydroxide treatment increased the concentration of hydroxyl groups on the surface but acid treatment increased the concentration of ether, phenol and lactone groups. The products used for copper adsorption. Base-treated carbons had higher adsorption capacity than acid-treated carbons. Langmuir isotherms were plotted and results were in good agreement with this type of isotherm.

Lima and Marshall (2005) produced activated carbon from broiler manure with steam activation and characterized the products. BET surface area, true density and surface charge of the products were determined. The products had relatively low surface area and they had high attrition. The ash content of activated carbons was very high. Bulk density was not varied significantly with production conditions. Surface of the products had low negative charge. Adsorbents were used to adsorb copper. Activated carbon activated for 45 min had the highest adsorption capacity while carbons activated for more than 45 min had lower capacity. The results compared with the results for commercial activated carbons.

CHAPTER IV

EXPERIMENTAL WORK

4.1. Materials

Activated carbon samples used in this study were obtained in previous M.Sc. studies in this department. Their production conditions as reported by researchers (Abdallah, 2004, Yağşi, 2004 and Çuhadar, 2005) are given in Table 4.1. Activated carbons produced by Abdallah, Yağşi and Çuhadar were called as AAC, YAC and CAC, respectively. In addition, a commercial activated carbon procured from KUREHA (Japan) was also used. Activated carbons were crushed and sieved in particle size range of 35-60 mesh prior to adsorption experiments.

Activated carbon – cadmium sulfate ($3CdSO_4.8H_2O$) and activated carbon – lead nitrate ($Pb(NO_3)_2$) systems were used in the experiments. Cadmium sulfate and lead nitrate were in analytical reagent grade (Merck). Cadmium sulfate of 0.2282 g and lead nitrate of 0.1599 g were dissolved in 1 liter of distilled-deionized water to obtain 1-liter stock solutions of 100 mg/l of Cd and Pb, respectively.

Table 4.1: Production Conditions of Activated Carbons

Code	Reference	Precursor	Carbonization Time (min)	Carbonization Temperature (°C)	Activation Type	Activating Agent	Activation Temperature (°C)	Activation Time (min)
AAC8.1	[1]	Sulphonated styrene divinylbenzene copolymer	60	600	Physical	Steam	800	60
AAC8.2	[1]	Sulphonated styrene divinylbenzene copolymer	60	600	Physical	Steam	800	120
AAC8.6	[1]	Sulphonated styrene divinylbenzene copolymer	60	600	Physical	Steam	800	360
AAC9.6	[1]	Sulphonated styrene divinylbenzene copolymer	60	600	Physical	Steam	900	360
YAC4.1.5	[42]	Apricot Stone	90	400	Chemical	50% Phosphoric Acid	25	1440
YAC4.2	[42]	Apricot Stone	120	400	Chemical	50% Phosphoric Acid	25	1440
YAC4.3	[42]	Apricot Stone	180	400	Chemical	50% Phosphoric Acid	25	1440
CAC4.2	[9]	Hazelnut Shell	120	500	Chemical	40% Phosphoric Acid	25	1440
CAC5.2	[9]	Hazelnut Shell	120	500	Chemical	50% Phosphoric Acid	25	1440

pH of the solutions was adjusted with 0.1 N of hydrochloric acid and 0.1 N of sodium hydroxide (Merck).

Methylene blue trihydrate ($C_{16}H_{18}ClN_3S.3H_2O$) was purchased from Hoechst AG (Germany) to determine MBN of activated carbons used in this study. Methylene blue stock solution of 213.9 mg/l was prepared by adding 0.25 g of methylene blue trihydrate into 1 liter of distilled-deionized water.

4.2. Characterization of Activated Carbons

4.2.1. BET Surface Areas

BET surface areas of activated carbons were taken from the M. Sc. studies by Abdallah (2004), Yağşi (2004) and Çuhadar (2005) in Chemical Engineering Department in METU. BET areas reported in these studies were obtained by measuring nitrogen adsorption at 77 K by a commercial volumetric gas adsorption apparatus, ASAP 2000 (Micromeritics Co., USA).

4.2.2. Slurry pH

Slurry pH of each activated carbon sample was determined by adding 0.1 g of each sample to 10 ml of distilled-deionized water. The slurry was kept in HDPE bottle for 7 days at room temperature. After pH had stabilized, final pH of the slurry was recorded.

4.2.3. Methylene Blue Number (MBN)

MBN of activated carbons were determined by adding 0.1 g of each activated carbon to 50 ml of methylene blue solution which had a concentration of 213.9 mg/l. The flasks containing methylene blue solutions were shaken in water bath shaker at 120 rpm and at 25±1 °C for 96 hours. After equilibrium was reached, solutions were filtered and concentration of methylene blue in the filtrate was measured by Hitachi UV-3200 spectrophotometer at a wavelength of 600 nm. Values were corrected against the blank tests. The area of methylene blue molecule was assumed as 1.62 nm^2 (Valdes et al., 2002) and the surface of activated carbon occupied by methylene blue was calculated.

4.2.4. Isoelectric Points

Carbon samples were crushed and sieved in the size less than 10 µm and 0.04-0.05 g of each sample was added into 5 ml of suspensions which have different pH values to determine zeta potential and isoelectric points of activated carbons. Samples were stabilized 24 h for sedimentation of particles. After 24 h, equilibrium pH of each sample was recorded and zeta potential of samples was measured by using MALVERN Zetasizer Nano ZS90 at 25 °C. Samples of the suspensions were collected with plastic syringes and injected into the electrophoresis cell. Measurements were duplicated and averages of the results were used. Equilibrium graphs of pH vs. zeta potential were plotted. The pH value where the zeta potential is zero is determined as isoelectric point (pH_{IEP}).

4.4. Experimental Procedure

Experimental system is shown in Fig. 4.1. The system is a water bath shaker (Julabo, Germany) with thermostat and speed control.

Figure 4.1: Experimental System

Batch experiments are carried out in high-density polyethylene (HDPE) bottles containing 10 ml of aqueous solutions of different heavy metals. The initial pH of the solutions was adjusted and then measured by Beckman Expandomatic SS-2 pH meter. 25 mg of different activated carbons was added to each bottle. Blank tests were performed without activated carbon. All bottles were sealed to minimize evaporation and shaken at 120 rpm for 24 hours in water bath shaker. The batch experiments were performed at 25±1 °C. Solutions were filtered using 2 μm membrane filters to end the experiment. Then, pH of the solutions was measured again. Concentrations of Cd and Pb in the filtered solutions were analyzed by Philips PU9200X atomic absorption spectrometer at 228.8 and 217 nm, respectively. Values were corrected against the blank tests. The experimental conditions are given in Table 4.2.

Table 4.2: Experimental Conditions for Batch Experiments

Set	**Experimental Constants**		**Experimental Variables**	
1	Dose of Activated Carbon	2.5 g/l	pH	2, 3, 4, 5, 6, 7
	Volume of Aqueous Solution	10 ml		
	Initial Heavy Metal Concentration	50 mg/l		
	Temperature	25 °C	Heavy Metal	Cd, Pb
	Contact Time	24 h		
	Agitation Speed	120 rpm		
2	Dose of Activated Carbon	2.5 g/l	Initial Heavy Metal Concentration (mg/l)	10, 25, 50, 100
	Volume of Aqueous Solution	10 ml		
	pH	4		
	Temperature	25 °C	Heavy Metal	Cd, Pb
	Contact Time	24 h		
	Agitation Speed	120 rpm		

Finally, Langmuir and Freundlich equations were applied for adsorption equilibrium. Langmuir isotherms and Freundlich isotherms were obtained with the plots of C_e/q_e vs. C_e and $\ln q_e$ vs. $\ln C_e$, respectively. Experimental data obtained in the second set of sorption experiments to check the effect of initial concentration was used to plot these isotherms.

CHAPTER V

RESULTS AND DISCUSSION

5.1. Preliminary Experiments

Some preliminary runs were performed to determine experimental conditions such as activated carbon dosage, initial metal concentration, pH or contact time for the establishment of the equilibrium. These experiments were performed with a commercial activated carbon (KUREHA, Japan).

Firstly, kinetic experiments were performed with commercial activated carbon to determine the equilibrium time of adsorption. Cd was used in preliminary experiments. Cd solution with concentration of 500 mg/l was prepared. 0.25 g of commercial activated carbon was added into 50 ml of solution. Solution pH was adjusted to 3. Equilibrium was reached after 3.5 h. This experiment was repeated with volume of 250 ml of solution and activated carbon amount of 1.25 g but no significant difference was observed. Although equilibrium was reached in 3.5 h, 24 h was chosen as contact time in case long equilibrium time for other activated carbons.

Experiments at the solution pH values of 3, 5 and 8 were performed to observe the effect of pH on adsorption. 0.25 g of commercial activated carbon was added to 50 ml of 500 mg/l of Cd solution. Cd adsorption increased with increasing pH. But even at pH 5, precipitation was significant. It was known from literature survey that precipitation of metal hydroxides is proportional to concentration. Then, it was decided to perform experiments at lower heavy metal concentration.

Preliminary experiments for AAC were carried out with adding 0.1 g of each activated carbon into 20 ml of Cd solution which had 200 mg/l of heavy metal concentration at pH 4 and similar results with previous preliminary studies were obtained.

Blank experiments were carried out to observe where the precipitation starts. At the concentration of 100 mg/l, pH of Cd and Pb solutions was adjusted to several values from 2 to 9 and waited for 24 h. Precipitation occurred at pH 7 for Cd and at pH 6.5 for Pb. Range of pH for this study was determined as from 2 to 7. Precipitation was avoided in this range and heavy metal removal was related to adsorption process mainly.

Methylene blue stock solution with concentration of 213.9 mg/l was prepared for preliminary experiments of MBN. Firstly, stock solution was diluted to 42.8 mg/l and 0.1 g of commercial activated carbon was added into 50 ml of solution. All methylene blue was adsorbed by activated carbon just in 3 hours. Experiment was repeated with 0.025 g of activated carbon but again, all methylene blue was adsorbed in 24 h. It was decided not to dilute stock solution. 0.1 g of activated carbon was added into 50 ml of methylene blue solution and equilibrium was reached after 48 hours, but 96 h was chosen as contact time to make sure that equilibrium was reached for other activated carbons.

5.2. Characterization of Activated Carbons

The main aim of this part of the study was to investigate the characteristics of activated carbons by the methods of BET surface area, slurry pH, MBN and isoelectric point. These parameters give information about different properties of activated carbons.

5.2.1. Surface Area

BET surface area values given in previous thesis studies (Abdallah, 2004, Yağşi, 2004, Çuhadar, 2005) are shown in Figure 5.1. It can be seen from this figure that activated carbons produced from same precursor had close surface areas.

AAC had surface area varying between 457 and 615 m^2/g. Surface area of AAC increased from 457 to 527 m^2/g with increasing activation time from 1 to 6 h at activation temperature of 800 °C. Similarly, surface area increased from 527 to 615 m^2/g with increasing activation temperature from 800 to 900 °C in activation time of 6 h. These results showed that change in activation time and in activation temperature had slightly positive effect on BET surface area (Abdallah, 2004).

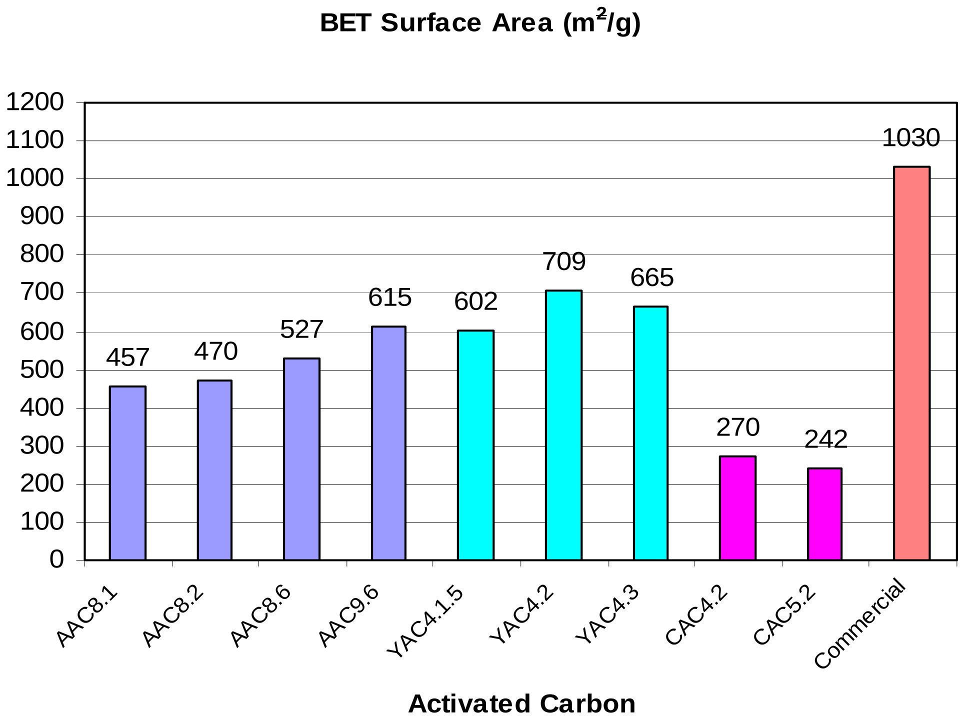

Figure 5.1: BET Surface Area of Activated Carbons

Surface area of YAC was slightly higher than surface area of AAC. It varied from 602 to 709 m^2/g. Increase in carbonization time from 1.5 to 2 h increased BET surface area from 602 to 709 m^2/g at 400 °C. But when the carbonization time increased from 2 to 3 h, BET surface area decreased from 709 to 665 m^2/g. This was probably because treatment at high temperature more than 2 h distorted the pore structure of activated carbon (Yağşi, 2004).

Surface area of CAC was quite low as compared to AAC and YAC types of activated carbons. In contrast to activation with more concentrated phosphoric acid solution, CAC5.2 had lower surface area than CAC4.2. The reason was that higher impregnation ratios could result in widening of micropores and formation of meso- and macropores giving lower surface areas (Çuhadar, 2005).

Surface area of commercial activated carbon was 1030 m^2/g (Obalı, 2003). This value was very high when compared to other types of activated carbons.

5.2.2. Slurry pH

Slurry pH values of activated carbons are shown in Figure 5.2. Slurry pH gives information about nature of surface of activated carbon since change in surface functional groups occurs during production period.

AAC had slurry pH in the range of 6.5-7.6. This indicated that the surface of this type of activated carbon was almost neutral. Precursor of this type of activated carbon was strongly acidic cation exchange resin but apparently, carbonization and activation by steam changed the slurry pH of AAC to higher pH values.

Slurry pH of YAC was between 3.7 and 4.3. This type of activated carbon has been produced by chemical activation of apricot stones. Treatment with phosphoric acid introduced oxygen containing functional groups and products became acidic.

Similarly, CAC has also been produced by chemical activation in the presence of phosphoric acid and this made their slurry pH values 3.0 and 3.2. This indicated that this type of activated carbon had strongly acidic surface.

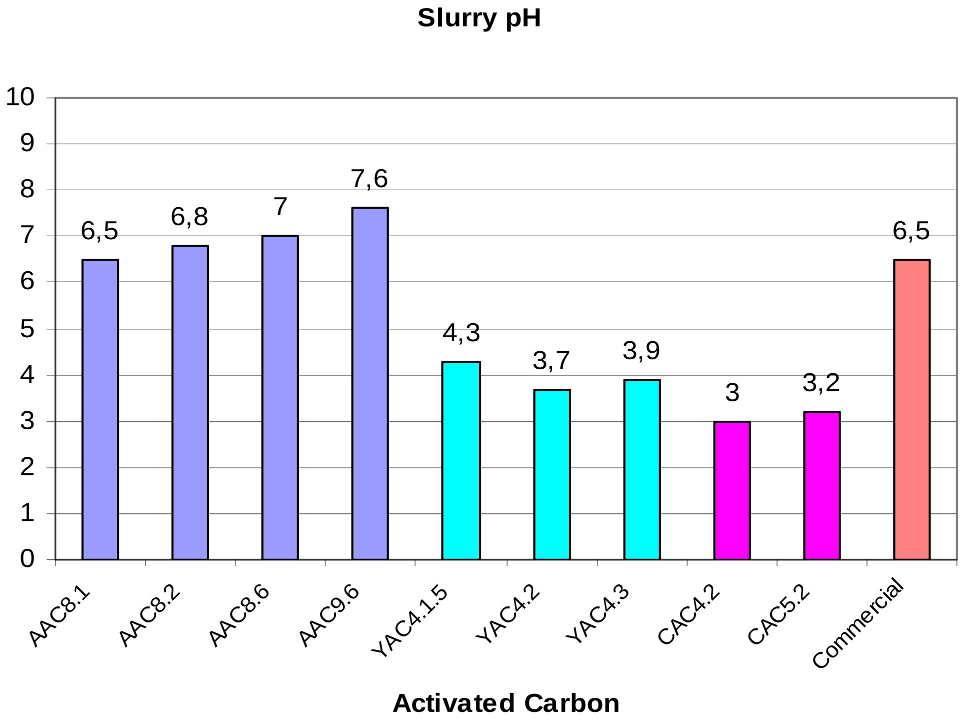

Figure 5.2: Slurry pH of Activated Carbons

Commercial AC had slurry pH of 6.5 and this showed that surface of this activated carbon was close to neutral.

5.2.3. Methylene Blue Number (MBN)

Methylene blue numbers of the activated carbon samples measured as described on section 4.2.3 are shown in Table 5.1. Experiments for methylene blue adsorption show the ability of adsorbent to adsorb on super micropores and mesopores and gives information about sizes of these pores.

AAC had MBN varying between 5.2 and 16.1 mg/g. Table 5.1 shows that MBN of AAC increased with increasing activation time and activation temperature. AAC 8.1, AAC8.2 and AAC8.6 had close MBN but MBN of AAC9.6 was more than twice of previous ones. YAC had greater MBN (12.9 – 23.3 mg/g) than AAC. Increase in carbonization time increased MBN of the YAC samples. MBN of CAC4.2 and CAC5.2 was 7.0 and 7.8 mg/g, respectively. These values were lower than that of YAC, but higher than that of AAC. MBN of commercial activated carbon was quite high (98.2 mg/g) as compared to other activated carbons.

Methylene blue is assumed to be adsorbed on pores of diameters larger than 1.5 nm (Attia et al., 2003). This indicates that surface area of super micropores and mesopores can be measured by methylene blue adsorption since surface area covered by methylene blue is known. Surface areas of these pores (S_{MB}) are shown in Table 5.1. AAC had S_{MB} varying from 15.9 to 49.0 m^2/g. Surface area of AAC9.6 occupied by methylene blue was almost threefold of AAC8.1, AAC8.2 and AAC8.6. YAC had higher S_{MB} (39.2 to 71.2 m^2/g) than AAC. Surface area of CAC accessible to methylene blue was relatively smaller (21.2 and 23.9 m^2/g) since their total surface areas were very small comparing to other samples. Calculations of these results are shown in Appendix B.

Ratio of S_{MB} to S_{BET} estimates the ratio of surface area of super micropores and mesopores to total surface area. High S_{MB}/S_{BET} ratio makes activated carbon preferable in adsorption of larger molecules. The opposite is true for smaller molecules. AAC8.1, AAC8.2 and AAC8.6 had lowest ratios among all activated carbons. This indicated microporosity character of AAC type of activated carbons. On the other hand, AAC9.6 had higher value than other AAC carbons. This showed that it had larger pores than other AAC activated carbons. Higher S_{MB}/S_{BET} ratios of YAC and CAC show that average pore diameters of these activated carbons were larger. This can be explained with widening of micropores during chemical activation. Almost one third of pores of commercial AC had diameter larger than 1.5 nm as shown by S_{MB}/S_{BET} ratio.

Table 5.1: Methylene Blue Adsorption of Activated Carbons

Activated Carbon	**MBN (mg/g)**	**S_{MB} (m^2/g)**	**S_{MB}/S_{BET}**
AAC8.1	5.2	15.9	0.035
AAC8.2	6.2	18.8	0.040
AAC8.6	7.1	21.7	0.041
AAC9.6	16.1	49.0	0.080
YAC4.1.5	12.9	39.2	0.065
YAC4.2	16.8	51.1	0.072
YAC4.3	23.3	71.2	0.107
CAC4.2	7.0	21.2	0.078
CAC5.2	7.8	23.9	0.099
Commercial	98.2	299.3	0.291

All activated carbons used in this study had S_{MB}/S_{BET} ratio lower than 1 indicating that monolayer adsorption.

5.2.4. Zeta Potential and Isoelectric Point

Figure 5.3 to 5.6 shows zeta potential of activated carbon samples as a function of equilibrium pH for AAC, YAC, CAC and commercial activated carbons. Zeta potential is an important parameter to characterize electrokinetic behavior of solid-liquid interface. Isoelectric point (pH_{IEP}) was taken as the point where zeta potential was zero and it reflects the character of external surface of activated carbon particles.

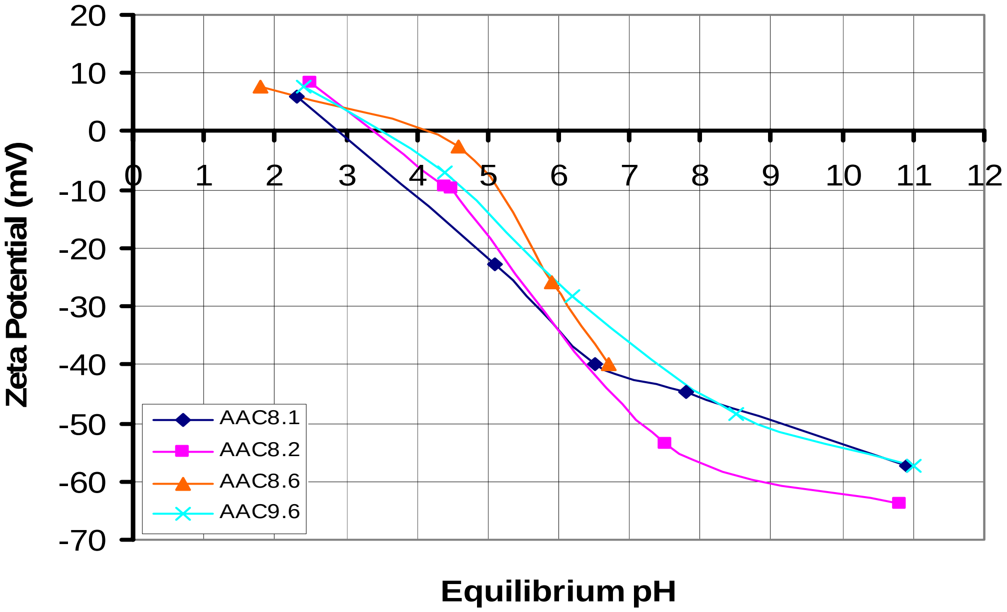

Figure 5.3: Zeta Potential of AAC

Figure 5.3 shows that zeta potential of all AAC activated carbons were close to zero in highly acidic range and pH_{IEP} was reached in the range of pH 3-4. This showed that external surface of AAC carbons was negatively charged even pH was 4. After this point, zeta potential decreased markedly. Negative zeta potential of AAC can be explained with that precursor of AAC was strongly acidic material and carboxylic functional groups on the external surface have remained although it has been carbonized at very high temperatures.

Figure 5.4 shows that surface of YAC4.1.5, YAC4.2 and YAC4.3 was negatively charged when pH was less than 2.1, 2.3 and 3.9, respectively. Above these values net surface charges were negative. YAC4.1.5 and YAC4.2 has very low pH_{IEP} as compared to YAC4.3. Low pH_{IEP} of YAC 4.1.5 and 4.2 indicated that number of oxygen containing groups on the surface increased during chemical activation process with phosphoric acid. Longer carbonization period decomposed these functional groups on the surface of YAC4.3 and pH_{IEP} increased.

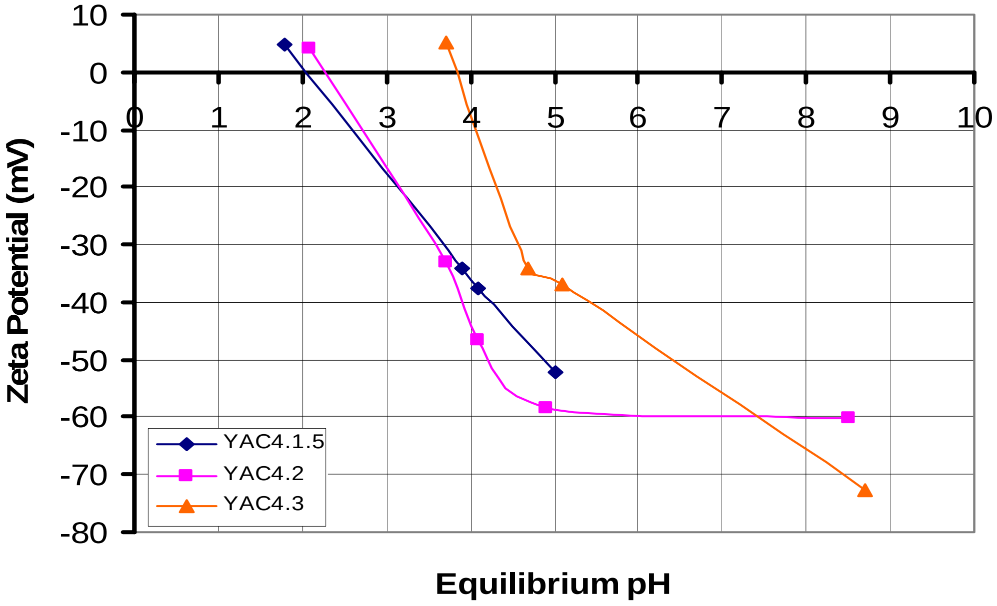

Figure 5.4: Zeta Potential of YAC

CAC has also been produced by chemical activation and isoelectric points of CAC4.2 and CAC5.2 were found to be as low as 1.5 and 2.1, respectively. In other words, this type of activated carbon had the lowest pH_{IEP} among all activated carbons. Again, chemical activation caused negatively charged surface at this type of activated carbon.

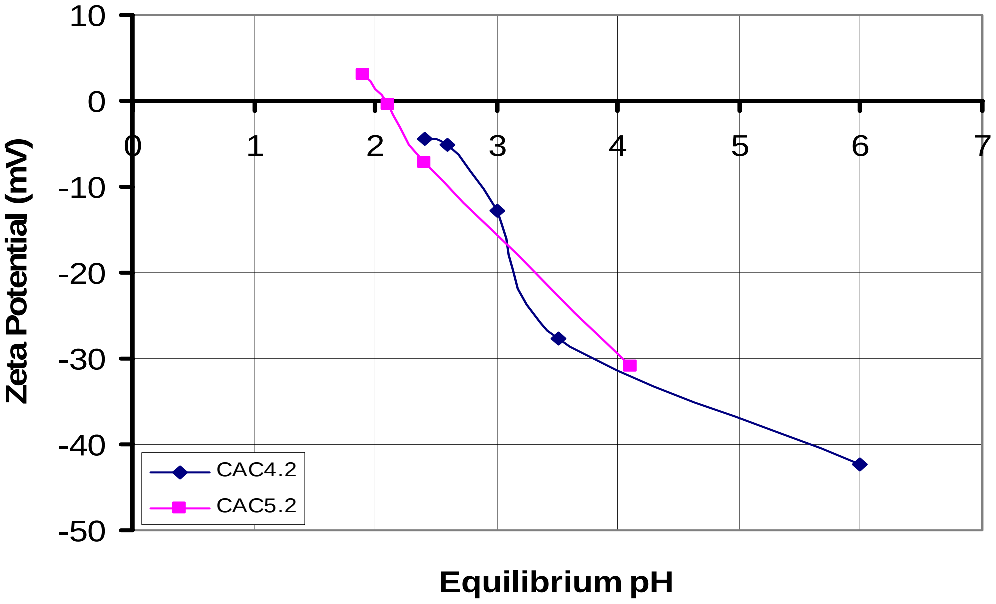

Figure 5.5: Zeta Potential of CAC

Commercial AC had also low zeta potential and low pH_{IEP} as shown in Figure 5.6. This makes adsorption of cations on commercial AC easier.

Isoelectric points of activated carbons used in this study were in the range of 1.5-4.1 and they were summarized in Table 5.2.

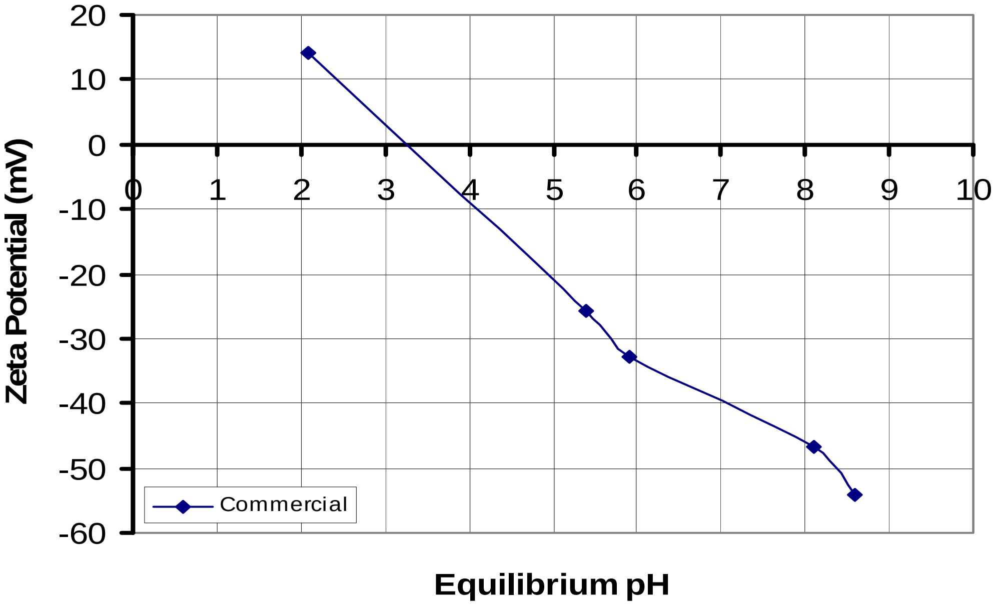

Figure 5.6: Zeta Potential of Commercial AC

Table 5.2: Isoelectric Points of Activated Carbons

Activated Carbon	pH_{IEP}
AAC8.1	3.0
AAC8.2	3.5
AAC8.6	4.1
AAC9.6	3.6
YAC4.1.5	2.1
YAC4.2	2.3
YAC4.3	3.9
CAC4.2	1.5*
CAC5.2	2.1
Commercial AC	3.4

* obtained by extrapolation

5.3. Batch Experiments

Batch experiments at different pH and initial adsorbate concentration, were done in order to determine the effects of these parameters. Two experiments (pH 4 at initial concentration of 50 mg/l and pH 4 at initial concentration of 100 mg/l) were repeated to check the reproducibility. The relative deviations of these repeated experiments were approximately 4% in average. This indicated that reproducibility was satisfactory. All numerical results can be seen in Appendix A.

5.3.1. Effect of pH on Heavy Metal Adsorption

The effect of pH on adsorption of Cd and Pb by various activated carbons was investigated by adsorption measurements in the pH range from 2 to 7. Activated carbon dosage was 25 mg per 10 ml of solution and initial heavy metal concentration was taken constant at 50 mg/l for both Cd and Pb.

The effect of initial pH on heavy metal adsorption onto AAC is shown for Cd in Figure 5.7 and for Pb in Figure 5.8. At pH 2, Cd removal by AAC was very low, because of high concentration of H^+ ions in the solution that prevented the exchange of Cd with protons on the carbon surface. In other words, adsorption of H^+ ions on suitable active sites led to low amounts of heavy metal removal (Seco et al., 1997). In addition, net surface charge was positive at low pH and there was repulsive electrostatic interaction between activated carbon surface and heavy metal ions at these pH values (Basso et al., 2002). This case also reduced heavy metal adsorption. These effects were reduced with increasing pH and maximum capacities were reached at pH 4. They remained essentially constant between pH 4 and 6 and then they sharply decreased at pH 7 where the hydrolysis of Cd started. Removal efficiency of AAC was quite low as compared to other activated carbons possibly because of its very high slurry pH. In other words, positively charged surface reduced capacity of activated carbons to adsorb cations.

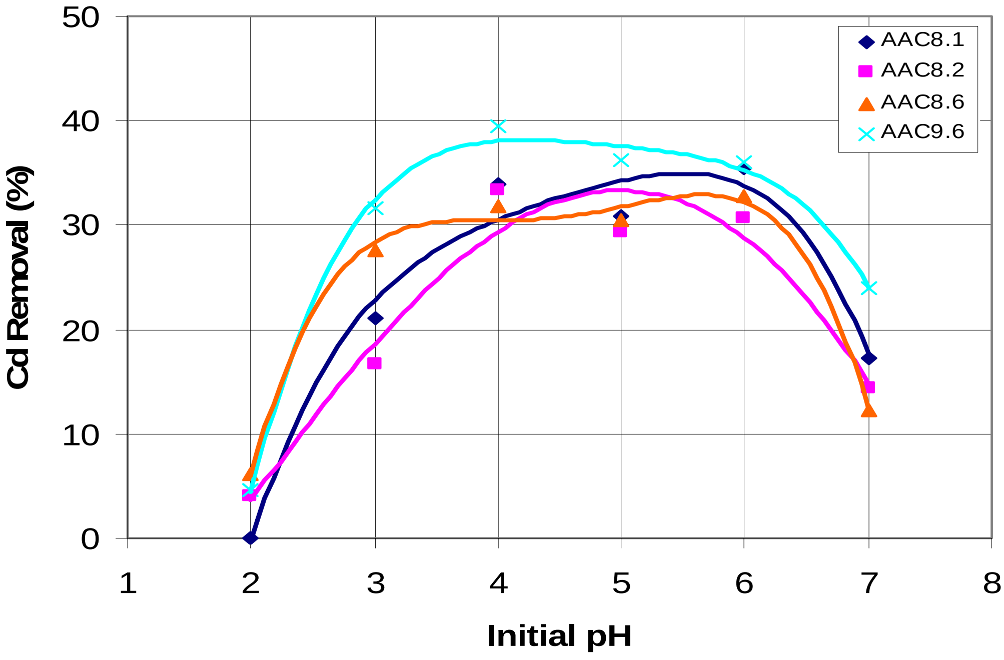

Figure 5.7: Effect of pH on Cd Adsorption by AAC

Pb adsorption capacities of AAC carbons were almost zero at pH 2. Figure 5.8 shows that percent removal for Pb increased and reached to maximum by the range of pH 5-6. In contrast to significant precipitation of Pb indicated by final concentration of blank experiment at pH 7, percent Pb removal by AAC didn't change. AAC9.6 had higher Pb capacity than other AAC carbons since mass transfer resistance was lower because of its larger pores indicated by its S_{MB}/S_{BET} ratio.

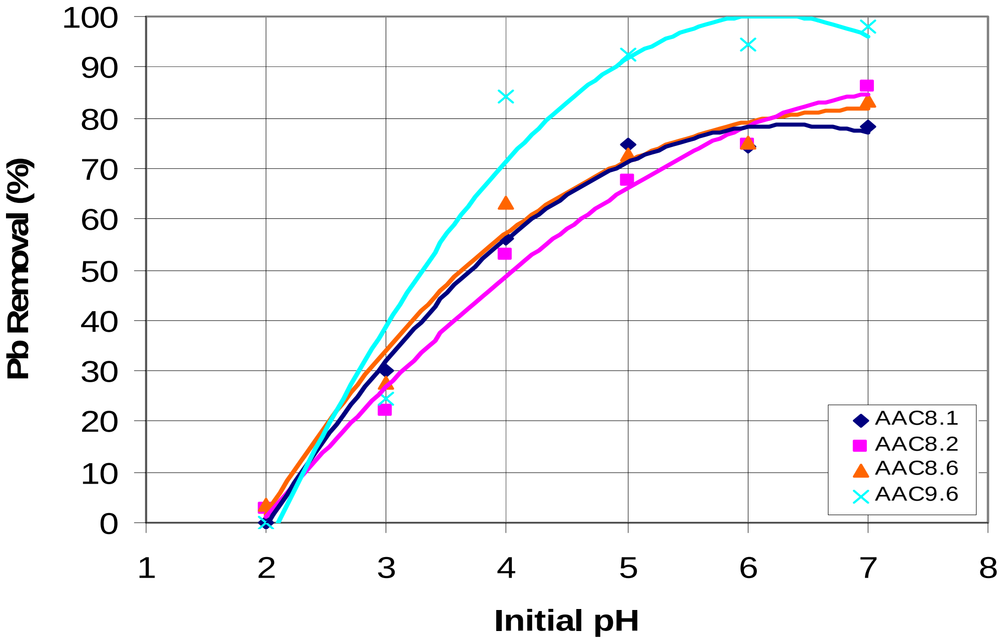

Figure 5.8: Effect of pH on Pb Adsorption by AAC

As seen from Figure 5.9, pH had similar effect on Cd adsorption by YAC in spite of larger surface area than AAC. Cd removal by YAC4.1.5, YAC4.2 and YAC4.3 increased from 7.6%, 5.1% and 6.5% to 37%, 37% and 26%, respectively when pH of the solution increased from pH 2 to 6. After this point, they decreased sharply at pH 7. YAC4.3 had more positively charged surface indicated by its higher pH_{IEP} than that of other YAC carbons. This made adsorption of cations harder because of repulsive electrostatic interaction. This was the reason why YAC4.1.5 and YAC4.2 had close but YAC4.3 had smaller Cd removal efficiency.

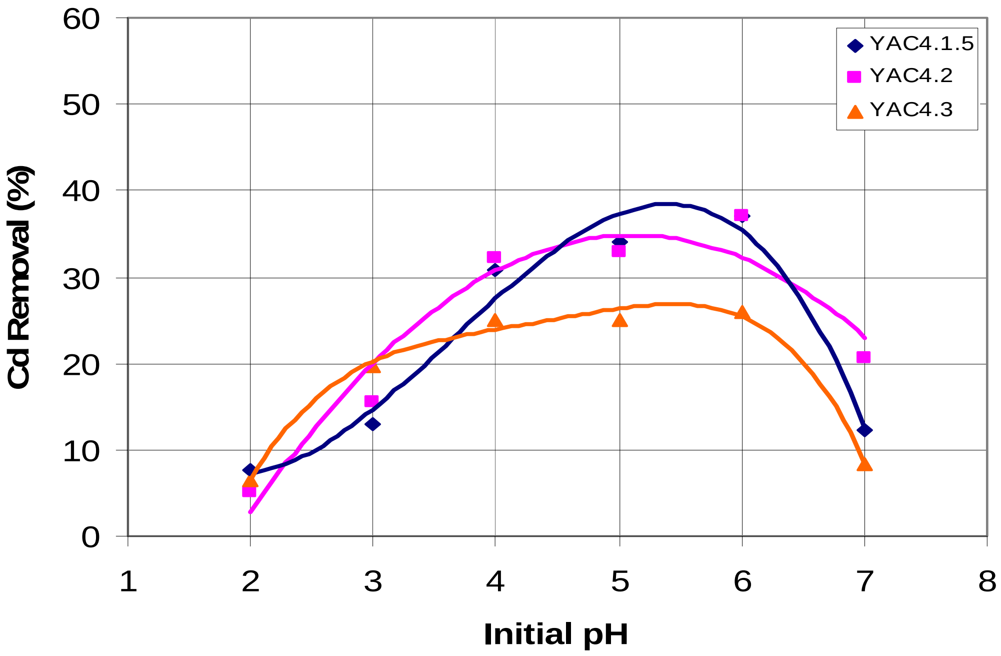

Figure 5.9: Effect of pH on Cd Adsorption by YAC

Pb adsorption by YAC was very low at pH 2. Concentration of H^+ ions and positive surface charge decreased as pH increased and maximum percent removal was reached at pH 5. After this pH, Pb removal by YAC was almost constant by pH 7. S_{MB}/S_{BET} ratios of YAC type of activated carbons showed that pores of YAC4.3 were larger and penetration into these pores was easier. On the other hand, pH_{IEP} of YAC4.1.5 and YAC4.2 showed that their surfaces were more negatively charged. These parameters possibly balanced each other and close removal percentages were obtained for each YAC carbon for Pb adsorption.

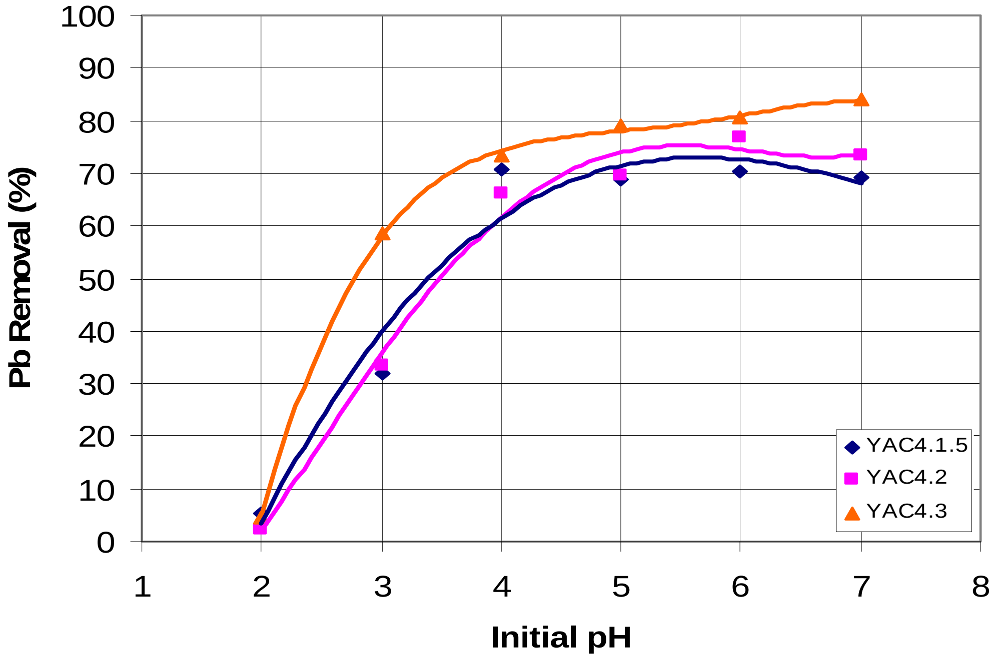

Figure 5.10: Effect of pH on Pb Adsorption by YAC

The effect of pH on adsorption of Cd and Pb by CAC can be seen in Figure 5.11 and Figure 5.12, respectively. CAC5.2 had greatest removal efficiency for the first set of sorption experiments among all activated carbons used in this study. More than 8% of Cd in the solution was adsorbed by CAC at pH 2. Removal percentages increased to 35% and 50% for CAC4.2 and CAC5.2, respectively at pH 4. Values were almost constant up to pH 6. But they decreased to 14% for CAC4.2 and 38% for CAC5.2 at pH 7. Removal efficiency of CAC5.2 was much higher than that of CAC4.2 for Cd removal. This was probably because CAC5.2 had larger pores as given by S_{MB}/S_{BET} ratio. Although CAC4.2 had lower isoelectric point and higher BET surface area, removal efficiency of CAC4.2 was higher since transfer of heavy metal ions into the pores easier.

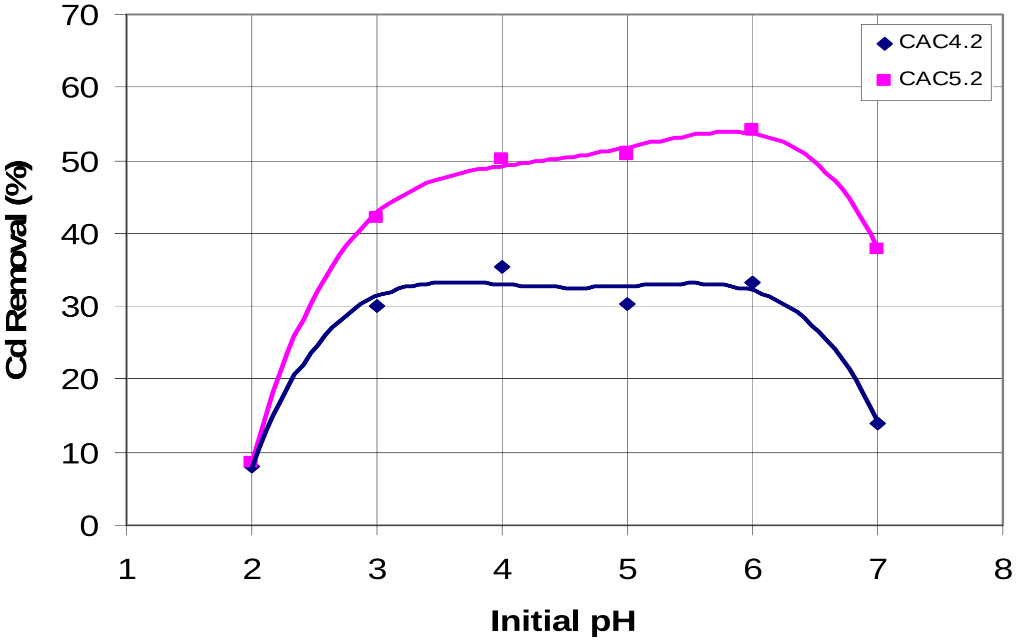

Figure 5.11: Effect of pH on Cd Adsorption by CAC

CAC had great efficiency to remove Pb from wastewater. Even at pH 2, more than 20% of Pb was adsorbed by CAC. Maximum removal was reached at pH 7 and almost all of Pb ions in the solution were removed. Pb removal efficiency of CAC5.2 was slightly over CAC4.2.

Removal efficiency of commercial AC at different pH is shown in Figure 5.13 and 5.14. Cd removal increased from 6% to 49% when initial pH increased from 2 to 5. It remained essentially constant by pH 7 in contrast to sudden decrease of Cd adsorption by other activated carbon types. This can be explained with its very high S_{MB}/S_{BET} ratio. This ratio showed that almost 30% of surface area of commercial AC lied in the pores of diameter larger than 1.5 nm. Adsorption on these larger pores possibly continued even micropores were blocked by adsorbed metal hydroxides at high pH.

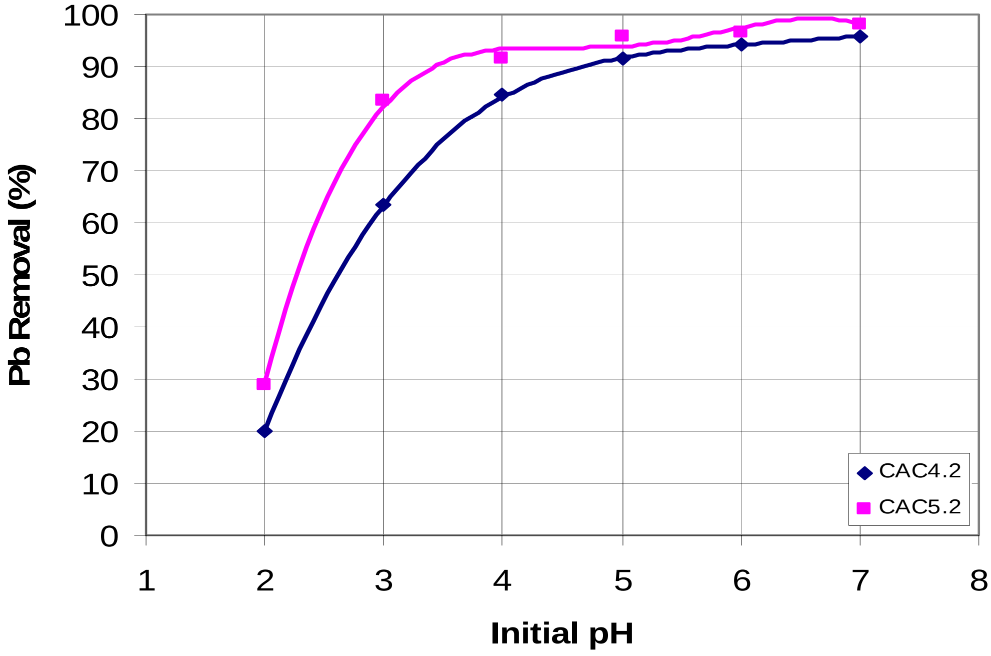

Figure 5.12: Effect of pH on Pb Adsorption by CAC

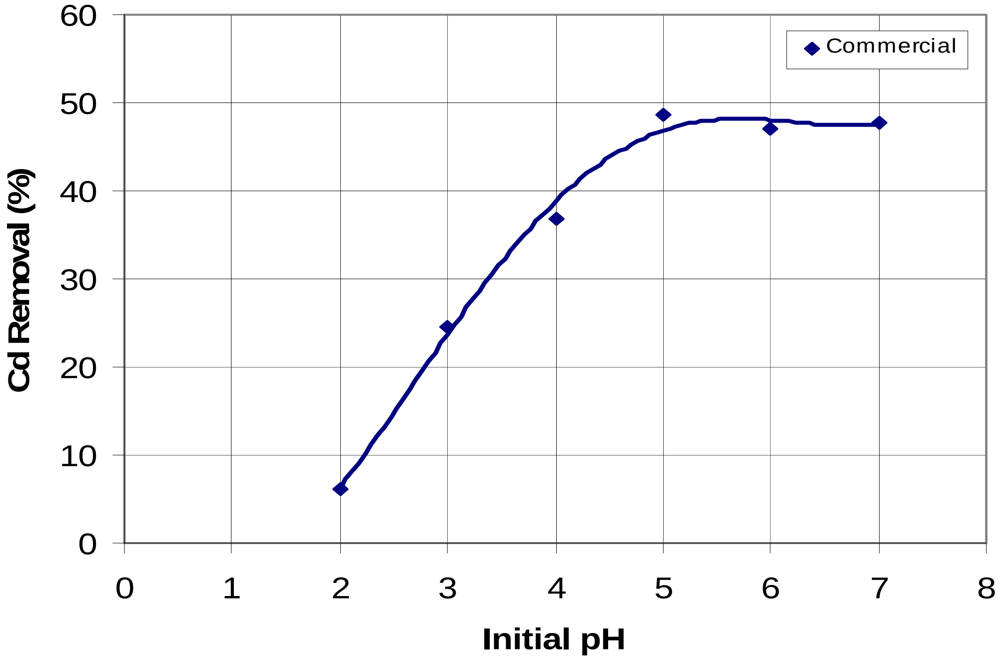

Figure 5.13: Effect of pH on Cd Adsorption by Commercial AC

On the other hand, increase in Pb removal was from 0% to 100% as pH increased from 2 to 7. These results were higher than those of AAC and YAC but they were very close to those of CAC.

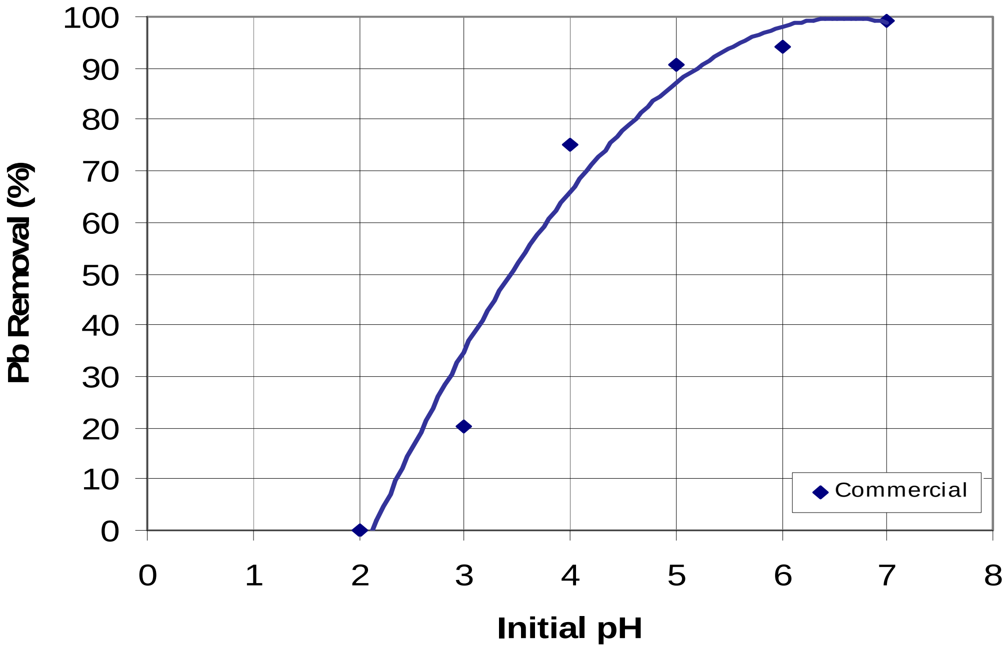

Figure 5.14: Effect of pH on Pb Adsorption by Commercial AC

Final pH values were also measured at the end of adsorption experiments (see in Appendix A). Final pH values were almost same with initial pH values until initial pH was 4. After this point, final pH was almost constant at specific values for each sample even initial pH increased. This point was also where removal efficiencies were reached maximum values almost for all activated carbons. This confirmed that ion exchange process between H^+ ions on the surface and heavy metal ions in the solution was the main adsorption mechanism. When maximum adsorption was reached, amount of H^+ ions released to the solution was stabilized and pH remained almost constant.

Cd has higher hydrated ionic radius, which is the radius of ion combined with water molecules in the solution, than Pb. Larger hydrated ionic radius of an ion gets penetration into pores harder. This was probably the reason why Pb removal efficiency was much higher than Cd removal efficiency for all activated carbons used in this study.

5.3.2. Effect of Initial Concentration on Heavy Metal Adsorption

The effect of initial metal concentration on adsorption was studied at four different initial concentrations from 10 mg/l to 100 mg/l. Activated carbon dosage was 25 mg per 10 ml of solution and initial pH was adjusted to 4 for both Cd and Pb.

The effect of initial concentration on Cd and Pb removal by AAC can be seen in Figure 5.15 and Figure 5.16, respectively. Initial heavy metal concentration showed significant effect on removal efficiencies of activated carbons. Cd removal by AAC was quite lower than literature values (Mohan and Singh, 2002, Moon and Lee, 2005). As seen from Figure 5.15, maximum Cd removal percentage was observed at initial concentration of 10 mg/l. They decreased with increasing initial concentration. AAC9.6 had the highest Cd removal percentage with 29% and AAC8.1 had the lowest Cd removal percentage with 20% at initial concentration of 100 mg/l.

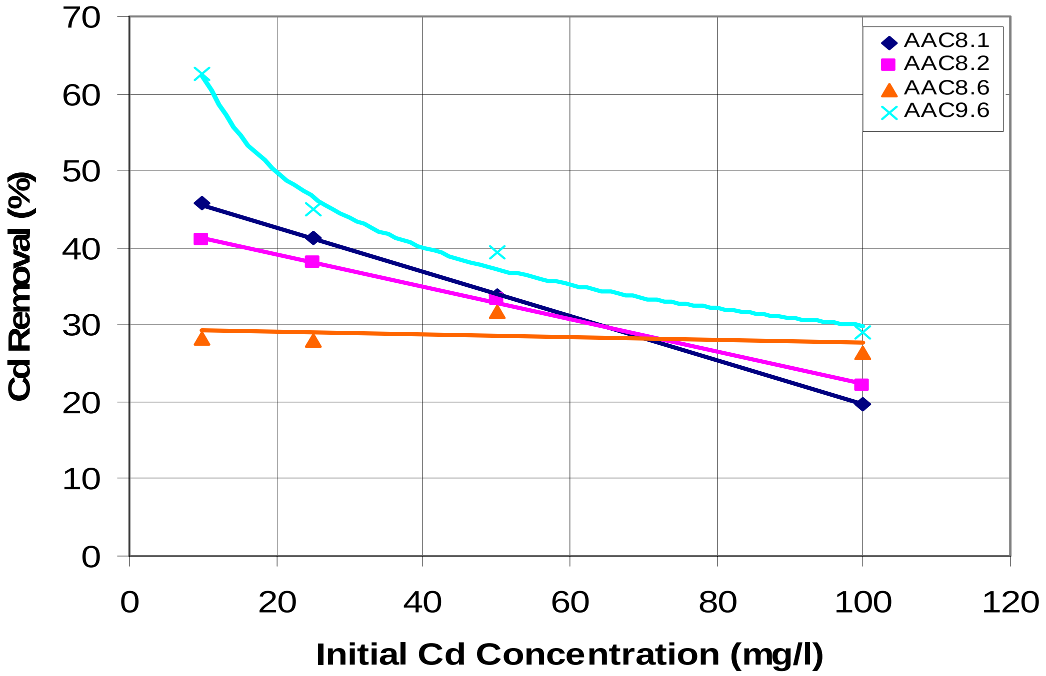

Figure 5.15: Effect of Initial Conc. on Cd Adsorption by AAC

AAC had higher capacity for Pb adsorption. All of AAC carbons adsorbed more than 70% of Pb in the solution at initial concentration of 10 mg/l. AAC9.6 adsorbed almost all Pb at that concentration. Increase in initial concentration decreased percent removal by AAC since saturation of active sites was proportional to the concentration of the solution. Pb removal by AAC8.1, AAC8.2 and AAC8.6 were much lower as compared to AAC9.6 as shown in Figure 5.16. This can be explained with narrower pores of these activated carbons indicated by their lower S_{MB}/S_{BET} ratio than AAC9.6. Narrow pores could be blocked by adsorbed Pb ions easily and surface sites could not become saturated.

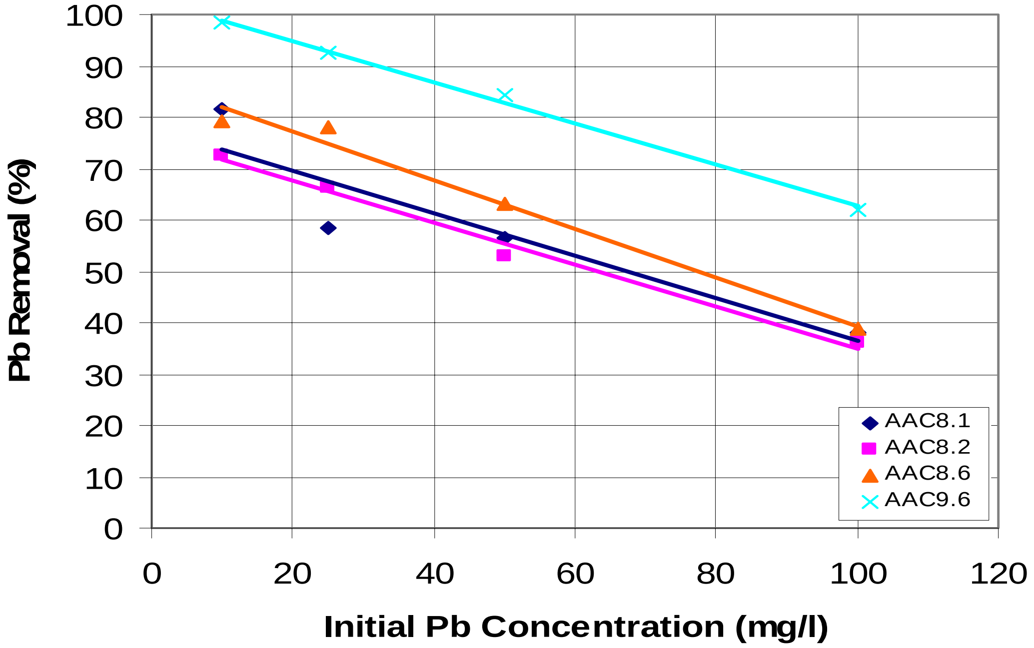

Figure 5.16: Effect of Initial Conc. on Pb Adsorption by AAC

Results of second set of sorption experiments for heavy metal removal by YAC are shown in Figure 5.17 and Figure 5.18. The results given in these figures were close to the results of AAC. Figure 5.17 shows that Cd removal percentage of YAC decreased from the range of 40-50% to about 25% as initial concentration increased from 10 to 100 mg/l.

Pb removal percentages of YAC were also negatively affected by increase in initial concentration as shown in Figure 5.18. Increase in initial concentration from 10 to 100 mg/l decreased percent removal from about 90% to the range of 45-55%.

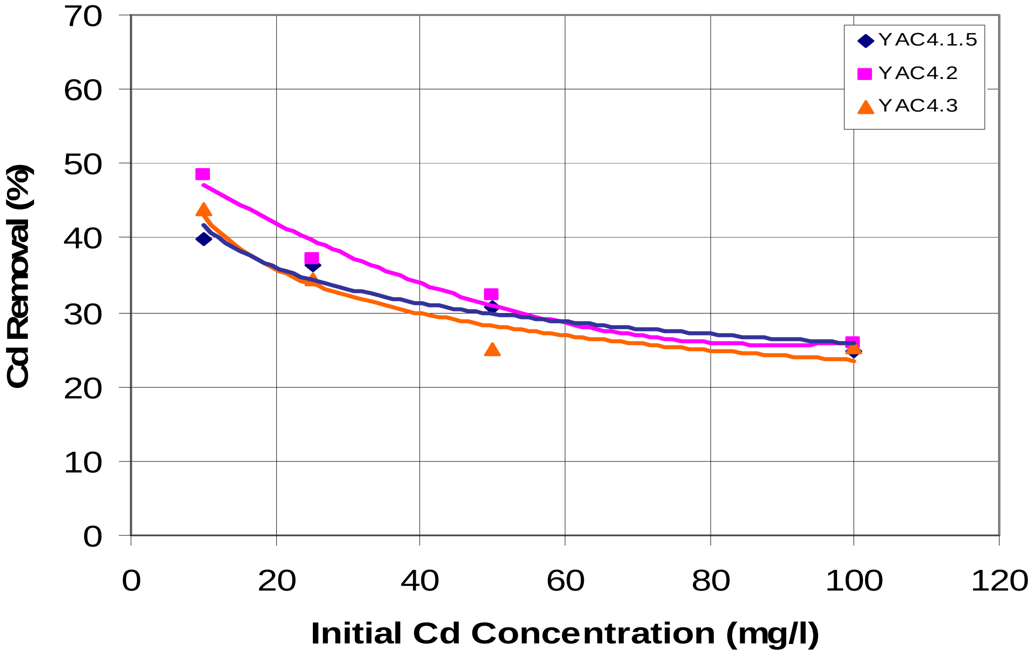

Figure: 5.17: Effect of Initial Conc. on Cd Adsorption by YAC

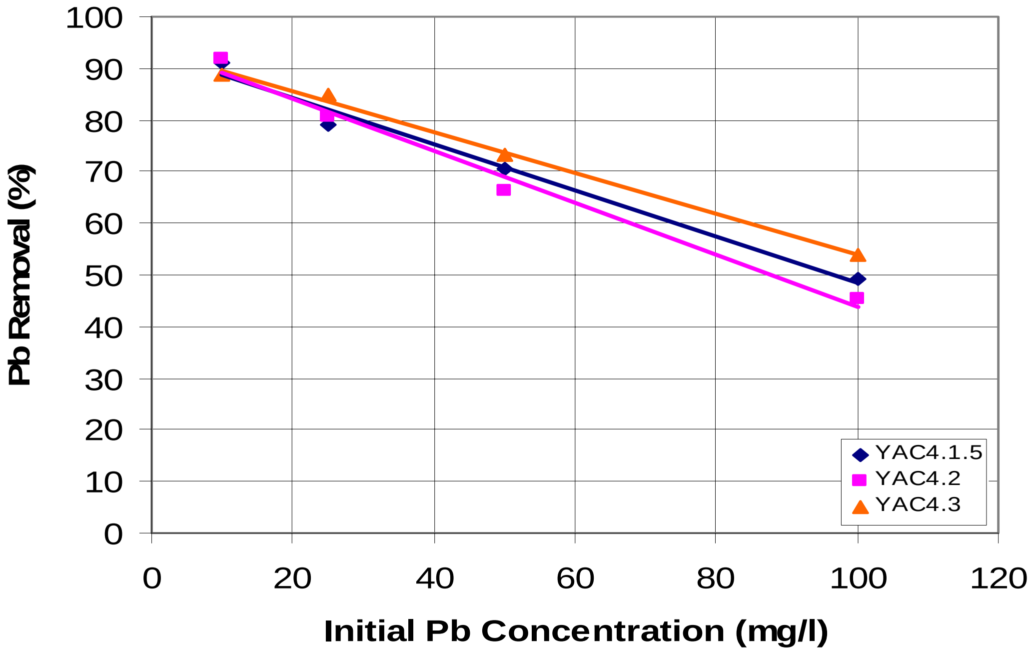

Figure 5.18: Effect of Initial Conc. on Pb Adsorption by YAC

YAC4.3 was expected to have higher removal efficiency because of its larger pores indicated by its higher S_{MB}/S_{BET} ratio but its adsorption capacity was not highly different from YAC4.1.5 and YAC4.2. This was probably because of its more positively charged surface indicated by its pH_{IEP}. When the surface was positively charged, repulsive electrostatic interaction prevented the adsorption of cations on suitable active sites.

Quite low pH_{IEP} and slurry pH of CAC showed that number of surface sites available for the adsorption of cations was much higher. This was the reason why CAC had highest removal efficiency among all activated carbons used in this study.

It is clear from Figure 5.19 that Cd removal by CAC decreased as initial concentration increased. Removal efficiency of CAC5.2 was higher markedly than that of CAC4.2 for Cd.

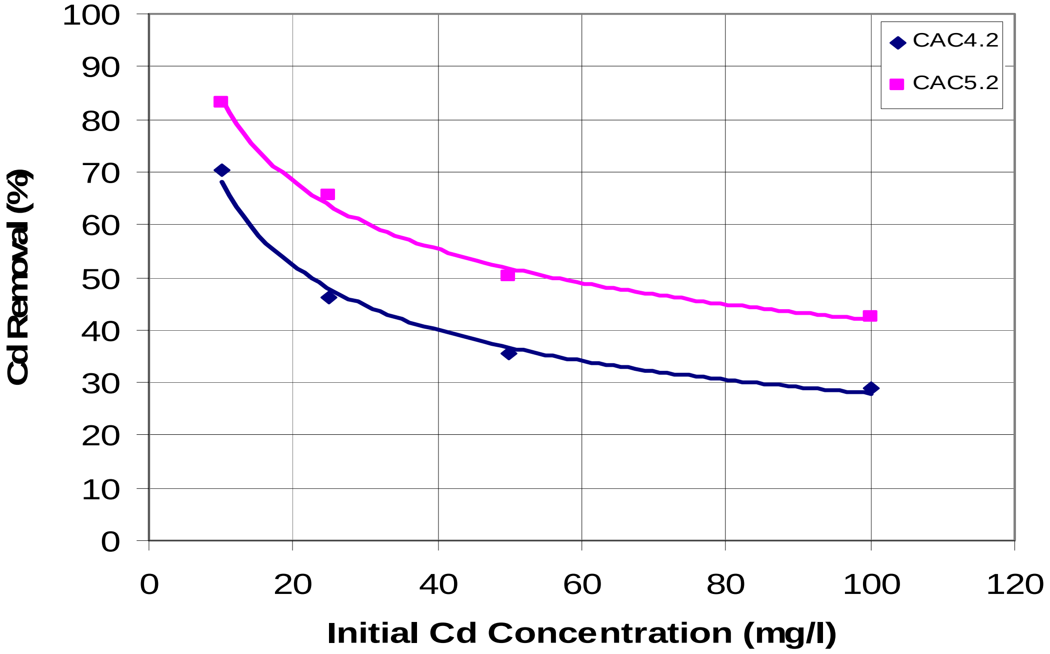

Figure 5.19: Effect of Initial Conc. on Cd Adsorption by CAC

On the other hand, Pb removal percentages of CAC4.2 and CAC5.2 were close to each other. They adsorbed almost all of Pb ions in the solution at initial concentration of 10 mg/l. The removal efficiencies decreased with increasing initial concentration and they reduced to 68% and 74% for CAC4.2 and CAC5.2, respectively.

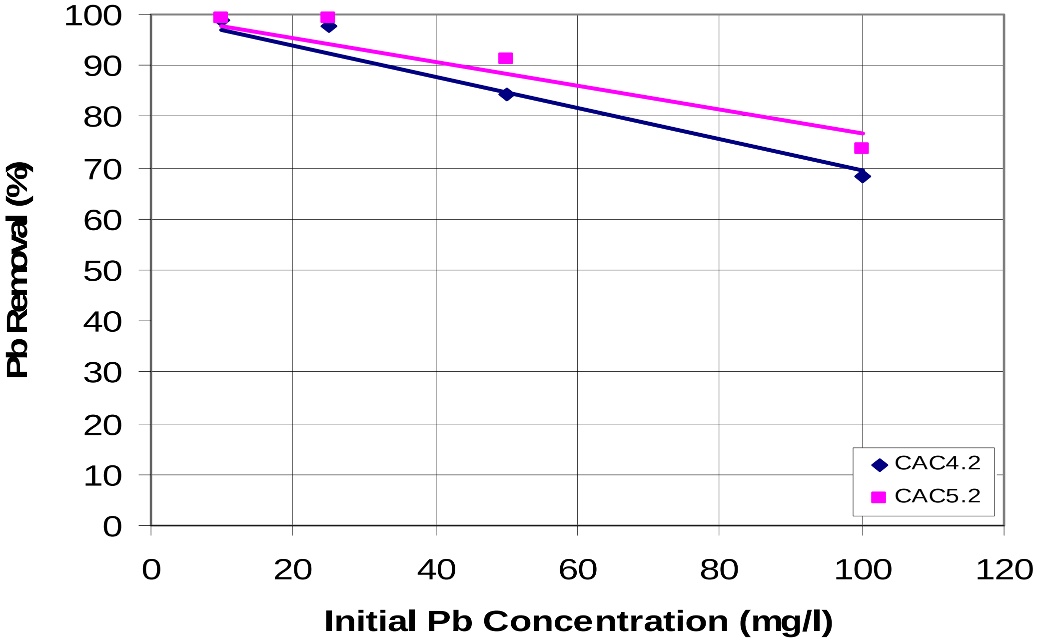

Figure 5.20: Effect of Initial Conc. on Pb Adsorption by CAC

Effect of initial concentration on adsorption by commercial AC is shown in Figure 5.21 and 5.22. Removal efficiency of commercial AC was higher than that of YAC and AAC except AAC9.6 but lower than that of CAC for both Cd and Pb.

Cd removal decreased from 68% to 30% with increasing initial concentration from 10 to 100 mg/l as seen from Figure 5.21. Similarly, decrease in Pb removal, which was from 98% to 53%, can be seen in Figure 5.22.

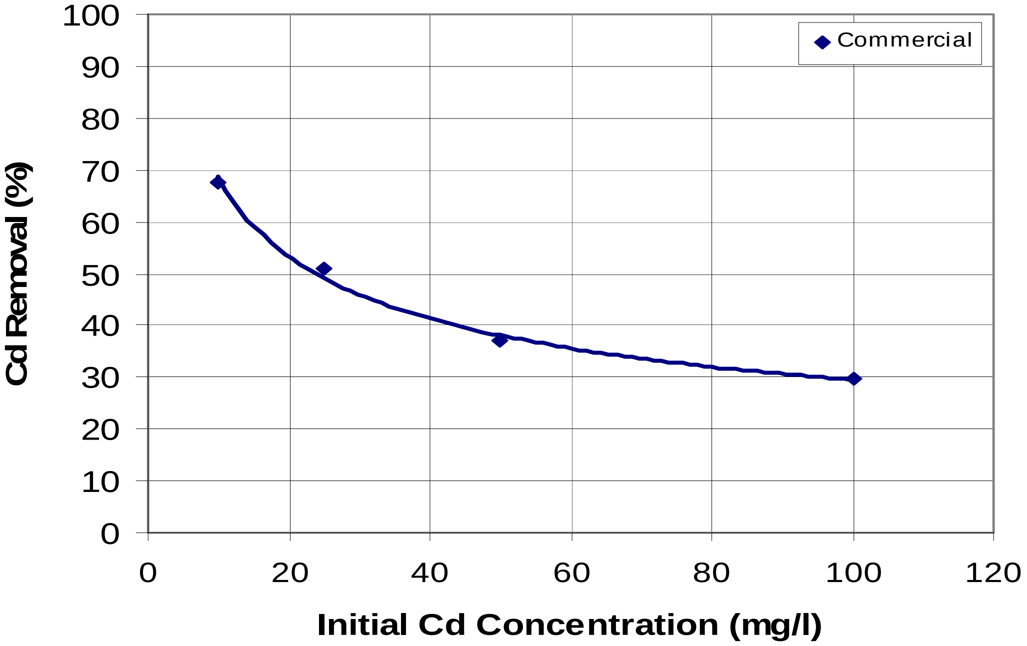

Figure 5.21: Effect of Initial Conc. on Cd Ads. by Commercial AC

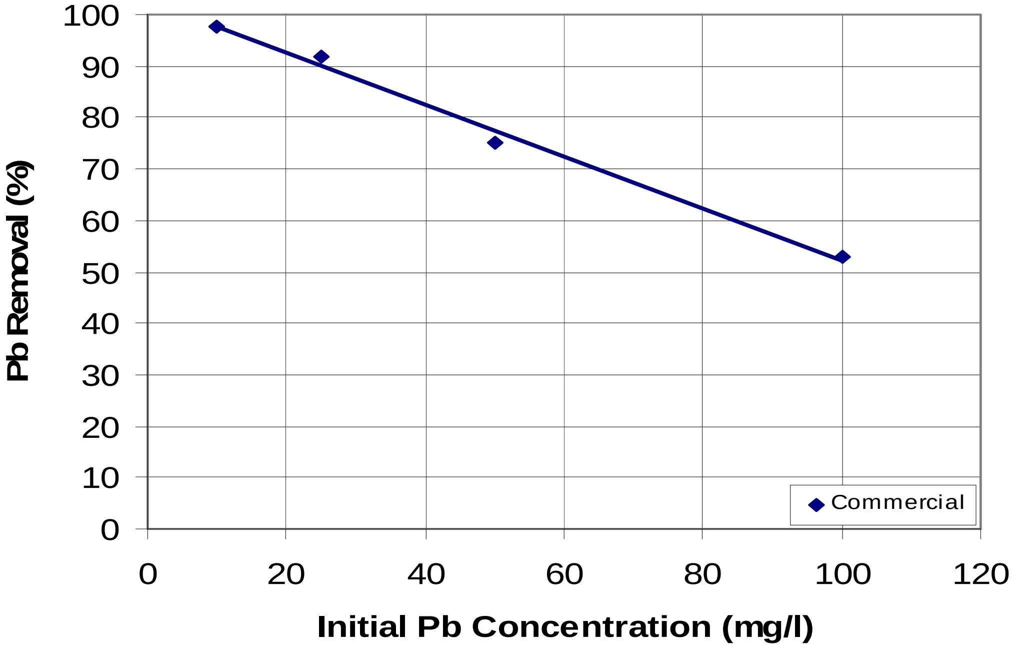

Figure 5.22: Effect of Initial Conc. on Pb Ads. by Commercial AC

5.3.3. Adsorption Isotherms

Nonlinear forms of adsorption isotherms of heavy metals on activated carbons were plotted with the experimental data given in section 5.3.2. These isotherms are compared in Figures 5.23 to 5.26 for adsorption of Cd and in Figures 5.27 to 5.30 for adsorption of Pb.

Linearized forms of the Langmuir and Freundlich isotherms were also plotted (given in Appendix C). Isotherm constants calculated from slope and intercept of the isotherms are summarized in Table 5.3 and in Table 5.4 for Cd and for Pb adsorption, respectively.

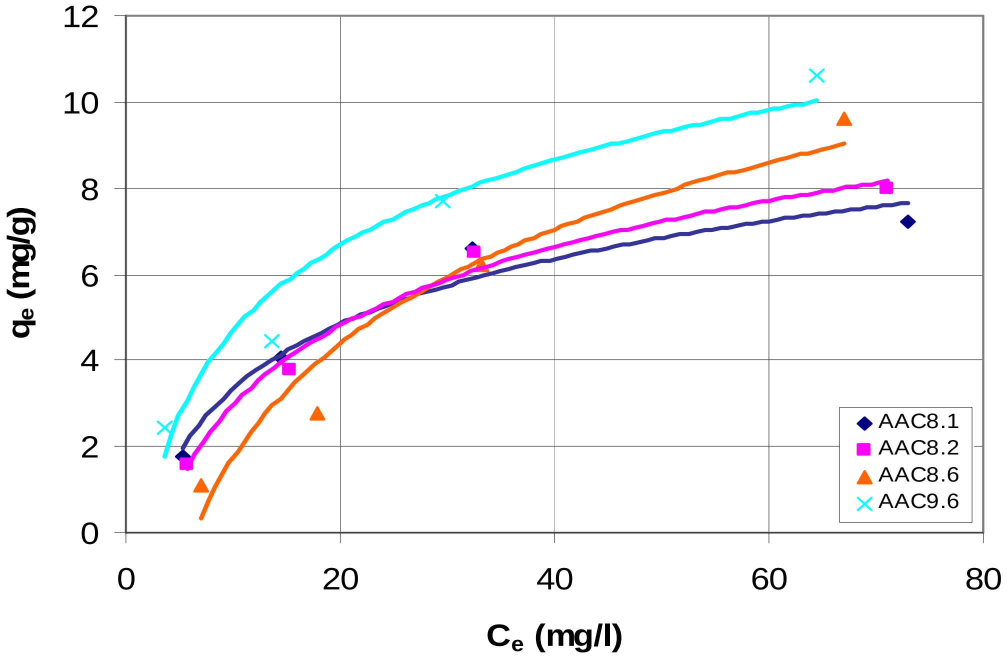

Figure 5.23: Adsorption Isotherms of Cd on AAC

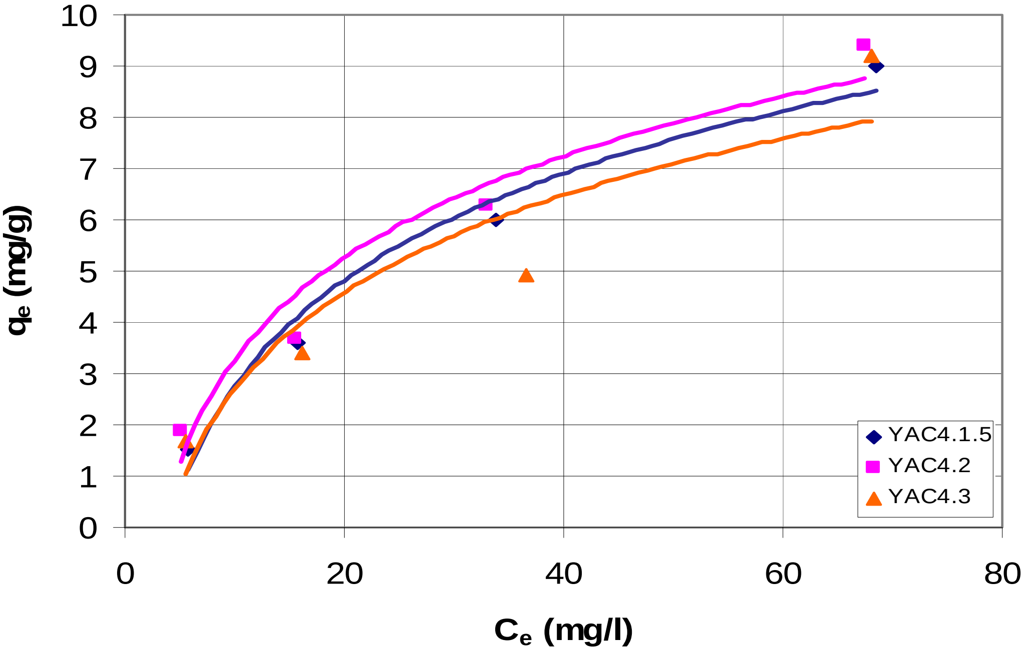

Figure 5.24: Adsorption Isotherms of Cd on YAC

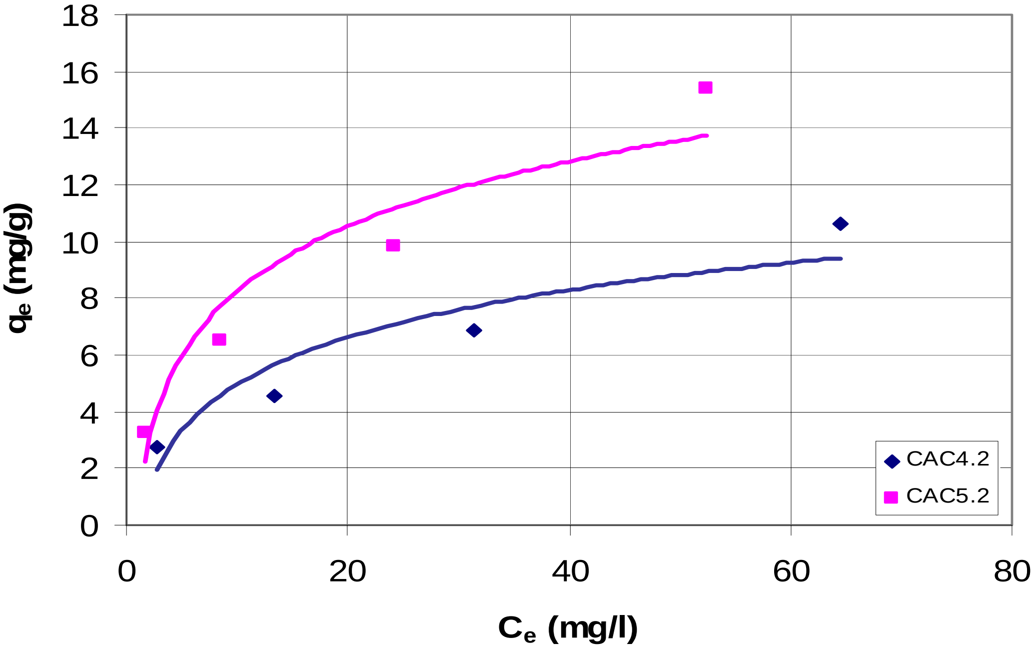

Figure 5.25: Adsorption Isotherms of Cd on CAC

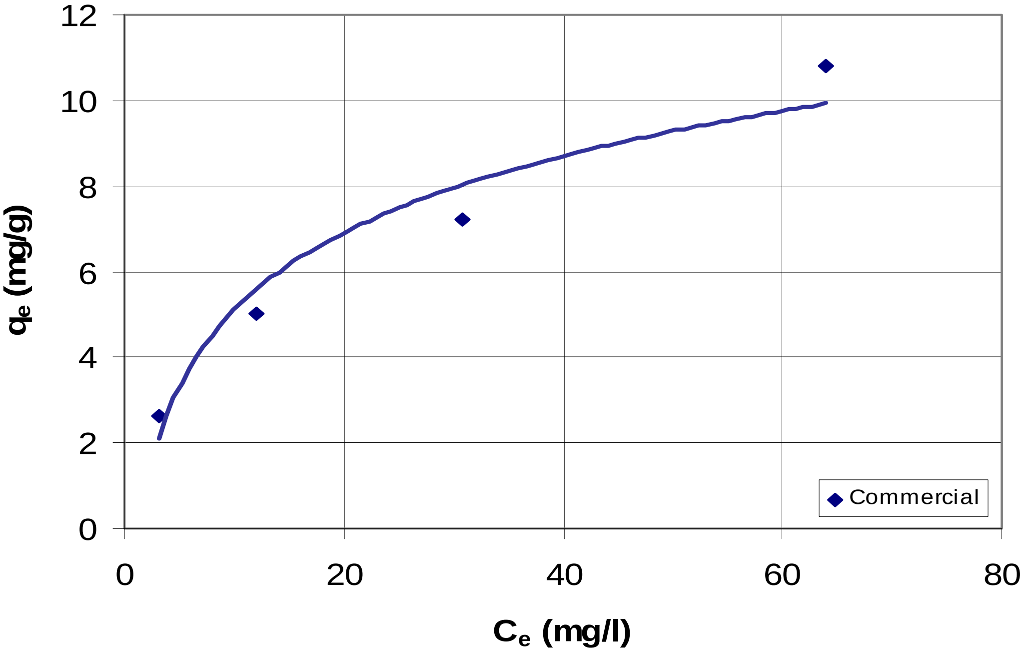

Figure 5.26: Adsorption Isotherm of Cd on Commercial AC

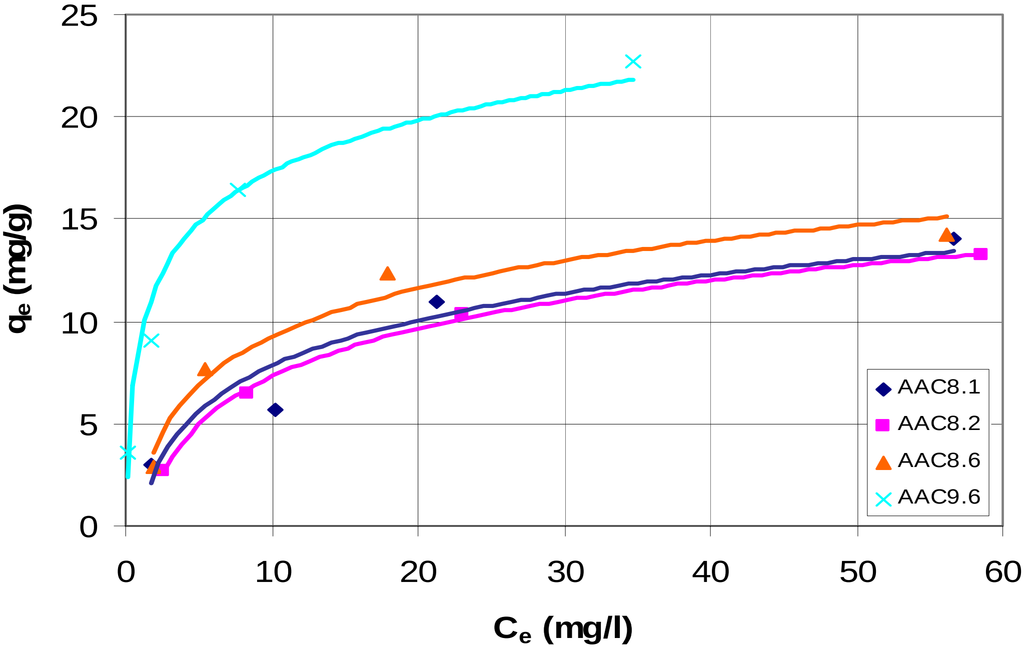

Figure 5.27: Adsorption Isotherms of Pb on AAC

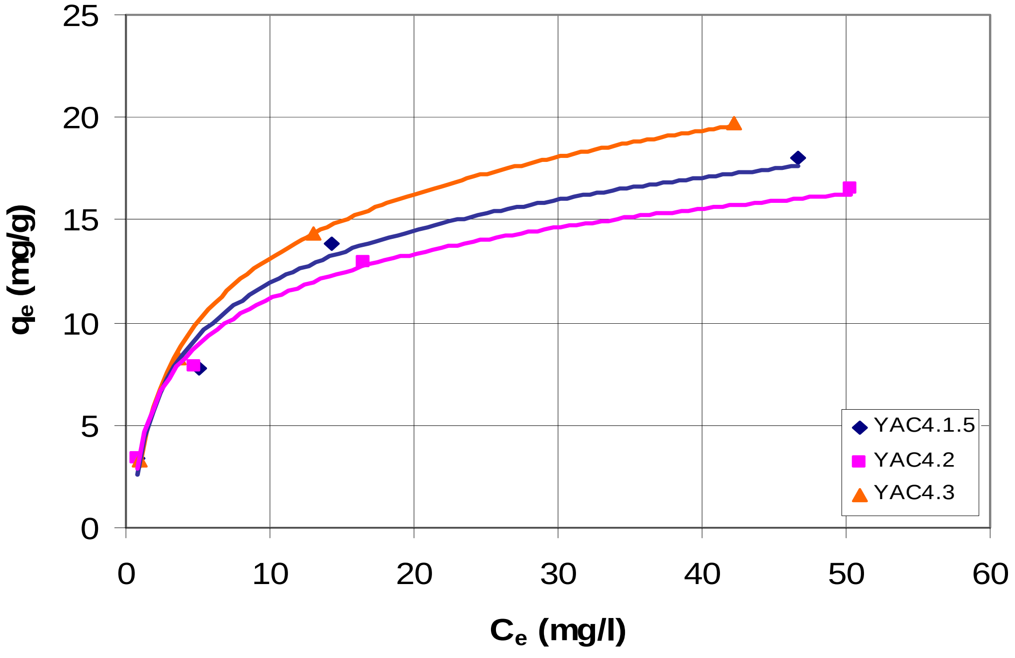

Figure 5.28: Adsorption Isotherms of Pb on YAC

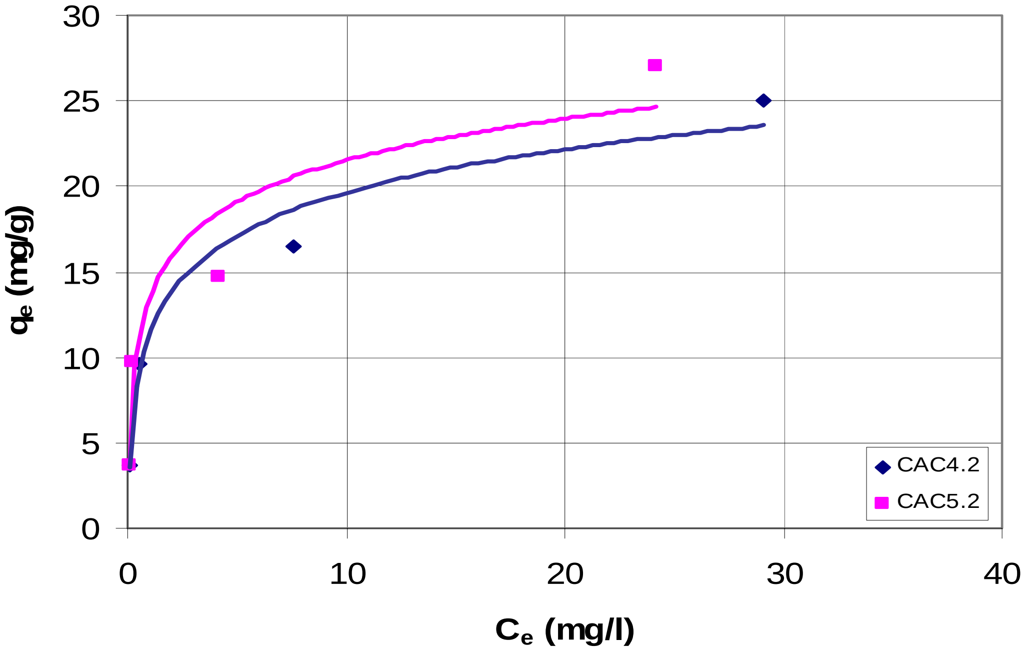

Figure 5.29: Adsorption Isotherms of Pb on CAC

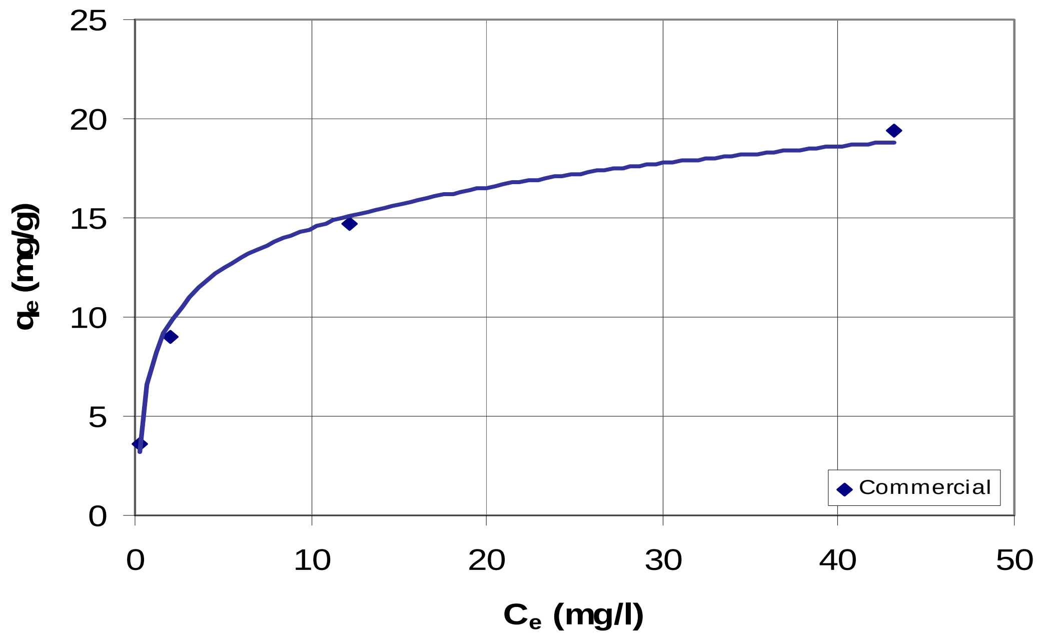

Figure 5.30: Adsorption Isotherm of Pb on Commercial AC

Table 5.3: Isotherm Constants for Cd Adsorption

Activated Carbon	**Langmuir**			**Freundlich**		
	Q (mg/g)	**b (l/mg)**	**R^2**	**n**	**K**	**R^2**
AAC8.1	9.3	0.054	0.9818	1.286	0.822	0.9161
AAC8.2	12.2	0.029	0.9766	1.518	0.560	0.9546
AAC8.6	112.4	0.001	0.1195	1.01	0.165	0.9867
AAC9.6	14.2	0.042	0.9640	1.898	1.205	0.9913
YAC4.1.5	16.3	0.018	0.9982	1.394	0.461	0.9912
YAC4.2	14.7	0.024	0.9596	1.598	0.682	0.9984
YAC4.3	15.1	0.018	0.7590	1.563	0.563	0.9808
CAC4.2	13.0	0.051	0.9175	2.336	1.647	0.9810
CAC5.2	18.3	0.074	0.9340	2.266	2.547	0.9950
Commercial	13.2	0.055	0.9542	2.171	1.555	0.9969

Table 5.4: Isotherm Constants of Pb Adsorption

Activated Carbon	Langmuir			Freundlich		
	Q (mg/g)	b (l/mg)	R^2	n	K	R^2
AAC8.1	17.1	0.076	0.9566	2.176	2.286	0.9640
AAC8.2	16.0	0.080	0.9999	1.963	1.889	0.9548
AAC8.6	16.0	0.148	0.9967	2.190	2.754	0.8757
AAC9.6	24.2	0.412	0.9947	2.844	7.161	0.9879
YAC4.1.5	20.3	0.160	0.9931	2.326	3.820	0.9810
YAC4.2	18.1	0.194	0.9953	2.597	4.025	0.9832
YAC4.3	22.7	0.150	0.9987	2.075	3.720	0.9556
CAC4.2	26.0	0.557	0.9843	3.071	8.800	0.9410
CAC5.2	28.2	0.700	0.9800	3.382	10.605	0.9135
Commercial	20.3	0.399	0.9940	3.155	6.393	0.9807

Langmuir and Freundlich isotherms were both capable to express heavy metal adsorption onto activated carbons in this study. As seen from the Figure 5.31, the data for Cd adsorption were better fitted by the Freundlich isotherm as compared to Langmuir isotherm as given by R^2 values, but Pb adsorption was described better by Langmuir isotherm as shown in Figure 5.32.

One of the major assumptions of Freundlich equation is heterogeneous surface composed of different classes of active sites. Better agreement of Freundlich isotherm with Cd adsorption indicated that Cd was adsorbed on some classes of active sites, not on all of available active sites. On the other hand, better agreement of Langmuir isotherm with Pb adsorption showed that Pb could be adsorbed on all classes of active sites. In other words, the surface of activated carbons behaved as homogenous for Pb adsorption.

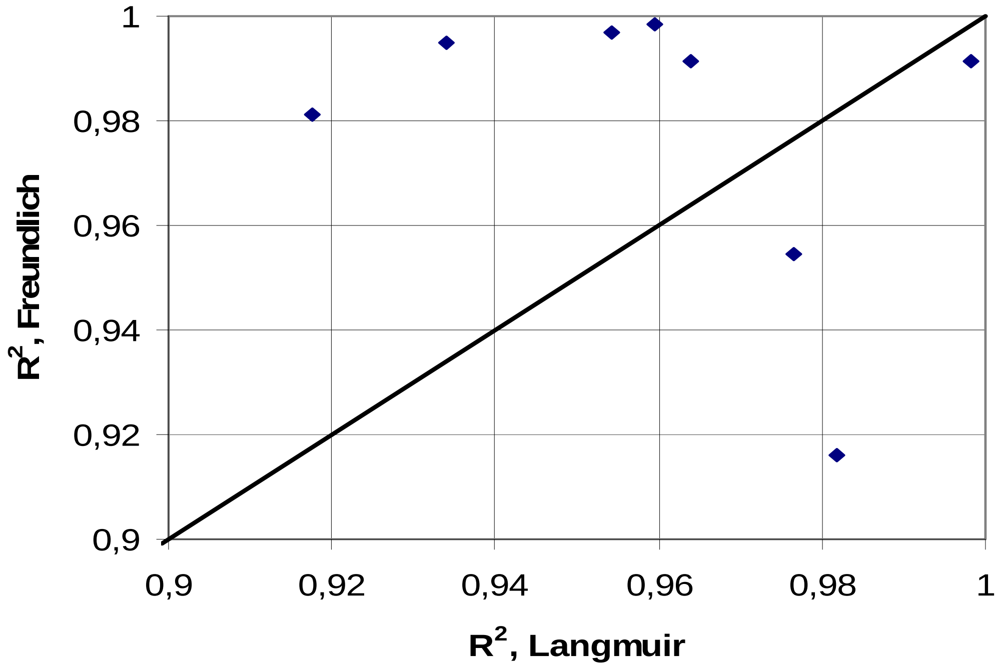

Figure 5.31: Comparison of R^2 Values for Cd Adsorption

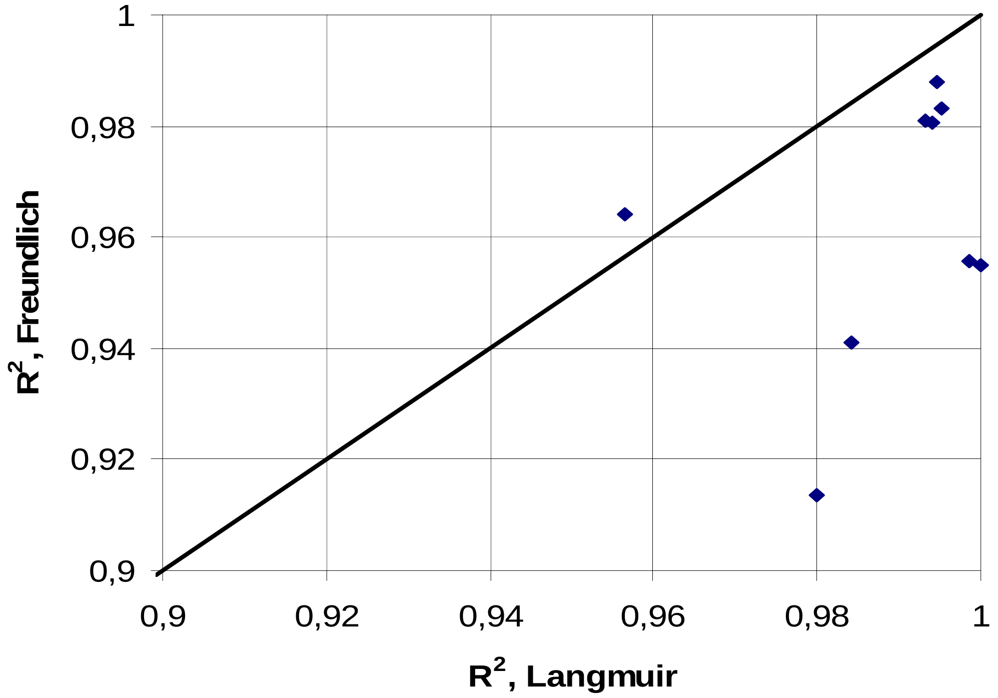

Figure 5.32: Comparison of R^2 Values for Pb Adsorption

CHAPTER VI

CONCLUSIONS

It was concluded from the results of this study that CAC had impressive performance in adsorption of heavy metals as compared to AAC and YAC type activated carbons, which had high potential. Heavy metal adsorption capacity of activated carbons was in decreasing order by CAC, Commercial AC, AAC and YAC, in general.

Precursor and production conditions are highly effective on adsorption capacity of activated carbons. Although CAC type of activated carbon had lowest surface area, adsorption capacities of these activated carbons were the highest ones. Thus, adsorption of heavy metals was not strongly dependent on surface area.

Results of methylene blue adsorption showed that chemical activation improved the porous structure of the products since pores of activated carbons produced by phosphoric acid activation were larger than the pores of activated carbons produced by physical activation.

Isoelectric points of all activated carbons used in this study were in the acidic range. These results indicated that net charge of external surface of activated carbon particles was negative even at low pH.

Probably the most important parameter that affects the adsorption process is pH. Results of first set of batch type experiments showed that heavy metal removal increased as pH increased. The optimum pH corresponding to maximum adsorption was in the range of 4-6 for both Cd and Pb.

The removal efficiencies of activated carbons were affected by the initial adsorbate concentration. Increase in initial concentration reduced the heavy metal removal percentages. In other words, lower concentration yielded greater removal efficiencies.

Both Langmuir and Freundlich expressions were able to describe the adsorption of Cd and Pb on activated carbons in this study. Constants of Langmuir and Freundlich isotherms indicated that activated carbons were more effective to adsorb Pb.

REFERENCES

1. Abdallah, W., “Production and Characterization of Activated Carbon from Sulphonated Stryrene Divinylbenzene Copolymer”, M. Sc. Thesis in Chemical Engineering, Middle East Technical University, Ankara, Turkey. (2004)

2. Attia, A. A., Girgis, B. S. and Khedr, S. A., “Capacity of activated carbon derived from pistachio shells by H_3PO_4 in the removal of dyes and phenolics”, Journal of Chemical Technology and Biotechnology, vol. 78, pp 611-619. (2003)

3. Basso, M. C., Cerrella, E. G. and Cukierman, A. L., “Activated carbons developed from a rapidly renewable biosource for removal of cadmium (II) and nickel (II) ions from dilute aqueous solutions”, Industrial & Engineering Chemistry Research, vol. 41., pp 180-189. (2002)

4. Bello, G., Cid, R., Garcia, R. and Arriagada, R., “Retention of Cr (VI) and Hg (II) in Eucalyptus globulus- and peach stone-activated carbons”, Journal of Chemical Technology and Biotechnology, vol. 74, pp 904-910. (1999)

5. Canter, L. W. and Knox, R. C., Ground Water Pollution Control, Lewis Publishers, Inc., Chelsea, Mich. (1985)

6. Carrubba, R. V., Urbanic, J. E., Wagner, N. J. and Zanitsch, R. H. AIChE Symp. Ser. Vol. 80, pp 76–83. (1984)

7. Clarke, P. J. et al. SAE Trans. vol. 76, pp 824–837. (1967)

8. Chen, J. P. and Wu, S., "Acid/base treated activated carbons: characterization of functional groups and metal adsorptive properties", Langmuir, vol. 20, pp 2233-2242. (2004)

9. Çuhadar, Ç., "Production and Characterization of Activated Carbon from Hazelnut Shell and Hazelnut Husk", M. Sc. Thesis in Chemical Engineering, Middle East Technical University, Ankara, Turkey. (2005)

10. Dabek, L., "Sorption of zinc ions from aqueous solutions on regenerated activated carbons", Journal of Hazardous Materials, vol. 101, no. 2, pp 191-201. (2003)

11. El-Gazar, W., "Removal of Lead from Water by Activated Carbon", M. Sc. Thesis in Chemical Engineering, Middle East Technical University, Ankara, Turkey. (1996)

12. Hassler J. W., Activated Carbon, Chemical Publishing Co., Inc., New York, pp 1-14. (1963)

13. Hassler J. W., Forest Products J. 8, 25A-27A. (1958)

14. Hassler J. W., Purification with Activated Carbon, Chem. Pub. Co., New York. (1974)

15. Jüntgen H., "New applications for carbonaceous adsorbents", Carbon, vol. 15, pp 273-283. (1977)

16. Kadirvelu, K., Kavipriya, M., Karthika, C., Radhika, M., Vennilamani, V. and Pattabhi, S., "Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions", Bioresource Technology, vol. 87, pp 129-132. (2003)

17. Kirk Othmer, Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley and Sons Inc. (2001)

18. Koyuncu, A., Çevre Mühendisliği Kimyası, SAM-Çevre Teknolojileri Merkezi Yayınları, İstanbul. (1999)

19. Lima, I. M. and Marshall, W. E., "Granular activated carbons from boiler manure: physical, chemical and adsorptive properties", Bioresource Technology, vol. 96. pp 699-706. (2005)

20. McEnaney, B. and Mays, T.J., Introduction to Carbon Science, Butterworths, London. (1989)

21. Mohan, D. and Chander S., "Single component and multi-component adsorption of metal ions by activated carbons", Colloids and Surfaces A: Physicochemical and Engineering Aspects, vol. 177, pp 183-196. (2001)

22. Mohan, D. and Singh, K. P., “Single and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse-an agricultural waste”, Water Research, vol. 36, pp 2304-2318. (2002)

23. Moon, C. and Lee, J., “Use of curdlan and activated carbon composed adsorbents for heavy metal removal”, Process Biochemistry, vol. 40, no. 3-4, pp 1279-1283. (2005)

24. Obalı, Z., “Heteropolyacid Catalysts for Etherification of Isoolefins”, M. Sc. Thesis in Chemical Engineering, Middle East Technical University, Ankara, Turkey. (2003)

25. Ouki, S. K. and Neufeld, R. D., “Use of activated carbon for the recovery of chromium from industrial wastewaters”, Journal of Chemical Technology and Biotechnology, vol. 70, pp 3-8. (1997)

26. Öztürk, A., “Production and Characterization of Activated Carbon from Pyrolysis of Copolymers”, M. Sc. Thesis in Chemical Engineering, Middle East Technical University, Ankara, Turkey. (1999)

27. Park, S. J. and Jung, W. Y., "Characterization of activated carbons based on polymeric resin", Journal of Colloid and Interface Science vol. 250, pp. 196–200. (2002)

28. Park, G. I., Lee, J. K., Ryu, S. K. and Kim, J. H., “Effect of two-step surface modification of activated carbon on the adsorption characteristics of metal ions in wastewater I: Equilibrium and

batch adsorptions", Carbon Science, vol. 3, no. 4, pp 219-225. (2002)

29. Puziy, A. M., Poddubnaya, O. I., Martinez-Alonso, A., Suarez-Garcia, F. and Tascon, J. M. D., "Synthetic carbons activated with phosphoric acid I: Surface chemistry and ion binding properties", Carbon, vol. 40, pp1493-1505. (2002)

30. Rajeshwarisivaraj, Sivakumar, S., Senthilkumar, P. and Subburam, V., "Carbon from cassava peel, an agricultural waste, as an adsorbent in the removal of dyes and metal ions from aqueous solution", Bioresource Technology, vol. 80, pp 233-235. (2001)

31. Rajeshwarisivaraj, Sivakumar, S., Senthilkumar, P. and Subburam, V., "Carbon from cassava peel, an agricultural waste, as an adsorbent in the removal of dyes and metal ions from aqueous solution", Bioresource Technology, vol. 80, pp 233-235. (2001)

32. Seco, A., Marzal, P. and Gabaldon, C., "Adsorption of heavy metals from aqueous solutions onto activated carbon in single Cu and Ni systems and in binary Cu-Ni, Cu-Cd and Cu-Zn systems", Journal of Chemical Technology and Biotechnology, vol. 68, pp 23-30. (1997)

33. Shekinah, P., Kadirvelu, K., Kanmani, P., Senthilkumar, P. and Subburam, V., "Adsorption of lead (II) from aqueous solution by activated carbon prepared from *Eichhornia*", Journal of

Chemical Technology and Biotechnology, vol. 77, pp 458-464. (2002)

34. Shim, J. W., Park, S. J. and Ryu, S. K., “Effect of modification with HNO_3 and NaOH on metal adsorption with pitch-based activated carbon fibers”, Carbon, vol. 39, pp 1635-1642. (2001)

35. Sincero, A. P. and Sincero, G. A., Physical-Chemical Treatment of Water and Wastewater, CRC Press, London (2002)

36. Smisek, M. And Cerny, S., Active Carbon Manufacture, Properties and Aplications, Elsevier Pub., Comp., New York. (1970)

37. Teker, M. and İmamoğlu, M., “Adsorption of copper and cadmium ions by activated carbon from rice hulls”, Turkish Journal of Chemistry, vol. 23, pp 185-191. (1999)

38. Toles, C. A., Marshall, W. E., Wartelle, L. H. and McAloon, A., “Steam- or carbon dioxide-activated carbons from almond shells: physical, chemical and adsorptive properties and estimated cost of production”, Bioresource Technology, vol. 75, pp 197-203. (2000)

39. Valdes, H., Sanchez-Polo, M., Rivera-Utrilla, J. And Zaror, C. A., “Effect of ozone treatment on surface properties of activated carbon”, Langmuir, vol. 18, pp 2111-2116. (2002)

40. Weber Jr., W. J., Physicochemical Processes for Water Quality Control, John Wiley and Sons, New York. (1972)

41. Xiao, B. and Thomas K. M., “Competitive adsorption of aqueous metal ions on an oxidized nanoporous activated carbon”, Langmuir, vol. 20, pp 4566-4578. (2004)

42. Yağşi, N. U., “Production and Characterization of Activated Carbon from Apricot Stones”, M. Sc. Thesis in Chemical Engineering, Middle East Technical University, Ankara, Turkey. (2004)

43. Zawadzki, J., Chemistry and Physics of Carbon, Vol. 21, Marcel Dekker, Inc., New York. (1989)

APPENDIX A

EXPERIMENTAL DATA FOR HEAVY METAL ADSORPTION

Table A.1: Exp. Data for Cd Adsorption at Different pH

Activated Carbon	**Final Cd Concentration (mg/l)**					
	pH=2	**pH=3**	**pH=4**	**pH=5**	**pH=6**	**pH=7**
AAC8.1	50.25	39.25	32.25	33.00	31.00	37.25
AAC8.2	47.50	41.50	32.50	33.75	33.25	38.50
AAC8.6	46.50	36.00	33.25	33.25	32.25	39.50
AAC9.6	47.25	34.00	29.50	30.50	30.75	34.25
YAC4.1.5	45.75	43.25	33.75	31.50	30.25	39.50
YAC4.2	47.00	42.00	33.00	32.00	30.25	35.75
YAC4.3	46.25	40.00	36.50	35.75	35.50	41.25
CAC4.2	45.50	34.75	31.50	33.25	32.00	38.75
CAC5.2	45.25	28.75	24.25	23.50	22.00	28.00
Commercial	46.50	37.50	30.75	24.50	25.38	23.50
Blank	49.50	49.75	48.75	47.75	48.00	45.00

Table A.2: Exp. Data for Pb Adsorption at Different pH

Activated Carbon	**Final Pb Concentration (mg/l)**					
	pH=2	**pH=3**	**pH=4**	**pH=5**	**pH=6**	**pH=7**
AAC8.1	50.90	33.40	21.35	11.85	12.30	8.12
AAC8.2	47.80	37.20	23.00	15.20	12.10	5.20
AAC8.6	47.40	34.50	17.95	12.85	12.00	6.18
AAC9.6	50.70	36.10	7.70	3.60	2.60	0.76
YAC4.1.5	46.50	32.50	14.35	14.52	14.15	11.42
YAC4.2	48.10	31.80	16.55	14.25	11.20	9.92
YAC4.3	47.00	19.90	13.05	9.80	9.40	5.96
CAC4.2	39.40	17.50	7.60	4.05	2.70	1.56
CAC5.2	35.00	7.90	4.20	1.95	1.70	0.70
Commercial	49.63	38.10	12.15	4.45	2.86	0.22
Blank	49.20	47.80	48.85	46.80	48.00	37.16

A.1. Sample Calculation of Percent Removal

Pb adsorption by YAC4.2 at pH=4 and at C_0=50 mg/l:

Concentration of Blank Experiment = 48.85 mg/l

Final Concentration of Solution = 16.55 mg/l

$$\% \text{ Removal} = \frac{C_{blank} - C_{final}}{C_{blank}} x100 = \frac{48.85 - 16.55}{48.85} x100 \qquad \text{(Eq. A.1)}$$

% Removal = 66.12% removal

Table A.3: Exp. Data for Cd Ads. at Different Initial Conc.

Activated Carbon	**Final Cd Concentration (mg/l)**			
	C_0=10 mg/l	**C_0=25 mg/l**	**C_0=50 mg/l**	**C_0=100 mg/l**
AAC8.1	5.26	14.50	32.25	73.00
AAC8.2	5.73	15.30	32.50	71.00
AAC8.6	6.96	17.80	33.25	67.00
AAC9.6	3.63	13.60	29.50	64.50
YAC4.1.5	5.83	15.70	33.75	68.50
YAC4.2	5.00	15.50	33.00	67.50
YAC4.3	5.43	16.20	36.50	68.00
CAC4.2	2.86	13.30	31.50	64.50
CAC5.2	1.63	8.50	24.25	52.50
Commercial	3.13	12.10	30.75	64.00
Blank	9.69	24.70	48.75	91.00

Table A.4: Exp. Data for Pb Ads. at Different Initial Conc.

Activated Carbon	**Final Pb Concentration (mg/l)**			
	C_0=10 mg/l	**C_0=25 mg/l**	**C_0=50 mg/l**	**C_0=100 mg/l**
AAC8.1	1.69	10.16	21.35	56.63
AAC8.2	2.51	8.26	23.00	58.63
AAC8.6	1.89	5.37	17.95	56.13
AAC9.6	0.16	1.83	7.70	34.75
YAC4.1.5	0.81	5.10	14.35	46.63
YAC4.2	0.74	4.76	16.55	50.25
YAC4.3	1.03	3.68	13.05	42.25
CAC4.2	0.12	0.54	7.60	9.13
CAC5.2	0.06	0.23	4.20	4.13
Commercial	0.06	1.97	12.15	43.10
Blank	9.16	24.44	48.85	91.63

A.2. Sample Calculation of Adsorption Capacity

Cd Adsorption by CAC5.2 at pH=4 and at C_0=10 mg/l:

Concentration of Blank Experiment = 9.69 mg/l

Final Concentration of Solution = 1.63 mg/l

$$\text{Adsorption Capacity} = \frac{(C_{blank} - C_{final}) \times V_{sol}}{m_{AC}} \qquad \text{(Eq. A.2)}$$

$$\text{Adsorption Capacity} = \frac{(9.69 - 1.63)\ \text{mg/l} \times 0.01\ \text{l sol.}}{0.025\ \text{g AC}} = 3.22\ \text{mg/g}$$

Table A.5: Experimental Data of Reproducibility Tests

	pH=4 C_0=50 mg/l				pH=4 C_0=100 mg/l			
Activated Carbon	**$[Cd]_{final}$ (mg/l)**	**RD (%)**	**$[Pb]_{final}$ (mg/l)**	**RD (%)**	**$[Cd]_{final}$ (mg/l)**	**RD (%)**	**$[Pb]_{final}$ (mg/l)**	**RD (%)**
AAC8.2	30.50	-6.15	22.50	-2.17	68.85	-3.03	55.60	-5.17
AAC9.6	31.00	+5.08	7.50	-2.60	64.50	0	33.20	-4.46
YAC4.1.5	35.00	+3.70	15.20	+5.92	70.00	+2.19	49.5	+6.15
YAC4.2	31.75	-3.79	17.55	+6.04	67.00	-0.74	51.40	+2.29
YAC4.3	36.00	-1.37	12.50	-4.21	70.50	+3.68	41.50	-1.78
CAC4.2	32.25	+2.38	7.80	+2.63	63.00	-2.33	30.2	+3.67
Commercial	30.50	-0.81	12.75	+4.94	61.50	-4.07	44.60	+3.48
Blank	48.75	0	48.85	0	91.00	0	91.63	0

RD : Relative Deviation

$[Cd]_{final}$: Final Cd Concentration

$[Pb]_{final}$: Final Pb Concentration

Table A.6: pH Change in Cd Adsorption Experiments

Activated Carbon	pH	pH = 2	pH = 3	pH = 4	pH = 5	pH = 6	pH = 7
AAC8.1	**Initial**	2.2	3.2	3.8	4.8	6.2	6.9
	Final	2.3	3.4	4.2	4.3	4.0	4.1
AAC8.2	**Initial**	2.2	3.1	3.8	4.9	6.2	6.9
	Final	2.3	3.4	3.9	3.9	4.0	4.0
AAC8.6	**Initial**	2.2	3.1	4.1	4.9	6.0	6.8
	Final	2.3	3.5	4.2	3.8	4.0	4.0
AAC9.6	**Initial**	2.2	3.2	4.1	5.2	6.2	6.9
	Final	2.3	3.8	4.5	4.6	5.0	4.6
YAC4.1.5	**Initial**	2.2	3	3.9	4.9	5.9	7.1
	Final	2.2	2.9	3.5	3.7	3.7	3.7
YAC4.2	**Initial**	2.2	3.0	4.1	4.8	6.2	6.9
	Final	2.3	3.0	3.8	3.9	3.7	3.8
YAC4.3	**Initial**	2.2	3.0	3.8	5.2	5.9	6.8
	Final	2.3	3.0	3.4	3.8	3.7	3.8
CAC4.2	**Initial**	2.2	3.0	3.8	4.8	6.0	6.9
	Final	2.2	2.8	3.2	3.5	3.4	3.4
CAC5.2	**Initial**	2.2	3.0	4.0	4.8	5.9	6.9
	Final	2.2	2.9	3.2	3.3	3.3	3.3
Commercial	**Initial**	2.2	3.0	3.9	4.8	5.8	6.8
	Final	2.2	3.1	4.5	5.0	4.5	4.4
Blank	**Initial**	2.2	3.1	4.0	5.1	6.0	6.9
	Final	2.2	3.1	3.9	5.0	5.8	6.8

Table A.7: pH Change in Pb Adsorption Experiments

Activated Carbon	**pH**	**pH = 2**	**pH = 3**	**pH = 4**	**pH = 5**	**pH = 6**	**pH = 7**
AAC8.1	**Initial**	2.2	3.1	4.0	5.2	6.2	6.8
	Final	2.3	3.3	4.0	3.8	3.9	4.0
AAC8.2	**Initial**	2.2	3.0	4.0	5.1	6.0	7.1
	Final	2.2	3.1	3.9	3.9	4.0	4.3
AAC8.6	**Initial**	2.2	3.1	4.0	5.2	6.1	6.9
	Final	2.2	3.2	3.9	4.0	4.1	4.1
AAC9.6	**Initial**	2.2	3.0	3.9	5.2	5.9	6.9
	Final	2.2	3.1	4.1	4.4	4.3	4.4
YAC4.1.5	**Initial**	2.2	3.0	4.0	5.2	6.0	7.1
	Final	2.2	2.9	3.5	3.7	3.6	3.6
YAC4.2	**Initial**	2.2	3.0	4.1	5.1	6.2	7.0
	Final	2.1	2.9	3.5	3.7	3.7	3.8
YAC4.3	**Initial**	2.2	2.9	4.0	4.9	6.0	7.1
	Final	2.2	3.0	3.4	3.6	3.6	3.8
CAC4.2	**Initial**	2.2	2.8	3.9	5.1	6.0	7.0
	Final	2.2	2.8	3.2	3.4	3.3	3.3
CAC5.2	**Initial**	2.2	3.1	4.0	4.9	6.1	7.1
	Final	2.2	2.8	3.2	3.3	3.3	3.4
Commercial	**Initial**	2.1	3.0	3.9	5.1	6.1	7.2
	Final	2.2	3.4	3.9	4.1	4.2	4.6
Blank	**Initial**	2.2	3.0	4.1	4.9	6.0	7.1
	Final	2.2	2.9	4.0	4.9	5.9	5.5

APPENDIX B

EXPERIMENTAL DATA FOR METHYLENE BLUE NUMBER

A chemical compound absorbs the light at specific wavelengths and this is a function of its electronic structure. In addition, intensity of absorption of light is related to the amount of the molecules between the light source and the detector. A UV spectrometer measure the amount of ultraviolet and visible light absorbed by a sample placed in the spectrometer.

A calibration curve must be prepared before measuring amount of methylene blue adsorbed by activated carbons. Data for calibration samples and calibration curve can be seen in Table B.1.

At the end of experiments, samples were taken and all samples except sample for commercial AC diluted to one of one hundredth prior to measurement. These samples were measured by UV spectrometer. Results of UV measurements can be seen in Table B.2.

Table B.1: Data for Calibration Samples

Methylene Blue Concentration (mg/l)	**Absorbance**
0	0
0.86	0.1089
2.14	0.2889
4.28	0.6863
5.13	0.7317
6.84	0.9285
8.56	1.1796

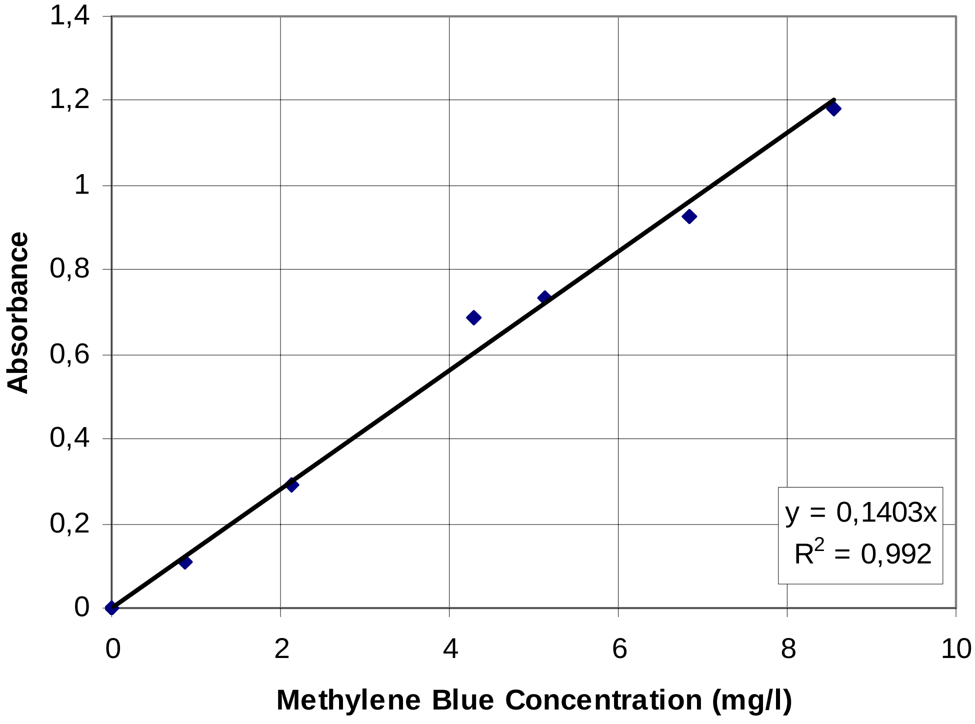

Figure B.1: Calibration Curve for MBN Experiments

Table B.2: Results of UV Measurements

Activated Carbon	**Dilution**	**Absorbance**
AAC8.1	1/100	0.2615
AAC8.2	1/100	0.2588
AAC8.6	1/100	0.2561
AAC9.6	1/100	0.2310
YAC4.1.5	1/100	0.2400
YAC4.2	1/100	0.2291
YAC4.3	1/100	0.2106
CAC4.2	1/100	0.2566
CAC5.2	1/100	0.2541
Commercial	1/1	0.0613
Blank	1/100	0.2761

B.1. Sample Calculation of MBN and S_{MB} / S_{BET}

Methylene Blue Adsorption by YAC4.3:

Concentration of Blank Experiment = 196.8 mg/l

Final Concentration of Solution = 150.1 mg/l

$$\text{MBN} = \frac{(C_{\text{blank}} - C_{\text{final}}) \text{ x } V_{\text{sol}}}{m_{\text{AC}}} \qquad \text{(Eq. B.1)}$$

$$\text{MBN} = \frac{(196.8 - 150.1) \text{ mg/l x } 0.05 \text{ l sol.}}{0.1 \text{ g AC}} = 23.3 \text{ mg/g}$$

$$S_{MB} = \frac{\text{MBN x MB Surface Area x Avagadro No.}}{\text{MB Molecular Weight}} \qquad \text{(Eq. B.2)}$$

$$S_{MB} = \frac{(23.4 \text{ mg/g}).(1.62\text{x}10^{-18} \text{ m}^2\text{/molecule}).(6.02\text{x}10^{23})}{319.86 \text{ g/mol}}$$

S_{MB} = 71.2 m^2/g

$$S_{MB}/S_{BET} = \frac{71.2\ m^2/g}{665\ m^2/g} = 0.107 \qquad \text{(Eq. B.3)}$$

APPENDIX C

LINEARIZED ADSORPTION ISOTHERMS

C.1. Linearized Isotherms of Cd Adsorption

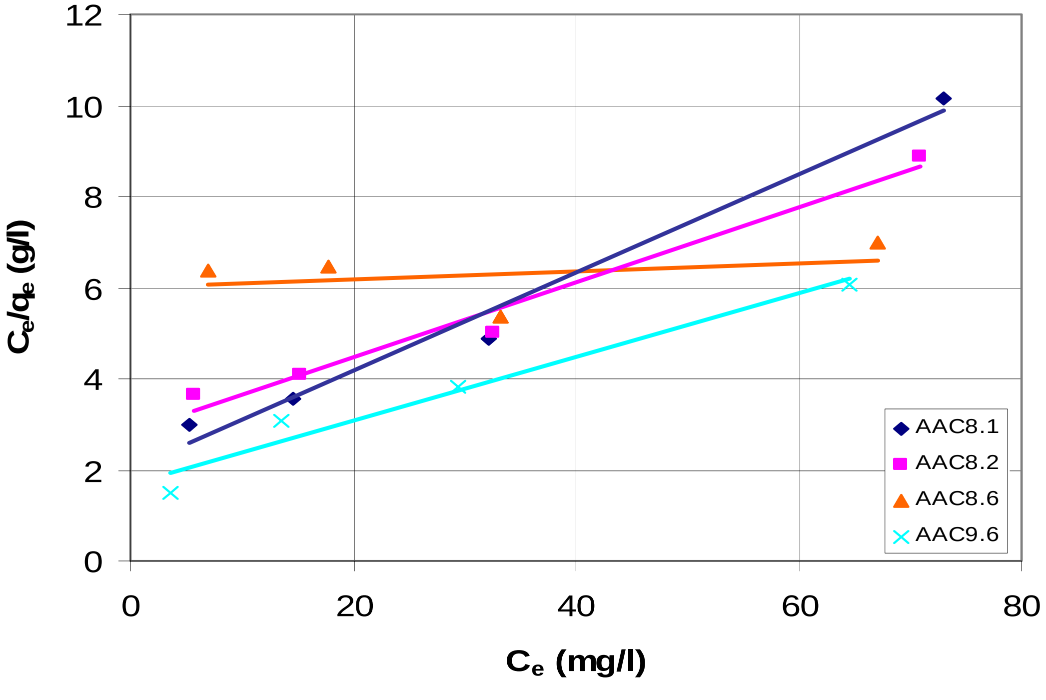

Figure C.1: Linear Forms of Langmuir Isotherms of Cd on AAC

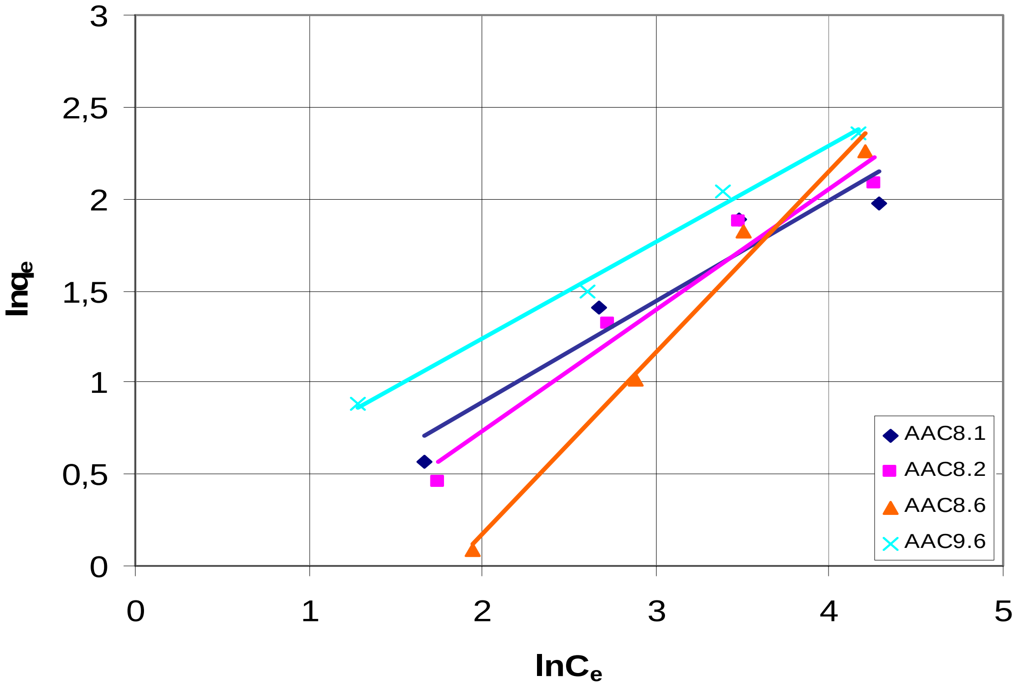

Figure C.2: Linear Forms of Freundlich Isotherms of Cd on AAC

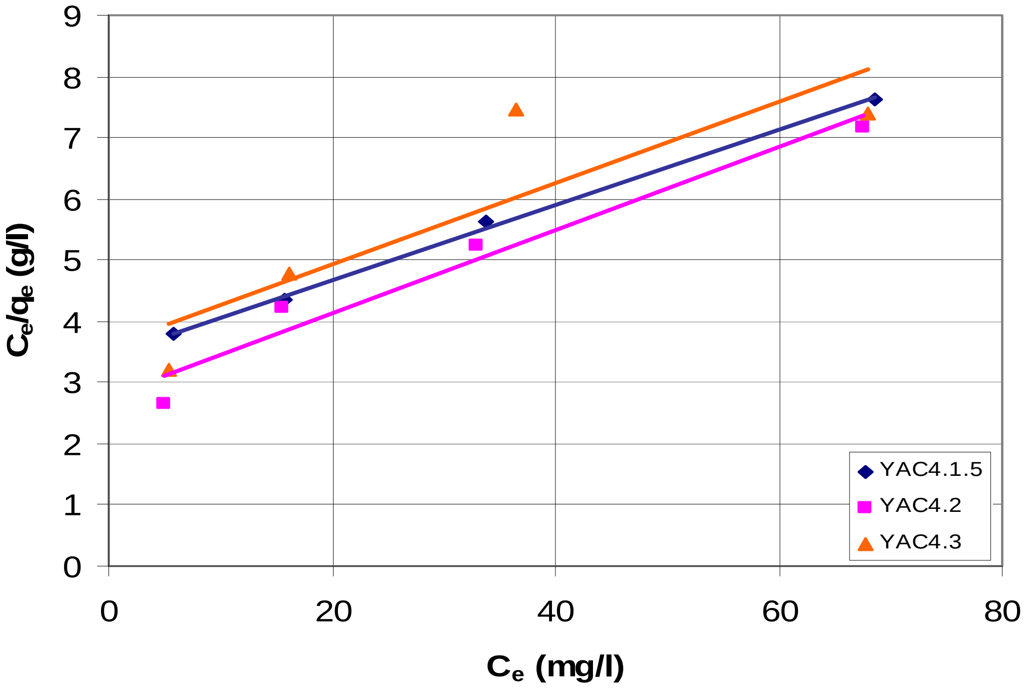

Figure C.3: Linear Forms of Langmuir Isotherms of Cd on YAC

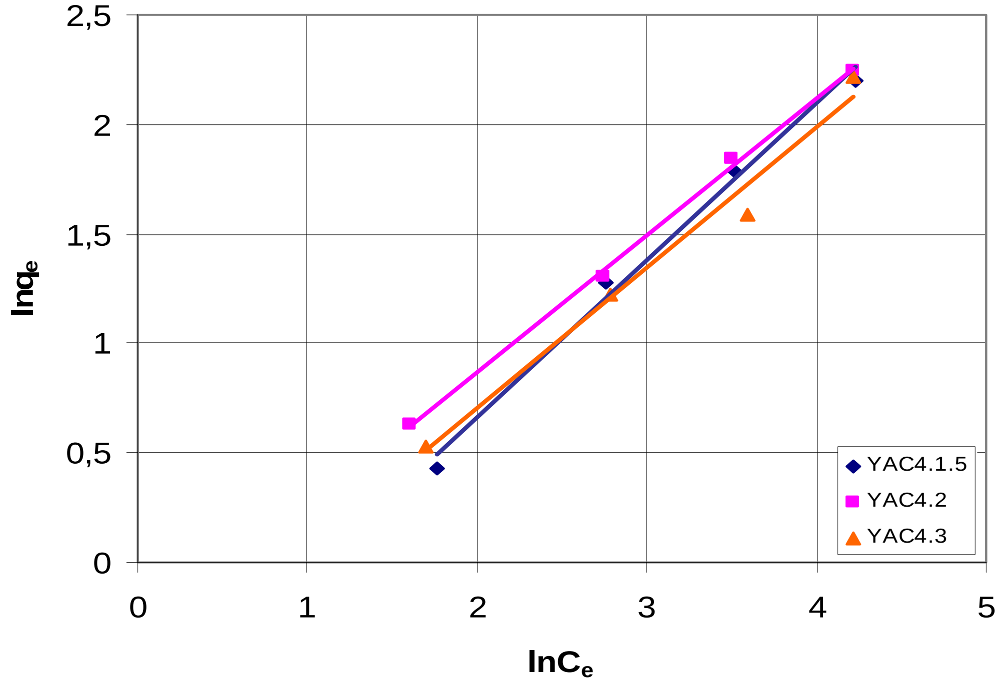

Figure C.4: Linear Forms of Freundlich Isotherms of Cd on YAC

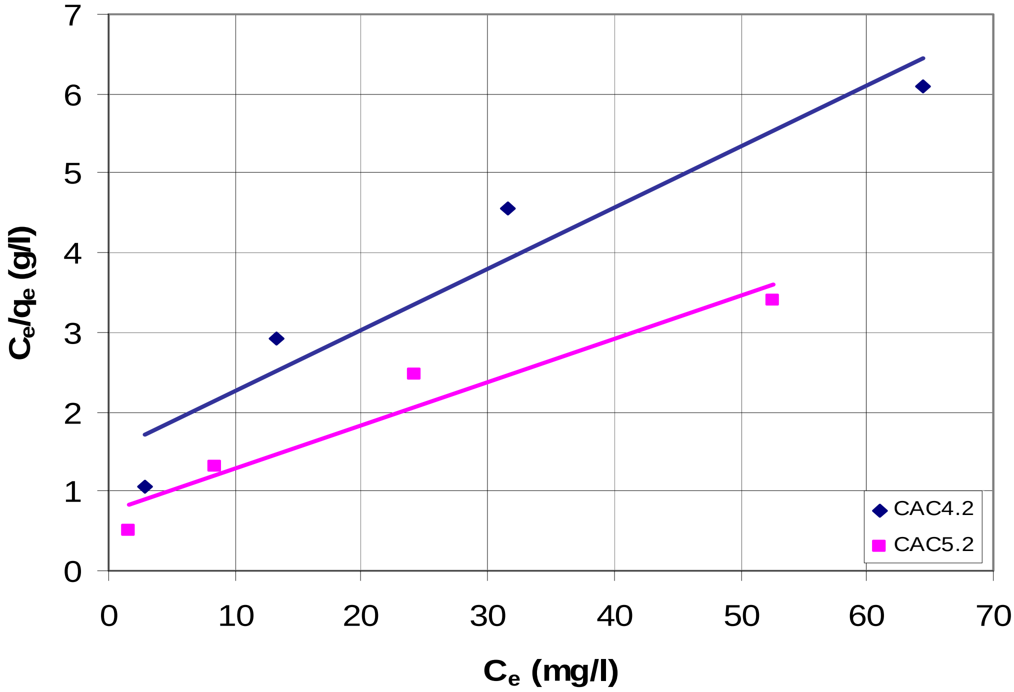

Figure C.5: Linear Forms of Langmuir Isotherms of Cd on CAC

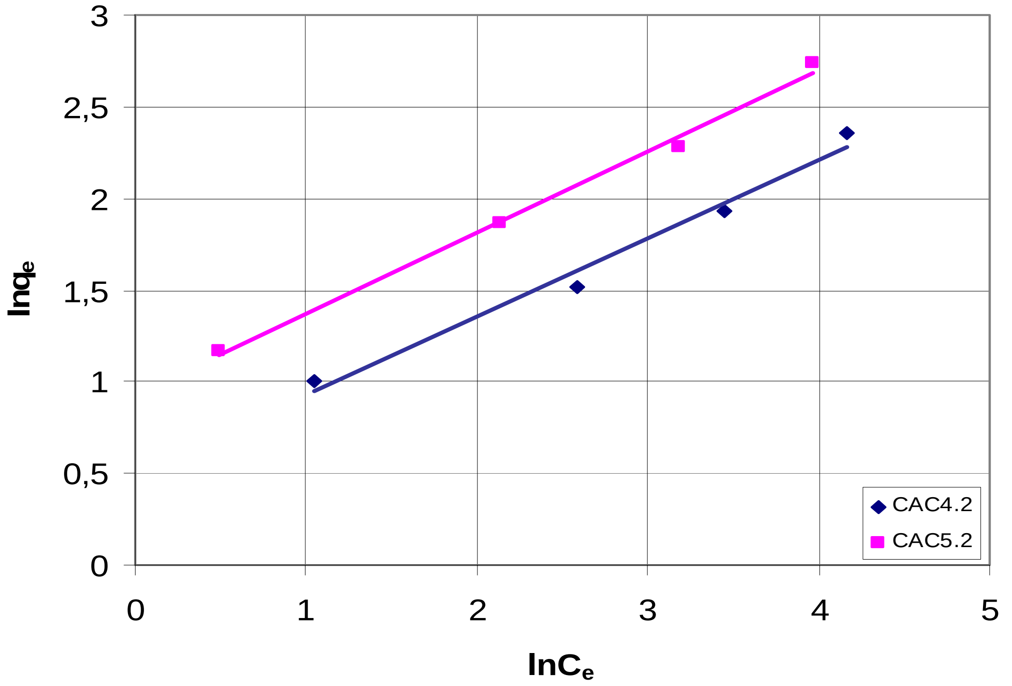

Figure C.6: Linear Forms of Freundlich Isotherms of Cd on CAC

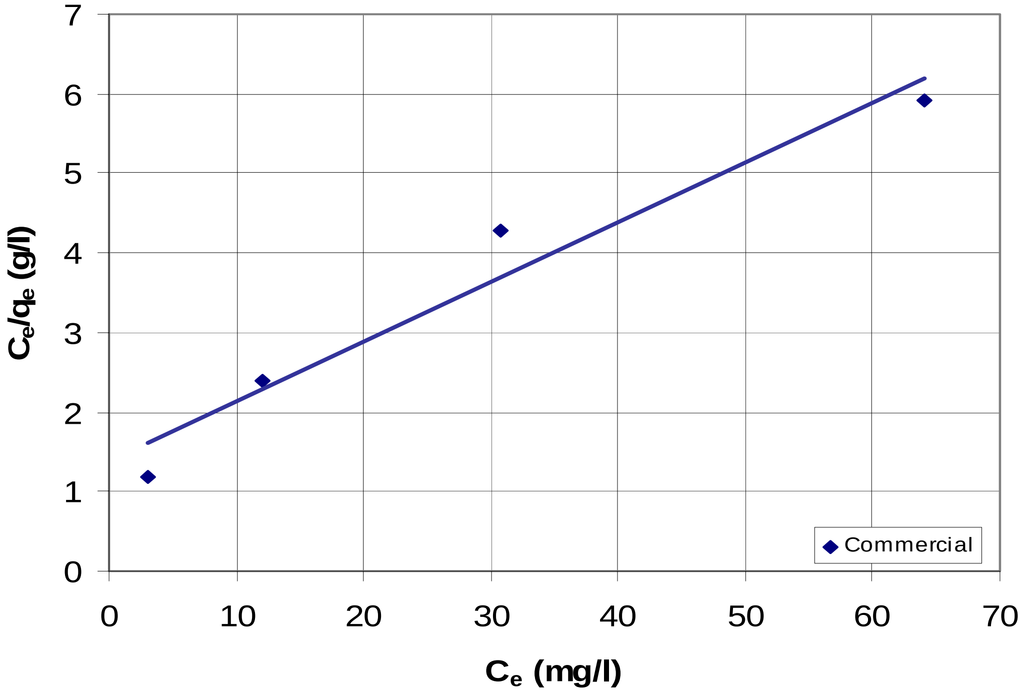

Figure C.7: Linear Form of Langmuir Isotherm of Cd on Commercial AC

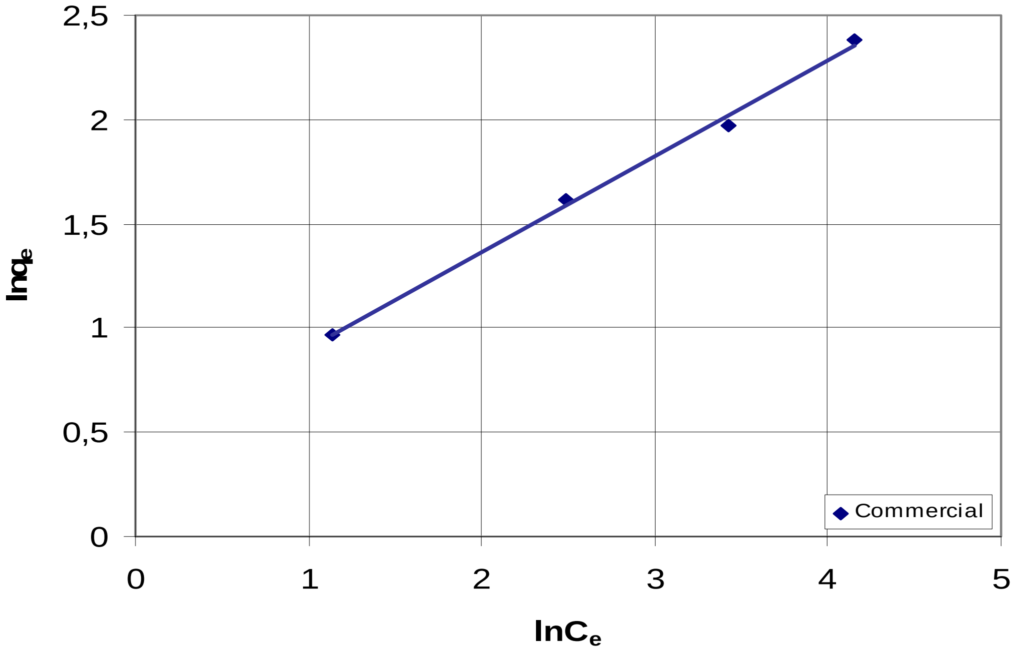

Figure C.8: Linear Form of Freundlich Isotherm of Cd on Commercial AC

C.2. Linearized Isotherms of Pb Adsorption

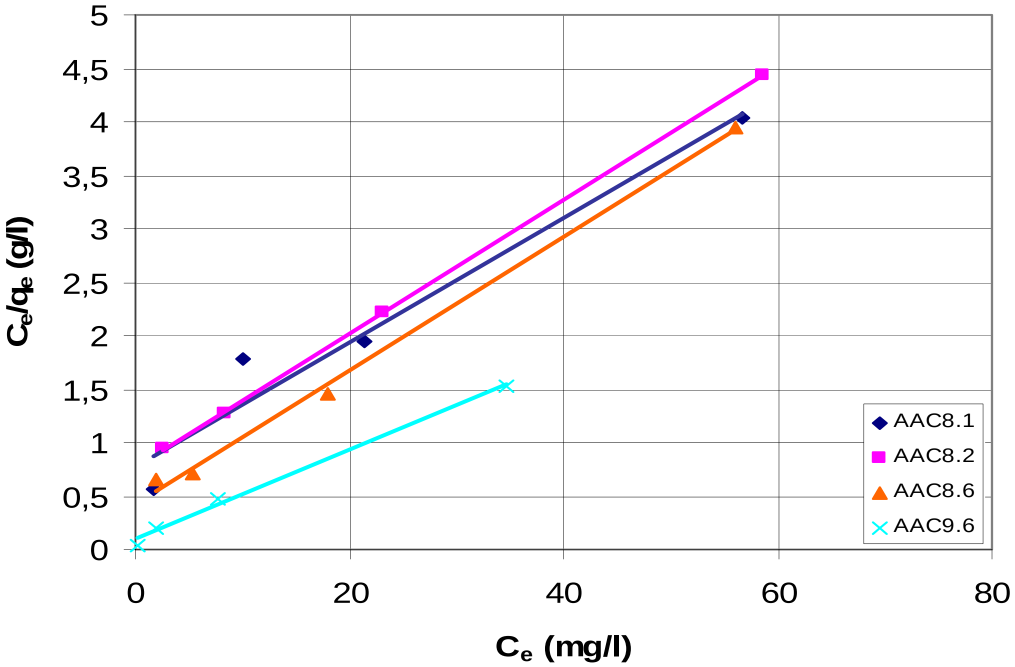

Figure C.9: Linear Forms of Langmuir Isotherms of Pb on AAC

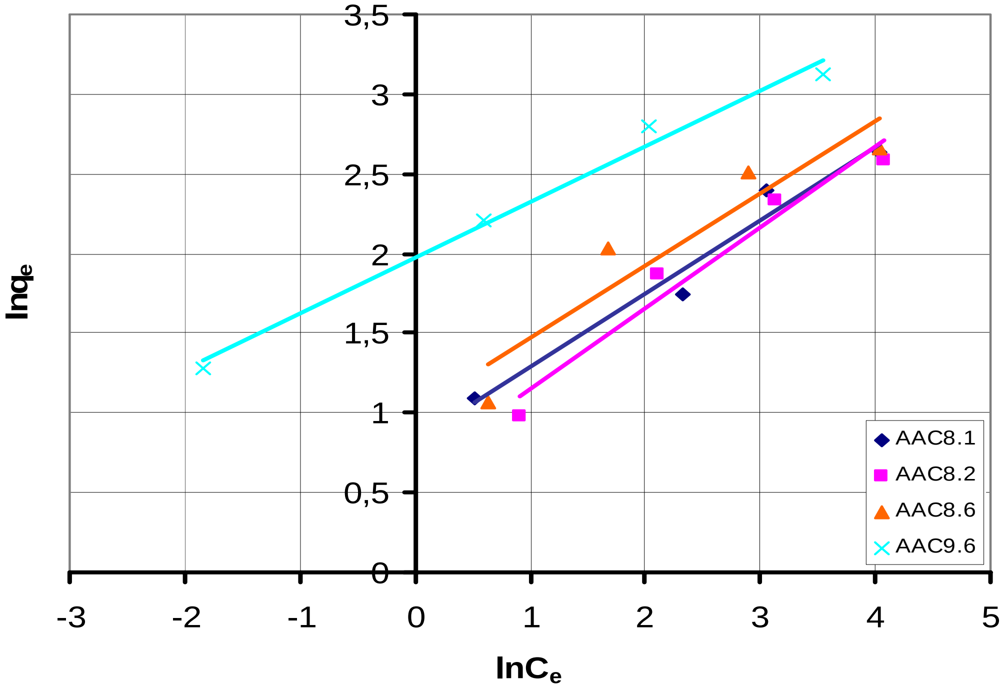

Figure C.10: Linear Forms of Freundlich Isotherms of Pb on AAC

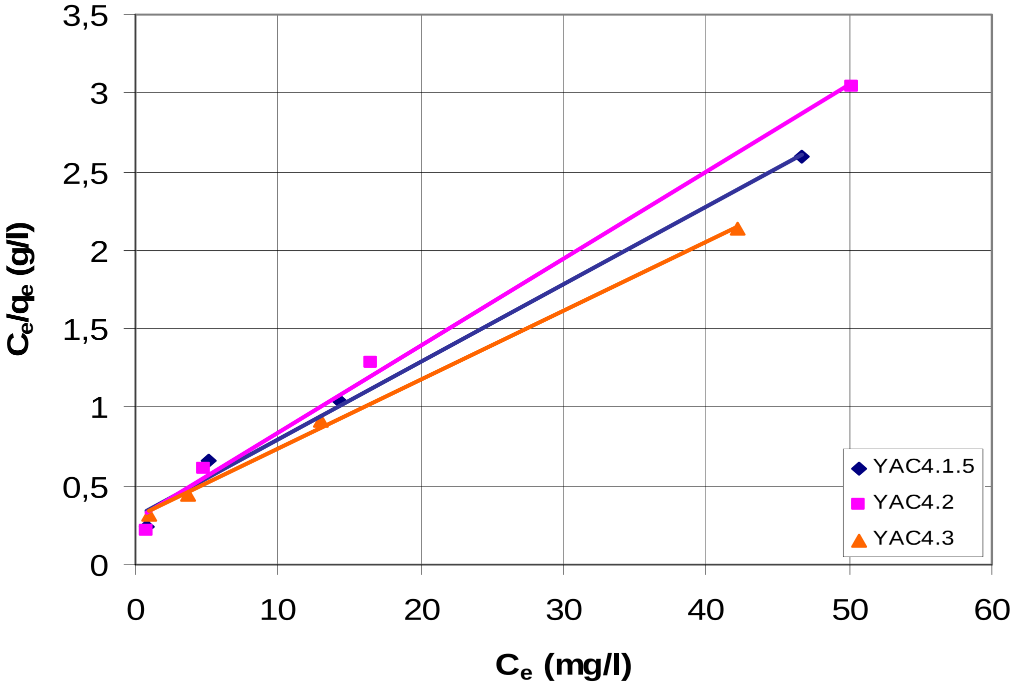

Figure C.11: Linear Forms of Langmuir Isotherms of Pb on YAC

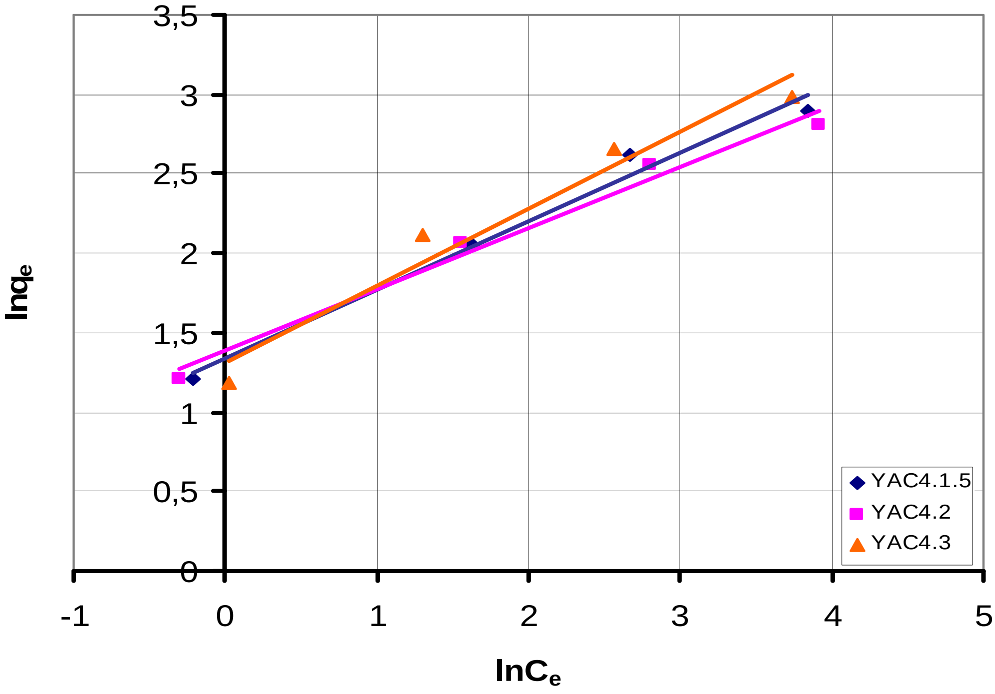

Figure C.12: Linear Forms of Freundlich Isotherms of Pb on YAC

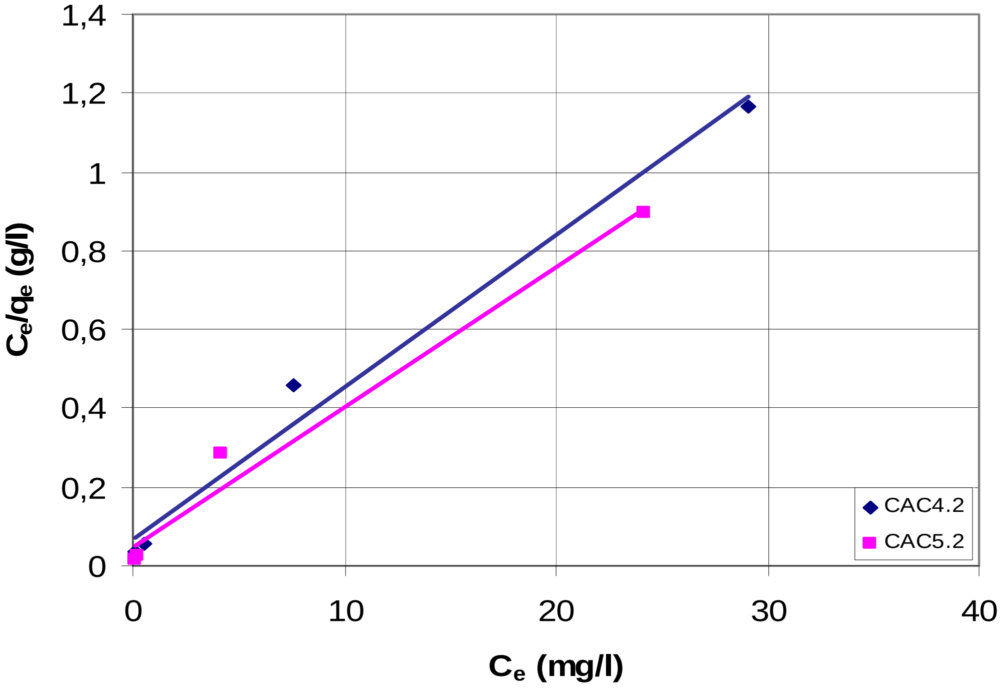

Figure C.13: Linear Forms of Langmuir Isotherms of Pb on CAC

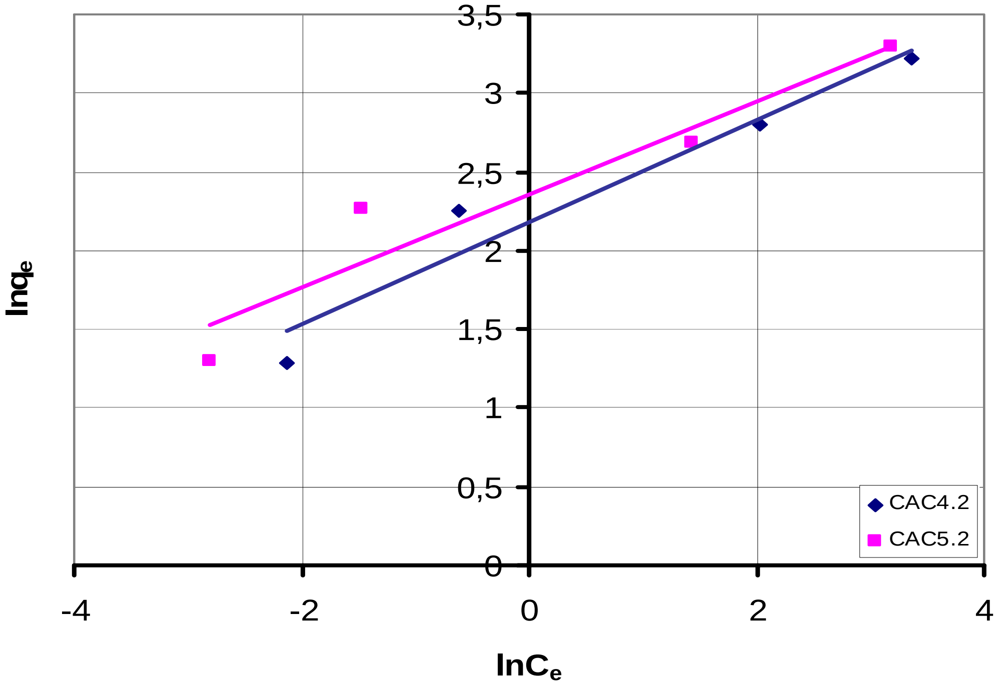

Figure C.14: Linear Forms of Freundlich Isotherms of Pb on CAC

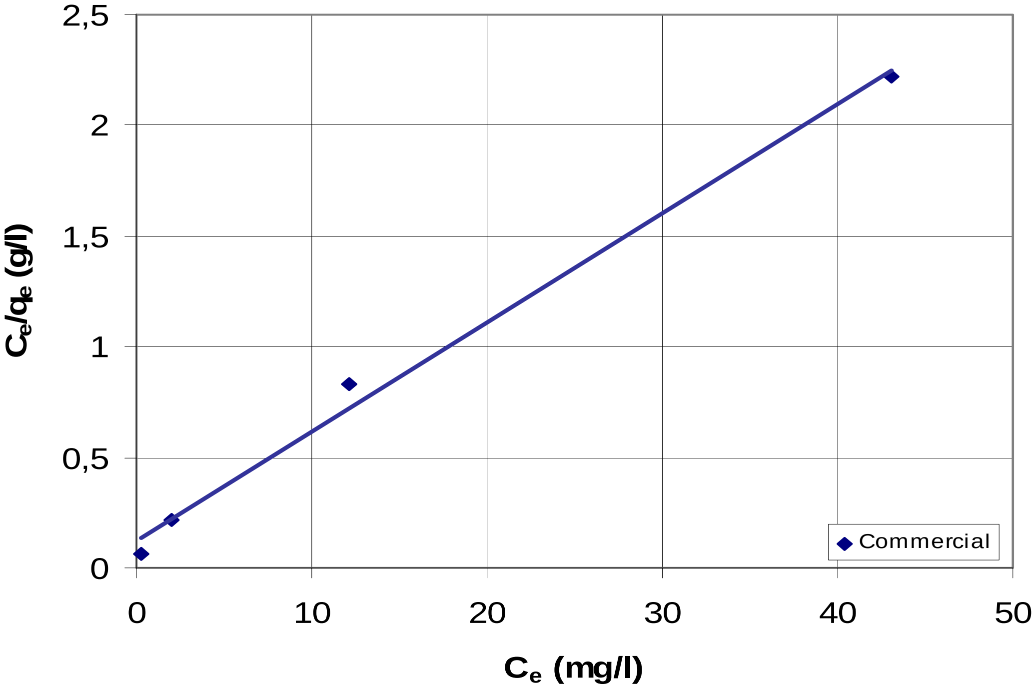

Figure C.15: Linear Form of Langmuir Isotherm of Pb on Commercial AC

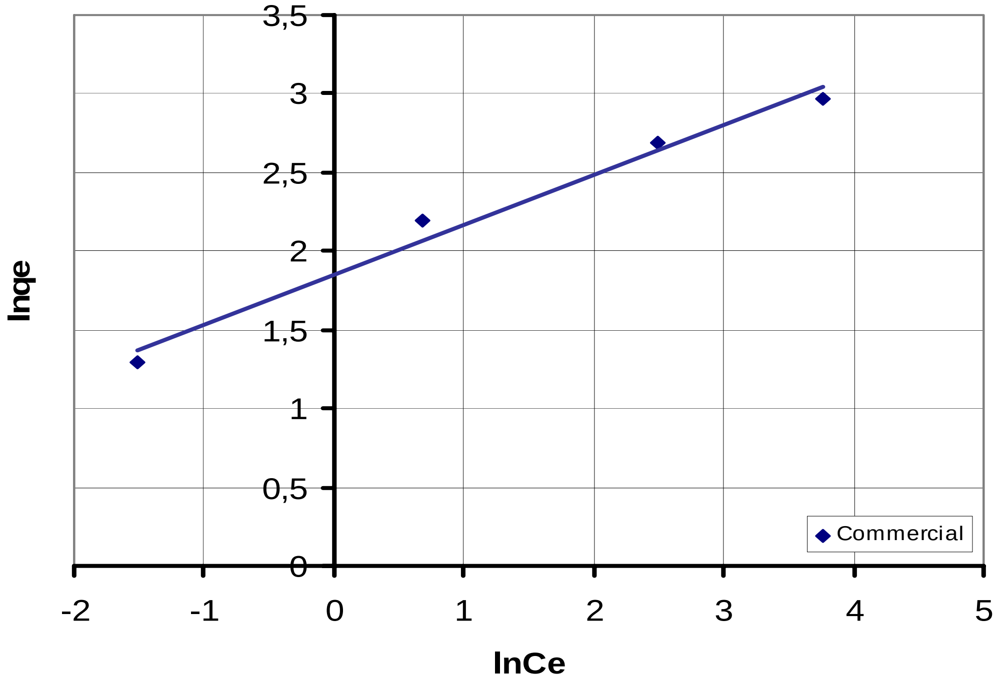

Figure C.16: Linear Form of Freundlich Isotherm of Pb on Commercial AC