

Chapter 1

INTRODUCTION

1.1 Introduction

In recent years there has been a growing concern with environmental protection. Environmental contamination due to heavy metals is caused by several industries, metal plating, mining, painting, and car radiator manufacturing, and also by agricultural sources such as fertilizers and fungicidal sprays. The presence of the toxic metals in the environment is a major concern because of their toxicity and threat for human life and for the environment, especially when tolerance levels are exceeded. Some of these are capable of being assimilated, stored and concentrated by organisms. Moreover, they are accumulated in the human body, causing erythrocyte destruction, nausea, salivation, diarrhea and muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformity. Since cadmium and lead are among the most toxic of elements, it necessitates the use of experimental methods to reduce their presence in contaminated aqueous solution to non-toxic quantities.

Various treatment technologies have been developed for the purification of water and wastewater contaminated by cadmium and lead. The most commonly used methods for the removal of these metal ions from industrial effluents including: chemical precipitation, solvent extraction, oxidation, reduction, dialysis/electrodialysis, electrolytic extraction, reverse osmosis, ion-exchange,

evaporation, cementation, dilution, adsorption, filtration, flotation, air stripping, steam stripping, flocculation, sedimentation, soil flushing/washing chelation, etc. Among these, adsorption has evolved as the front line of defense and especially for those, which cannot be removed by other techniques. Selective adsorption utilizing biological materials, mineral oxides, activated carbon, or polymer resins, has generated much excitement among researchers, environmental engineers and scientists.

At the present time, activated carbons occupy a prominent position among current adsorbents as versatile and universal materials, due to their distinguished properties: (1) physical properties e.g. their well-developed porous structures and large internal surface and (2) chemical nature comprised of hydrophobic graphene layers and hydrophilic surface functional groups. These porous materials can be used for the adsorption of a wide range of species from both gas or liquid phases. However, adsorption from the liquid phase is more complex and the fundamental principles are much less well understood compared with gas-phase adsorption (Haghseresht, et al., 2002).

A variety of activated carbons are available commercially but they are very costly. Therefore, there are many researcher have attempted to produce and develop the activated carbons extensively. All of the productions involve activation process by using many carbonaceous materials as precursors. Precursors of activated carbons are either of botanical origin (e.g. wood, coconut shells and nut shells) or of degraded and coalified plant matter (e.g. peat, lignite and all ranks of coal). Agricultural wastes are considered as very important feed-stocks in virtue of two facts: they are renewable sources and low cost materials.

Continuing our activities in this direction, we have derived a new low-cost activated carbon from bagasse and pericarp of rubber fruit (an agricultural waste material) by using chemical activation with zinc chloride ($ZnCl_2$). The aim of this work is to study the adsorption of cadmium and lead ions on activated carbons obtained in aqueous solution. The influence of experimental conditions and the adsorption isotherm will be investigated systematically. Experimental results will be analyzed to provide an understanding of the adsorption mechanism by using physical chemistry knowledge for help.

1.2 Preliminary knowledge and theoretical sections

1.2.1 Definition of activated carbon

Activated carbon mainly consists of elementary carbon in a graphite alike structure. It can be produced by heat treatment, or "activation", of raw materials such as wood, coal, peat and coconuts shell. During the activation process, the unique internal pore structure is created, and it is this pore structure which provides activated carbon its outstanding adsorptive properties.

Related to the type of application, three major product groups exist:

Granular Activated Carbon (GAC) - irregular shaped particles with sizes ranging from 0.2 to 5 mm. This type is used in both liquid and gas phase applications.

Powder Activated Carbon (PAC) - pulverized carbon with a size predominantly less than 0.18 mm (US Mesh 80). These are mainly used in liquid phase applications and for flue gas treatment.

Pelleted Activated Carbon - extruded and cylindrical shaped with diameters from 0.8 to 5 mm. These are mainly used for gas phase applications because of their low pressure drop, high mechanical strength and low dust content.

Utilities of activated carbon

Activated carbon, the common factor in hundreds of different applications just a grab from the numerous applications: decolourisation of sugar and sweeteners, drinking water treatment, gold recovery, production of pharmaceuticals and fine chemicals, catalytic processes, off gas treatment of waste incinerators, automotive vapour filters, colour/odour correction in wines and fruit juices, additive in liquorice, etc.

In its numerous applications, activated carbon represents a number of different functionalities:

Adsorption: the most well-known mechanism, through chemisorption or physical adsorption (Van der Waals forces).

Reduction: e.g. removal of chlorine from water is based on chemical reduction reactions.

Catalysis: activated carbon can catalyse a number of chemical conversions, or can be a carrier of catalytic agents (e.g. precious metals).

Carrier of biomass: supported material in biological filters.

Carrier of chemicals: e.g. slow release applications colourant, activated carbon's function in decolourizing.

1.2.2 The activation process of activated carbon

Activation refers to the development of the adsorption properties of carbon. Raw materials such as wood, nut shells, coconut shells and coal do have some adsorption capacity, but this is greatly enhanced by the activation process.

Chemical activation

One of the key steps in the production of activated carbons is chemical activation through the impregnation of the raw material with chemicals such as phosphoric acid, potassium hydroxide, or ZnCl_2 . These additives are known to enhance carbonization, resulting in improved development of the pore structure. Chemical activation is usually limited to woody precursors. Among the activating agents used for the production of activated carbon from carbonaceous material, ZnCl_2 has been proven to be one of the most effective impregnants. ZnCl_2 acts as a dehydrating agent, influencing the decomposition of carbonaceous material during the pyrolysis, thus restricting the formation of tar and increasing the carbon yield. The degradation of cellulose material and the aromatization of the carbon skeleton upon ZnCl_2 treatment result in the creation of the pore structure. These pores are the interstices left vacant upon the removal of ZnCl_2 from the carbon matrix by intensive washing. The studies have clearly demonstrated that the amount of ZnCl_2 used during chemical activation significantly impacts the structural characteristics of the carbons (Byrne and Marsh, 1995).

Physical activation

This method is the development of porosity by gasification with an oxidizing gas at 700-1100 °C. Commonly used gases are carbon dioxide (CO₂), steam and air. They can be used singly or in combination. Several types of oven can be used in the manufacture of activated carbon, i.e. rotary kilns, multiple heart furnaces and fluidized beds. The type of oven used determines the properties of the activated carbon produced (Derbyshire, et al, 1995).

1.2.3 Porosity: definitions

Based on the experience of adsorption chemistry, total porosity is classified into three groups. The origins and structure of porosities are elaborated upon below. IUPAC classifies porosities as follows:

- Micropores width less than 2 nm
- Mesopores width between 2 and 50 nm
- Macropores width greater than 50 nm

It has also been useful to classify micropores further into ultra- (<0.5 nm width) and super- (1.0-2.0 nm) micropores, these definitions being relevant when considering adsorption behavior. Micropores are considered as being about the size of adsorbate molecules and accommodate one, two or perhaps three molecules. Mesoporosity is wider than micropores. Macroporosity has little interest for the surface chemist. They are transport pores to the interior of particles and are considered as external surface. Some activated carbons contain all of these sizes of porosity associated with the botanical composition of the material. The pore size distribution is highly important for the practical

application; the best fit depends on the compounds of interest, the matrix (gas, liquid) and treatment conditions. The desired pore structure of an activated carbon product is attained by combining the right raw material and activation conditions (Byrne and Marsh, 1995).

1.2.4 Adsorption

The adsorption is a process where molecules from the gas phase or from solution bind in a condensed layer on a solid or liquid surface. The molecules that bind to the surface are called *the adsorbate* while the substance that holds the adsorbate is called *the adsorbent*. The process when the molecules bind is called *adsorption*. Removal of the molecules from the surface is called *desorption*. There are two different types of adsorption:

[1] **Chemisorption** (or chemical adsorption), where there is direct chemical bond between the adsorbate and the surface. This bond cannot be broken by only increased temperature. This behavior is usually irreversible process.

[2] **Physisorption** (or physical adsorption), where the adsorbates were held by physical (i.e., Van der Waals) forces. These forces can be eliminated (removal of molecules from surface of adsorbent) when increasing temperature. Therefore, physisorption can be called reversible process.

Chemisorption and physisorption are usually distinguishable from each other without any great difficulty. Table A summarizes the main criteria.

Table A Criteria for distinguishing between chemisorption and physisorption.
(Bond, 1987)

Criteria	Chemisorption	Physisorption
Enthalpy of adsorption or heat of adsorption (ΔH_{ads})	>40 kJ mol ⁻¹ , usually around 600-700 kJ mol ⁻¹	0-40 kJ mol ⁻¹
Activation energy, E_a	Usually small	Zero
Increasing temperature	Irreversible	Reversible

The adsorption characteristics in solution phase between the adsorbent and adsorbate were explained by **the adsorption isotherm models** in general. Several models can be used to describe adsorption data. The two most frequently used for dilute solutions are the Langmuir and Freundlich isotherms.

Langmuir isotherm.

In dilute solution Langmuir model assumes the surface to consist of adsorption sites, each having an area σ^0 , all adsorbed species interact only with a site and not with each other, and adsorption is thus limited to a monolayer (this behavior is similar to gas phase). In the case of adsorption from solution, however, it seems more possible to consider an alternative phrasing of the model. Adsorption is still limited to a monolayer, but this layer is now regarded as an ideal two-dimensional solution of equal-size solute and solvent molecules of area, σ^0 . Thus, absence of lateral interaction (Adamson and Gast, 1997).

The Langmuir adsorption isotherm is given by

$$Q = \frac{Q_m b C_e}{1 + b C_e} \quad (\text{nonlinear form}) \quad (1)$$

where Q represents the amount of solute adsorbed per unit weight of adsorbent; Q_m is the amount of solute adsorbed per unit weight of adsorbent required for monolayer coverage of the surface, also called the monolayer capacity; C_e is the concentration of adsorbate in solution at equilibrium conditions; and b is an equilibrium constant related to the heat of adsorption, ($b \propto e^{(\Delta H/RT)}$) (Adamson and Gast, 1997).

Equation (1) is usually linearized by inversion to obtain the following form

$$\frac{1}{Q} = \frac{1}{Q_m} + \frac{1}{b Q_m} \frac{1}{C_e} \quad (\text{linear form}) \quad (2)$$

Many researchers have usually used equation (2) to analyse batch equilibrium data by plotting $1/Q$ versus $1/C_e$, which yields a linear if data conform to the Langmuir isotherm.

Once b is considered, this parameter can be rewritten as

$$b = b' e^{(\Delta H_{\text{ads}}/RT)} \quad (3)$$

equation (3) is so called van't Hoff equation, where ΔH_{ads} is enthalpy or heat of adsorption, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature in Kelvin and b' is pre-exponential factor constant.

The heat of adsorption (ΔH_{ads}) can be determined from slope of the observed linearity from the plot of $\ln b$ (or \log) versus $1/T$ that leads to heat process involved in adsorption at monolayer coverage.

Freundlich isotherm.

The Freundlich equation is unlike the Langmuir one, does not become linear at low concentrations but remain convex to the concentration axis. Therefore, it is not shown a saturation or limiting value (not become plateau). There is no assurance that the derivation of the Freundlich equation is unique. However, if the data fit this model, it is only likely that the surface is heterogeneous (Adamson and Gast, 1997).

The Freundlich adsorption equation is perhaps the most widely used for the description of adsorption in aqueous systems. The Freundlich equation is of the form

$$Q = K_f \cdot C_e^n \quad (\text{nonlinear form}) \quad (4)$$

where Q and C_e have the same definitions as previously presented for the Langmuir isotherm. K_f is the so-called unit capacity factor that shows adsorption capacity and n (dimensionless) is the empirical parameter that represents the heterogeneity of the site energies and also is indicative of the intensity of adsorption.

The logarithm of equation (4) given below is usually used to fit data as

$$\log Q = \log K_F + n \log C_e \quad (\text{linear form}) \quad (5)$$

Heat (enthalpy) of adsorption consideration

If the isotherm of adsorption can be fitted with Langmuir model adequately, the heat of adsorption process at monolayer coverage can be investigated from equation (3).

There is another propose that is usually used to explain heat of adsorption. Isothermal data obtained at different temperatures are used to estimate the isosteric heat of the process. Consequently, enthalpy changes associated with adsorption processes can be estimated using the Clausius-Clapeyron equation. In this way, the isosteric heats of adsorption, ΔH_{ads} , for various loadings (or amounts adsorbed) are calculated from equation (6) by means of the isosteres corresponding to each amount adsorbed (Adamson and Gast, 1997).

$$\left(\frac{d \ln C_e}{dT} \right)_Q = \frac{\Delta H_{ads}}{RT^2} \quad (6)$$

or

$$\Delta H_{ads} = -R \left[\frac{d \ln C_e}{d(1/T)} \right]_Q \quad (7)$$

In equation (6) and (7), ΔH_{ads} is the isosteric heat of adsorption (kJ mol^{-1}), a measure of the enthalpy change involved in the transfer of solute from the reference state to the adsorbed state at a constant solid-phase concentration; C_e and Q are the equilibrium aqueous-phase and solid-phase concentrations, respectively; R is the universal gas constant ($8.314 \text{ J K}^{-1}\text{mol}^{-1}$), and T is the temperature in Kelvin.

Aqueous-phase solute concentrations (C_e) at different temperatures are calculated at constant solid-phase solute concentration (Q) using the calculated isotherm parameters. A linear regression of $\ln C_e$ as a function of $1/T$ yields a single value of ΔH_{ads} and its coefficient of determination at a given Q .

1.3 Review of Literatures

There have been many researches concern in the adsorption of metal ions on activated carbon surface. This interest is due to the importance of the following process: surface chemistry, water chemistry, analytical chemistry, chemical engineering and environmental studies. Many researchers have studied adsorption of metal ions on activated carbon such as:

Gomez-Serrano, et al. (1998) studied comparatively the adsorption of mercury, cadmium and lead from aqueous solutions on heat-treat and sulphurized activated carbons. The adsorption isotherms for the various metals were measured at 25°C (298 K), using adsorptive solutions at two pH values.

The adsorption was much higher for mercury than for cadmium and lead for all adsorbents. The adsorption of mercury greatly increased for the samples of sulphurized carbon (carbon which have sulfur functional groups on its surface) and also, though less, for the sample prepared in nitrogen gas which incorporated nitrogen functional groups to activated carbon surfaces. This behavior could be explained by chemical interaction of the adsorbate with surface groups of the adsorbents. For acid-base reactions the Pearson 's theory on hard-soft acid-base (HSAB) (Pearson, 1988) established that hard acids prefer to coordinate to hard base, and soft acid to soft base, this interaction of the adsorptive surface groups is likely favored for mercury as compared to cadmium and lead. This would be so assuming the presence in the adsorbents of surface groups which behaved as soft base. The decrease of pH in the adsorptive solution to pH 2.0 drastically reduced the adsorption of mercury. The effect of pH change on the adsorption of cadmium and lead occurred with less adsorbents than for mercury.

Biniak, et al. (1999) studied the adsorption properties of a modified activated carbon with various oxygen- and/or nitrogen-containing surface groups toward copper ions. Previously de-ashed and chemically modified commercial activated carbon D-43/1 (Carbo-Tech, Essen, Germany) was used. The chemical properties of the modified carbon surface were estimated by standard neutralization titration with HCl, NaOH, and NaOC_2H_5 . The adsorption of Cu^{2+} ions on three modified activated carbons from aqueous CuSO_4 solution of various pH was measured. The carbon samples with adsorbed Cu^{2+} ions were analyzed by

spectroscopic methods (X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy). In addition, an electrochemical measurement (cyclic voltammetry) was performed using powdered activated carbon electrodes. While the modification procedures employed alter the surface only slightly, they strongly influence the surface chemical structure. Basic groups were predominant in the heat-treated samples; acidic functional groups were predominant in the oxidized sample. Both the copper cation adsorption studies and the spectral and electrochemical measurements showed that adsorbed ions interact with the carbon surface in different ways. The number of adsorbed ions depended on the nature and quantity of surface acid-base functionalities and on the pH equilibrium in aqueous solution.

Namasivayam, et al., (1999) investigated adsorption of mercury (II) from aqueous solutions on coirpith carbon under the varying conditions of agitation time, metal ion concentration, adsorbent dose and pH. Adsorption equilibrium reached in 10, 25, 30 and 40 min for 10, 20, 30 and 40 mg L⁻¹ Hg²⁺ concentration. Adsorption followed both Langmuir and Freundlich isotherms. The adsorption capacity was 154 mg g⁻¹. The percent removal increased with the increase of pH from 2 to 5 and remained constant up to pH 11. Desorption studies were also performed with dilute hydrochloric acid and potassium iodide solutions. The maximum percent recovery of Hg²⁺ was 63 with 0.5 M HCl and 84.0 with 2.0% KI solution. Higher desorption of Hg (II) by I⁻ is due to the formation of relatively more stable iodide complexes of Hg²⁺ compared to the chloride complexes.

Kadirvelu, et al. (2000) studied the adsorption of three metal ions, Cu^{2+} , Ni^{2+} , and Pb^{2+} on activated carbon cloths (ACC). Two adsorbents, CS 1501 (with more than 96% of micropore volume) and RS 1301 (with 32% of mesopore volume), were studied. Batch experiments were carried out to assess kinetic and equilibrium parameters. They allowed kinetic data, transfer coefficients, and maximum adsorption capacities to be computed. These parameters showed the fast external film transfer of metal ions on fibers because of their low diameter (10 μm). Intraparticle diffusion coefficients are lower than those obtained with a granular activated carbon (GAC), but maximum adsorption capacities agree with literature values for GAC. They showed the dependency of adsorption on metal ion size and ACC porosity, the largest cation Pb^{2+} being more adsorbed by the mesoporous cloth. The pH effect was also studied, and pH adsorption edges were determined. They were short, only 2 pH units, and located below the precipitation edges. A decrease of equilibrium pH with an increase of metal ion concentration, coupled with a regeneration study of saturated ACC by HCl, led them to propose an adsorption mechanism by ion-exchange between metal cations and H^+ ions at the ACC surface. Carboxylic groups seem especially involved in this mechanism, and precipitation between metal ions could happen.

Jia, et al., (2000) introduced various types of oxygen functional groups onto the surface of coconut shell derived activated carbon by oxidation using nitric acid. Fourier-transform infrared spectroscopy (FT-IR), temperature programmed desorption (TPD) and selective neutralization were used to characterize the surface oxygen functional groups. The oxidized carbons were

also heat treated to provide a suite of carbons where the oxygen functional groups of various thermal stabilities were varied progressively. The adsorption of cadmium ions was enhanced dramatically by oxidation of the carbon. The ratio of released protons to adsorbed cadmium ions on oxidized carbon was approximately 2, indicating cations exchange was involved in the process of adsorption. Na^+ exchange studies with the oxidized carbon gave a similar ratio. After heat treatment of the oxidized carbons to remove oxygen functional groups, the ratio of H^+ released to Cd^{2+} adsorbed and the adsorption capacity decreased significantly. Both reversible and irreversible processes were involved in cadmium ion adsorption with reversible adsorption having higher enthalpy. The irreversible adsorption resulted from cation exchange with carboxylic acid groups, whereas the reversible adsorption probably involved physisorption of the partially hydrated cadmium ion.

El-Hendawy, et al., (2001) studied preparation and adsorption of some compounds on activated carbon obtained from corncobs. Dried, crushed, corncobs were carbonized at $500\text{ }^{\circ}\text{C}$ and steam activated (in one- or two-step schemes), or activated with H_3PO_4 . The products were characterized by N_2 adsorption at 77 K, using the BET and DR methods. Adsorption capacity was demonstrated by the iodine and phenol numbers, and the isotherms of methylene blue and Pb^{2+} ions, from aqueous solutions. A distribution of porosity in the carbons was estimated within the various ranges (ultra-, super-, meso- and macropores). Simple carbonization yields a poor adsorbing carbon; only its uptake for iodine was high and proposed to be due to an addition reaction on

residual unsaturation of the parent lignocellulosic structures. Enhanced porosity was best associated with chemical activation and/or steam pyrolysis at 700 °C. These activated carbons proved highly porous and rich in mesopores, and showed high adsorption capacity for methylene blue and Pb^{2+} ions. Phenol uptake was found to depend on surface chemical nature of the carbon rather than its porous properties. Corncobs were postulated to be feasible as feedstock to produce good adsorbing carbons.

Jia, et al., (2002) investigated effects of nitrogen surface functional groups to metal ions adsorption. A commercially available coconut-shell-derived active carbon was oxidized with nitric acid and both the original and oxidized active carbons were treated with ammonia at 1073 K to incorporate nitrogen functional groups into the carbon. An active carbon with very high nitrogen content (9.4 wt%) was also prepared from a nitrogen-rich precursor, polyacrylonitrile (PAN). These nitrogen-rich carbons had points of zero charge (pH_{pzc}) similar to H-type active carbons. X-ray absorption near-edge structure (XANES) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, and temperature-programmed desorption (TPD) were used to characterize the nitrogen functional groups in the carbons. The nitrogen functional groups present on the carbon surface were pyridinic, pyrrolic (or indolic), and pyridonic structures. The adsorption of transition metal cations Cd^{2+} , Ni^{2+} , and Cu^{2+} from aqueous solution on the suite of active carbons showed that adsorption was markedly higher for carbons with nitrogen functional groups present on the surface than for carbons with similar pH_{pzc} values. In contrast, the adsorption characteristics of Ca^{2+} from aqueous

solution were similar for all the carbons studied. Flow microcalorimetry (FMC) studies showed that the enthalpies of adsorption of $\text{Cd}^{2+}(\text{aq})$ on the active carbons with high nitrogen contents were much higher than for nitric acid oxidized carbons studied previously, which also had enhanced adsorption characteristics for metal ion species. The enthalpies of adsorption of Cu^{2+} were similar to those obtained for Cd^{2+} for specific active carbons. The nitrogen functional groups in the carbons act as surface coordination sites for the adsorption of transition metal ions from aqueous solution. The adsorption characteristics of these carbons were compared with those of oxidized carbons.

Dastgheib, et al., (2002) modeled adsorption isotherms for activated carbon made from pecan shells. The experiment has been performed at 25 °C and an approximate pH of 3 for a number of metal ion solutes. It was found that the Sips and Freundlich equations were satisfactory for explaining the experimental data. The correlation of metal ion adsorption with the solute parameters of metal ion electronegativity and first stability constant of the metal hydroxide was investigated. In the case of most of the metal ions studied, higher electronegativities and stability constants corresponded to the higher adsorption levels of metal ions onto the activated carbon. A correlation was developed to predict the constants of the Freundlich equation from the selected parameters of the metal ions, and thus could predict the adsorption isotherms at constant pH. The developed correlation gave results with acceptable deviations from experimental data. A procedure was proposed for obtaining similar correlations for different conditions (temperature, pH, carbon type and dosage). The ratio of

equivalent metal ions adsorbed to protons released was calculated for the studied metal ions over a range of concentrations. In most cases, particularly at low concentrations, this ratio was close to one, confirming that ion exchange of one proton with one equivalent metal ion was the dominant reaction mechanism.

Sirichote, et al., (2002) studied the adsorptions of iron (III) from aqueous solution at room temperature on activated carbons obtaining from bagasse, pericarp of rubber fruit and coconut shell. The activated carbons were prepared by carbonization of these raw materials and followed by activation with $ZnCl_2$. The adsorption behavior of iron (III) on these activated carbons could be interpreted by Langmuir adsorption isotherm as monolayer coverage. The maximum amounts of iron (III) adsorbed per gram of these activated carbons were 0.66 mmol/g, 0.41 mmol/g and 0.18 mmol/g, respectively. Study of the temperature dependence on these adsorptions has revealed them to be exothermic processes with the heats of adsorption of about -8.9 kJ/mol, -9.7 kJ/mol and -5.7 kJ/mol for bagasse, pericarp of rubber fruit and coconut shell, respectively.

Strelko, et al., (2002) oxidized a commercial activated carbon Chemviron F 400 by using nitric acid in order to introduce a variety of acidic surface functional groups. Both unoxidized and oxidized carbon samples were characterized using nitrogen porosimetry (nitrogen adsorption isotherm), elemental analysis, pH titration, Boehm's titration, and electrophoretic mobility measurements. Results showed that oxidation treatment reduced surface area and pore volume. However, the carbon surface acquired an acidic character with carboxylic groups

being the dominant surface functional groups. The modified sample displayed cation-exchange properties over a wide range of pH values and exhibits poly-functional nature. Both carbon samples were challenged for the removal of transition metals such as copper (II), nickel (II), cobalt (II), zinc (II), and manganese (II). The affinity series $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ has been found to coincide with the general stability sequence of metal complexes (the Irving–Williams series). The higher preference displayed by carbons toward copper (II) is a consequence of the fact that copper (II) often forms distorted and more stable octahedral complexes.

Chen, et al., (2003) reported improvement of copper ion adsorption from aqueous solutions. In this study, citric acid was used to modify a commercially available activated carbon. The carbon was modified with 1.0 M citric acid, followed by an optional step of reaction with 1.0 M sodium hydroxide. It was found that the surface modification reduced the specific surface area by 34% and point of zero charge (pH_{pzc}) of the carbon by 0.5 units. Equilibrium results showed that citric acid modification increased the adsorption capacity to 14.92 mg Cu/g, which was 140% higher than the unmodified carbon. The initial solution with higher pH resulted in higher copper adsorption. The chemical surface modification adversely affected the copper adsorption rate. Adsorption kinetic mechanisms were investigated with an intraparticle diffusion model. It was found that the modification did not change both external diffusion and intraparticle diffusion.

Savova, et al., (2003) studied on the adsorption of manganese ions from aqueous solution on carbon obtained from a mixture of biomass products (apricot stones). They indicated the importance of acidic surface oxides for manganese ion adsorption that was predominantly site specific. The results showed that oxygen remaining from the raw material participates in the formation of surface oxides and indicated the possibility of controlling the content of acidic surface sites of the carbon surface by appropriate selection of the precursor composition and surface properties modification. The surface functionalities of oxidized carbon from a mixture of biomass products resembled the behavior of an ion-exchange resin. Oxidized carbon obtained from a 50:50 mixture of tar from steam pyrolysis of apricot stones and furfural contained a balance of surface area and high surface concentration of functional groups was favorable for adsorption of positively charged manganese ions.

1.4 Objectives

- 1.4.1 To produce activated carbons from bagasse and pericarp of rubber fruit (an agricultural waste material) by using chemical activation with zinc chloride (ZnCl_2).
- 1.4.2 To characterize some physical (especially porous texture) and chemical properties of the obtained activated carbons.
- 1.4.3 To study the adsorption properties of cadmium, Cd^{2+} and lead, Pb^{2+} ions on the obtained activated carbons by controlling conditions.
- 1.4.4 To elucidate adsorption mechanism of above metal ions on the activated carbons by incorporating 1.4.2 and 1.4.3 for help.