STUDIES OF COPPER-IMPREGNATED ACTIVATED CARBON FOR CYANIDE REMOVAL

by

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LIST OF ABBREVIATION

AC	Activated Carbon
ACKK	Activated Carbon Kekwa K
ACKP	Activated Carbon Kekwa P
ACVA	Activated Carbon Versatec A
ACVC	Activated Carbon Versatec C
ACVH	Activated Carbon Versatec H
ASTM	American Standard Test Method
atm	Atmosphere
BET	Surface Area Analysis (Breneure Emelt Teller)
C	Carbon
Cu	Copper
CN	Cyanide
CIAC	Copper-Impregnated Activated Carbon
EDX	Energy Disperse X-Ray
FT-ir	Fourier Transform Infrared Spectrophotometer
GAC	Granular Activated Carbon
MSC	Molecular-Sieve Carbon
PAC	Powder Activated Carbon

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STUDIES OF COPPER-IMPREGNATED ACTIVATED CARBON FOR CYANIDE REMOVAL

Abstract

In the present work, two types of locally manufactured granular activated carbon from Kekwa Industry (KI66G and P1814G) and Versatec Industry carbon (A, C and H) were used to study their cyanide adsorption capacity. Batch experimental work carried out shows that cyanide can be removed using copper impregnated activated carbon. For Versatec carbon (ACVC), with carbon dosage of 15 g/L, the highest cyanide adsorption efficiencies of 97 % and 98.4 % are achieved from $Cu(I)Cl_2$ and $Cu(II)SO_4$ impregnated carbon respectively at similar CN:Cu molar ratio of 1.25 : 1.95. About 38.14 mg CN/g C is removed in just 3 hours at pH 6 for $Cu(II)SO_4$ impregnated carbon. Cyanide concentration at equilibrium reaching to 31.54 mg CN/g C for both the Cu(I) and Cu(II) impregnated carbon. The effect and performance of impregnated copper chloride on carbon was found to be broadly similar to carbon impregnated with copper sulphate. The smaller particle size Kekwa carbon type P (ACKP) with copper impregnated from $Cu(II)SO_4$ exhibits a higher percentage of CN removal of about 96.58 % in 100 ppm CN, in just 120 minutes at pH 8, resulting in CN removal of about 30.48 mg CN / g C. The CN:Cu molar ratio is about 1.50:1.95. In 50 ppm of CN concentration, CN removal efficiency is about 94.97 and 95.67% in just 120 minutes at pH 6 with $Cu(I)Cl_2$ and $Cu(II)SO_4$ impregnated carbon respectively. In 100 ppm CN, the best achievable cyanide removed for both the virgin carbons are at a lower percentage in the range of 21.0% to 22.16 % for ACKP and ACVC respectively in 120 minutes. In the column studies, ACVC shows a higher performance of CN removal which is about 94.93% in just 15 minutes at pH 6 with carbon dosage of 15 g/L, 1.67%

Cu (from $CuSO_4$) in 100 ppm CN solution as compared to ACKP of about 91.8 % CN removed. SEM/EDX analysis evidently showed the presence of copper on the impregnated activated carbon. Infrared examinations shows that the adsorption of cyanide has occurred and that the copper species exists in the form of $Cu(CN)_3^{2-}$ complex on the carbon. BET surface area analysis for ACVC gave the highest measured value of 982.16 m^2/g which evidently shows the highest percentage of copper adsorbed (74.4%) on carbon, enhances and optimizes the existing properties of the carbon giving a greater cyanide removal efficiency of 98.4%.

KAJIAN TERHADAP KARBON TERAKTIF TERJERAP-ISI KUPRUM BAGI PENYINGKIRAN SIANIDA

Abstrak

Dalam kajian ini, dua jenis karbon teraktif tempatan jenis granul yang dihasilkan oleh Kekwa Industri (KI66G and P1814G) dan Versatec Industri (A, C dan H) telah digunakan untuk mengkaji keupayaan penjerapan sianida. Ujian kelompok menunjukkan sianida boleh disingkirkan menggunakan karbon teraktif terjerap isi kuprum. Bagi karbon Versatec (ACVC), dengan dos karbon sebanyak 15 g/L, kecekapan penjerapan sianida yang tertinggi adalah pada 97% dan 98.4% bagi karbon terjerap isi $Cu(I)Cl_2$ dan $Cu(II)SO_4$ masing-masing pada nisbah molar CN:Cu yang sama iaitu 1.25 : 1.95. Sebanyak 38.14 mg CN/g C telah disingkirkan dalam masa 3 jam pada pH 6 bagi karbon terjerap isi $Cu(II)SO_4$. Kepekatan sianida pada keseimbangan adalah sebanyak 31.54 mg CN/g C terjerap bagi kedua-dua jerap isi Cu(I) dan Cu(II). Keberkesanan dan prestasi karbon teraktif terjerap isi kuprum klorida adalah hampir sama dengan karbon terjerap isi kuprum sulfat. Karbon Kekwa jenis P (ACKP), bersaiz partikel lebih kecil dengan terjerap isi $Cu(II)SO_4$ mempamerkan peratus penyingkiran sianida yang lebih tinggi sebanyak 96.58% dalam 100 ppm CN dalam masa 120 minit pada pH 8, memberikan penyingkiran sebanyak 30.48 mg CN / g C. Nisbah kemolaran CN:Cu adalah 1.50:1.95. Dalam 50 ppm CN, peratus penyingkiran adalah sebanyak 94.97 dan 95.67% dalam masa 120 minit pada pH 6 dengan karbon terjerap isi $CuCl_2$ dan $CuSO_4$ masing-masing. Dalam 100 ppm CN, penyingkiran sianida yang paling baik bagi kedua-dua jenis karbon tanpa jerap isi (virgin carbon) pula adalah dalam julat yang agak rendah iaitu dari 21.0% kepada 22.16% bagi ACKP dan ACVC masing-masing dalam masa 120 minit. Dalam kajian kolum, ACVC menunjukkan prestasi penyingkiran CN yang lebih tinggi iaitu sebanyak 94.93% dalam masa 15 minit pada pH 6 dengan dos karbon sebanyak 15 g/L, 1.67% (Cu terjerapisi dari $CuSO_4$) dalam 100 ppm CN berbanding dengan ACKP iaitu sebanyak 91.8% CN telah disingkirkan. Analisis SEM/EDX membuktikan kehadiran kuprum pada karbon teraktif terjerapisi kuprum. Pemeriksaan infra-merah menunjukkan berlakunya penjerapan CN ke atas karbon dan spesi kuprum wujud sebagai kompleks $Cu(CN)_3^{2-}$ pada karbon. Analisis luas permukaan BET bagi ACVC memberikan nilai luas permukaan karbon yang tertinggi iaitu sebanyak 982.18 m^2/g, dengan peratus penjerapan kuprum tertinggi (74.4%) pada karbon menambahkan dan mengoptimumkan sifat sedia ada karbon memberikan keupayaan penyingkiran CN yang lebih baik sebanyak 98.4%.

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CHAPTER 1
INTRODUCTION

1.1 Research Background

Waste water discharged by industrial activities is often contaminated by a variety of toxic or otherwise harmful substances which have negative effects on the water environment. For example, of metal finishing industry and electroplating units is one of the major sources of heavy metals such as (Zn, Cu, Cr, Pb etc.) and cyanide pollutants which contribute greatly to the pollution load of the receiving water bodies and therefore increase the environmental risk (Monser and Adhoum, 2002).

Cyanide present in effluent water of several industries. Cyanidation has dominated the gold mining industry. In view of the toxicity of cyanide, and the fact that cyanide is fatal in small dosages, authorities have been forced to tighten up plant discharge regulations. It is therefore vital to recover as much cyanide as possible, not only to meet standard requirements, but to strive towards obtaining lower levels of free cyanide (CN^-) in tailing and plant effluent. (Monser and Adhoum, 2002).

The solubility of gold in cyanide solution was recognized as early as 1783 by Scheel (Sweeden) and was studied in the 1840s and 1850s by Elkington and Bagration (Russia), Elsner (German) and Faraday (England). Elkington also had a patent for the use of potassium cyanide solutions for electroplating of gold and silver.

Cyanide is a singly-charged anion containing unimolar amounts of carbon and nitrogen atoms triply-bounded together. It is a strong ligand, capable of complexing at low concentrations with virtually any heavy metal. Because the health and survival of plants and animals are dependent on the transport of these heavy metals through their tissues, cyanide is very toxic.

Several systems have been adopted for the reduction of cyanide in mill discharges. There are SO_2 assisted oxidation, natural degradation, acidification-volatilization-reneutralization, oxidation and biological treatment. However, in the first three processes, cyanide reduction does not appear to meet the strict regulatory requirements, and as for the fourth process, it is limited to certain climate conditions. The next best process used, is the oxidation with hydrogen peroxide where the cyanide concentration is reduced to low enough levels, but this process requires an expensive reagent which cannot be reused. (Williams and Petersen, 1996).

Adams, (1994) used activated carbon for the removal of free cyanide from solution, but observed that copper-impregnated carbon yielded far better cyanide removal. However, Adams, (1994), did not test other metal impregnated carbons or different metal loadings on the carbon. The use of a metal impregnated carbon system would therefore be more effective in reducing cyanide concentrations in solution.

Due to the problem mentioned above, the study on using activated carbon in the removal of free cyanide is being done in our laboratory. The adsorption onto activated carbon has found increasing application in the treatment of wastewater, as well as for the recovery of metals from cyanide leached pulps. Activated carbon has a great potential for cyanide waste treatment both in gold extraction plants and effluent from metal finishing plants and hence, it forms a subject studied in the present work.

Characterization of activated carbon shows that surface area has an effect although the reactivity of the surface as a result of oxygenated functional groups, e.g. carboxylate and phenolate is thought to be significant in the sorption of metal cations. Pore size distribution has been used to describe the internal structures and adsorption capacities of activated carbons. (Davies et al, 1999). The highly active surface properties of the activated carbon are attributed to the chemical functional groups and the internal surface areas, which typically range from 500 to 3000 m^2/g. (Tansel and Nagarajan, 2002).

(Adams, 1994) studied the effect of copper in the adsorption of cyanide onto activated carbon. It was found that the removal capacity was highly improved by the presence of copper (Monser and Adhoum, 2002). It is the aim of this research to investigate the use of impregnated activated carbon for the removal of cyanide for dilute solutions. Furthermore, specific attention will be paid to factors influencing the performance of the impregnated carbon system, so as to optimize the system in terms of cyanide removal.

1.2 Significant of Research

From the research done, the author would expect the investigation to give further knowledge and understanding of how activated carbon contribute to the waste water treatment, according to their good characteristic of large surface area and hard-dense that can be regenerated and reuse. It is hope that design will be able to achieve the objectives in order to minimize the heavy metal concentration in the industrial waste disposal and to achieve optimum adsorption of activated carbon. This research program is an environmental friendly project. It emphasizes on the importance of conversation of environmental surroundings. Thought this, it is hopeful that both research and industry will reap mutual benefits.

1.3 Research Objective

- To study the characteristic of a locally manufactured granular activated carbon from Kekwa Industry and Versatec Industry for cyanide removal.
- To develop a process of copper-impregnation on the local activated carbon for cyanide removal.
- To study the cyanide adsorption capacity of the copper-impregnated activated carbon.
- To study the parameters affecting the adsorption capacity of the copper-impregnated activated carbon (CIAC) such as pH, CN : Cu molar ratio, Cu : C ratio, and varying the concentration of cyanide, weight and type of carbons, the carbon particle size, copper salts and percentage of copper impregnated onto the AC (activated carbon).

1.4 Scope of Research

This project was done in different set of experiment parameter by using copper impregnated activated carbon to study the factors affecting the adsorption of cyanide such as pH, weight and type of carbon, particle size of carbon, the molar ratio of cyanide to copper and also copper to carbon ratio in 50, 100 and 200 ppm of cyanide solution. This ratio is important to exhibit the ability of cyanide adsorption within the appropriate ratio to design a simple operation and to provide a cost effective solution. In addition, activated carbon is known to have large surface area and hard dense characteristic that can be regenerated and reuse the carbon. Cyanide also can be recovered by using the cyanide distillation apparatus.

In this research, two different sources of copper were used for impregnation on AC i.e. copper (I) chloride and copper (II) sulphate. The impregnation was done in the three percentage of copper impregnated (0.5, 1.0 and 1.67%). Batch CN adsorption test were done at different set of parameters as discussed in the research objective above. The tests were carried out to investigate the CN removal efficiency and the adsorption capacity of CN on the CIAC.

CHAPTER 2
THEORY AND REVIEW

2.1 Adsorption Theory, Concepts, and Models

Adsorption phenomena are operative in most natural physical, biological, and chemical systems, and adsorption operations employing solid such as activated carbon and synthetic resins are used widely in industrial applications and for purification of waters and wastewaters (Walter and Weber, 1985).

The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that face is the adsorbate. Adsorption is thus different than absorption, a process in which material transferred from one phase to another interpenetrates the second phase to form a “solution”. The term sorption is a general expression encompassing both processes.

A quantitative equilibrium distribution between phase concentrations is defined for each combination of a specific adsorbate, adsorbent, and set of system conditions. The character of the distribution, which markedly affects the feasibility of adsorption as a separation process for a particular application, is influenced by a variety of factors relating to the properties of the adsorbate, the adsorbent and the system in which adsorption occurs (Walter and Weber, 1985).

Factors determining the characteristics of phase partition equilibria and the rates at which these equilibria are attained in various types of adsorption operations are rooted in process concepts underlying the adsorption of substances at surfaces and interfaces, and illustrate how these concepts relate to the design and operation of adsorption systems.

Although adsorption operations are utilized in the separation of substances from a variety of gases and liquids at a variety of interfaces and surfaces, adsorption from liquids at solid surfaces is not only the most common category of these but also the one which involves the most comprehensive range of factor.

2.2 Adsorption Principles

2.2.1 Surface Interactions

Adsorption at a surface or interface is largely the result of binding forces between the individual atoms, ions, or molecules of an adsorbate and the surface, all of these forces having their origin in electromagnetic interactions (Weber, 1972; Weber and Vliet, 1980). Four principal types of adsorption – exchange, physical, chemical, and specific – may be distinguished. Exchange adsorption, or ion exchange, involves electrostatic attachment of ionic species to sites of opposite charge at the surface of an adsorbent, with subsequent displacement of these species by other ionic adsorbates of greater electrostatic affinity. Physical adsorption results from the action of van der Waals forces, which are comprised of both London dispersion forces and classical electrostatic forces. Chemical adsorption involves a reaction between an adsorbate and an adsorbent resulting in a change in the chemical form of the adsorbate. The resulting chemisorptive bond is usually stronger than that derived from the physical van der Waals forces. Attachment of adsorbates molecules at functional groups on adsorbent surfaces can also results from specific interactions which do not result in adsorbate transformation. (Walter and Weber, 1985).

These interactions designated “specific adsorption”, exhibit a range of binding energies ranging from values commonly associated with physical adsorption to the higher energies involved in chemisorption. The net dispersion, electrostatic, chemisorptive, and functional-group interactions broadly define the affinity of an adsorbent for a specific adsorbate.

The extent of adsorption also relates to certain properties of the adsorbate relative to the solution phase, notably those of surface tension and solubility (Weber, 1972). For example, many organic compounds can effectively lower the surface tension of water and the energy balance of aqueous system of such compounds of favors their partitioning to solid-water and gas-water interfaces. The extent of adsorption is greatly influenced by the solvophobicity or lyophobocity of a compound, that is, its “dislike” for, or insolubility in the solvent phase. The greater its solvophobocity with respect to a given solvent, the greater is the tendency of an adsorbate to be adsorbed from that solvent at interfaces with other phases. Bonding between substances and the solvent in which it is dissolved must be broken before adsorption from the solvent can occur. The greater the solubility of the compound, the stronger the bond, and the smaller the extent of adsorption (Weber jr ; 1985).

Adsorption from solution onto a solid thus can occur as a result of one or both of two characteristic properties for a given solvent-adsorbate-adsorbate system. The primary driving force may relate to the solvophobic or lyophobic character of the adsorbate or to a particular affinity of the adsorbate for the surface of the adsorbent. A number of parameters specific to a given system will therefore affect adsorption. These have been discussed in detail by Mattson and Mark (1971), Weber (1972), and Van Vliet and Weber (1980), and will be only briefly summarized here. For the adsorbate they include concentration, molecular weight, molecular size, molecular structure, molecular polarity, steric form or configuration, and the nature of background or competitive adsorbates. For the adsorbents the most important determinants of equilibrium capacity and rate of approach to this capacity include surface area, the physicochemical nature of the surface, the availability of that surface to adsorbate molecules or ions, and the physical size and form of the adsorbent particles. System parameters such as temperature and pH can also markedly influenced adsorption to the extent that they effect changes in any one or more of the aforementioned parameters (Weber, jr; 1985).

2.3 Adsorbate-Solvent Properties

An inverse relationship between extent of adsorption of a substance from a solvent and its solubility in that solvent can be generally anticipated. For example, the water solubility of organic compounds within a particular chemical class decreases with increasing molecular size or weight because the compounds becomes more hydrocarbon like as the number of carbon atoms becomes greater. Thus adsorption from aqueous solution increases as a homologous series is ascended, largely because the expulsion of increasingly large hydrophobic molecules from water permits an increasing number of water-water bonds to reform (Walter and Weber, 1985).

Molecular size can also affect adsorption rates if this are controlled by intraparticle diffusive mass transport within porous adsorbents, which generally is more rapid the smaller the molecule. It must be emphasized that rate dependence on molecular size can be generalized only within a particular chemical class or homologous series. Large molecules of one chemical class may adsorb more rapidly than smaller ones of another if higher energies of driving forces for adsorption are involved.

Many organic compounds may exist as ionic species. Fatty acids, phenols, amines, and the variety of pesticides are a few materials which ionize in water under appropriate conditions pH. Frequently certain physical and chemical properties of compounds change upon ionization, and this can affect adsorbability. Most observations for amphoteric substances point to the generalization that as long as the adsorbing compounds are structurally simple and electrostatic or exchange reactions is not significant; adsorption from polar solutes such as water is greater for neutral species than for the corresponding ionic forms. The effects of ionization decrease as compounds become more complex.

A polar solute will be strongly adsorbed from a nonpolar solvent by a polar adsorbent, and at the opposite end of the spectrum, will prefer a polar solvent to a nonpolar adsorbent. Polarity of organic compound is a function of charge separation within the molecule. Almost any asymmetric compound will be more or less polar, but several types of functional groups tend to produce fairly high polarities in compounds. Example of these is hydroxyl, carboxyl, nitro, nitrile, carbonyl, sulfonate, and amine. Thus ethanol, C_2H_5OH, is polar, being incrementally negative at the hydroxyl group and correspondingly positive at the ethyl group. Salvation by water, for example, involves formation of a hydrogen bond between the positive hydrogen atoms of water and a negative group on a solute, along with some bonding in the reverse direction to the water oxygen. Water solubility is thus expected to increase with increasing polarity, and it follows that adsorption from aqueous solution generally decreases as polarity increases.

Adsorption reactions are normally exothermic, with changes in enthalpy of the order of those for condensation or crystallization reactions. The equilibrium extent or capacity of adsorption in a given system is thus generally found to increase with decreasing temperature. Conversely, because adsorption kinetics is generally controlled by diffusive mass transfer, rates of approach to equilibrium normally increase with increasing temperature (Walter and Weber, 1985).

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2.4 System Properties

Because hydrogen and hydroxide ions often interact with adsorbents commonly used in aqueous phase applications, the adsorption of other ions may thus be influenced by solution pH. Further to the extent to which adsorption differs between the conjugate forms of acidic or basic compounds; pH affects adsorption in that it governs degree of protolysis or “ionization” of such compounds. As noted earlier, neutral species (e.g., acetic acid and phenol molecules) tend to adsorb more strongly from the aqueous phase than do their corresponding ionic forms (e.g., acetate and phenolate ions).

The components of a mixture of adsorbates may mutually enhance adsorption, act relatively independently, or interfere with one another. Mutual reduction of both adsorption capacities and adsorption rates can be expected if the affinities of the adsorbates do not differ by orders of magnitude and if there are no specific interactions among them which enhance adsorption; this because the adsorption of more than one substance generally reduces the number of surface sites available to each. For diffusion controlled rates of adsorption by porous adsorbents, very slowly diffusing species in mixed adsorbate systems can depress rates of uptake of those which diffuse more rapidly. The reasons for such effects become more evident in an ensuing discussion of adsorption kinetics (Walter and Weber, 1985).

2.5 Adsorbent Properties

Adsorption is a surface phenomenon and practical commercial adsorbents are therefore characterized by large surface areas, the majority of which is comprised of internal surfaces bounding the extensive pores and capillaries of highly porous solids. Activated carbon is one of the most widely used porous adsorbents because of its capability for efficiently adsorbing a broad range of different types of adsorbates. While activated carbon's wide-spectrum adsorption capability is unmatched by any other material, certain synthetic adsorbents may offer distinct advantages in specifically defined cases. Notable examples are the analytical use of synthetic polymeric adsorbents for recovery of organics from water for identification and quantification purposes, the use of synthetic carbonaceous adsorbents derived from polymers for removal of specific organic substances (i.e., low molecular weight volatile halogenated hydrocarbons) from waters containing natural background organics, and the use of polymeric adsorbents for adsorbate recovery in high-concentration industrial process and waste treatment applications.

The performance characteristics of adsorbents relate in large measure to their intraparticle properties. Surface area and the distribution of area with respect to pore size generally are primary determinants of adsorption capacity. The nature of the intraparticle surface are markedly affects the types of adsorption interactions that will be operative for an adsorbent, and is a major distinguishing factor between activated carbons and synthetic adsorbents. Those properties which are important for adsorption have been discussed and summarized by Weber and Van Vliet (1980, 1981) for a variety of commercial adsorbents; highlights are presented below. The generic term “activated carbon” encompasses a broad range of amorphous carbon-based materials having high degrees of porosity and extensive surface areas. The large surface areas are associated with near-molecular size pores and capillaries formed with in the carbon granules by selective burning and oxidation of raw material during activation. Commercial carbons typically have total surface areas in the range from 450 to 1500 m^2/g as measured by the nitrogen adsorption method. However the actual surface area available for adsorption is dependent on the specific nature of the adsorbate, and can be considerably less than the total. The pore volumes of commercial carbons range from 0.5 to 1.5 cc/g. it is however, only that fraction of the pore volume contained in pores larger than about 10 Å which determines the effective capacity of carbons for liquid phase applications. The effective capacity thus depends on the distribution of area or volume with pore size, and the distribution of molecular sizes to be adsorbed

The surface chemistry of activated carbon is important in determining its activity or capacity for adsorption of a specific organic substance. The chemical properties of the surface depend on the raw material used, the type of activation process, and the conditions of essentially two different types. The bulk of the surface is comprised of basal plane areas. These are largely uniform nonpolar surface which support solvophobic and physical adsorptions. A much smaller but very important part of the total surface area is comprised of the heterogeneous edges of carbon planes to which carbon-oxygen functional groups formed by oxidation in the manufacturing process are attached. These groups enable activated carbon to undergo halogenation, hydrogenation, and oxidation, and to function as a specific adsorbent and catalyst in a variety of different reactions. They provide for a range of electrostatic, hydrogen bonding, functional group, and chemisorption adsorbent-adsorbate interaction which generally exceed physical or solvophobic interactions in tenacity and greatly extend the spectrum and degree of adsorbability of adsorbate on activated carbon. A particular benefit afforded by such interactions in enhanced adsorption performance at very low adsorbate concentrations in the solution phase, a significant factor in such application as potable water treatment where part-per-billion levels of organics are deemed undesirable.

Although it does not directly affect adsorption capacity, hardness, or durability, of individual adsorbent particles is an important property to be considered, at least for granular activated carbon (GAC) applications. This property largely determines the losses which will occur on each adsorption-regeneration cycle as a result of attrition during handling and burn-off during reactivation. Petroleum, lignite and bituminous coal-based carbons are typically used in GAC systems, while softer wood and peat-based materials find more use as powdered activated carbons (PACs). (Walter and Weber, 1985)

Synthetic adsorbents of various polymer matrix, pore structure and functional group characteristics are commercially available in the forms of beads or granules. The matrices commonly comprise insoluble three-dimensional hydrocarbon polymer networks of either aromatic nature, e.g., condensed phenol-formaldehyde or styrene divinyl benzene-or aliphatic nature, e.g., polymerized acrylic acid or methyl acrylic acid (Paleos, 1969; Snoeyink et al., 1974; Abrams, 1975). Pore size distributions can be controlled during manufacture by varying the amount of extender used in the polymerization reaction; this governs the degree of matrix crosslinking and ultimate porous structure. The macroporous and macroreticular synthetic adsorbents thus form contain no ion exchange functional groups and are designated polymeric adsorbents. Ion exchange properties can be imparted to the adsorbents by incorporation of appropriate functional groups in the polymer matrices. Such macroporous ion exchange resins have been reported to have some potential for organics removal in municipal water and waste water treatment, (Rebhun and Kaufman, 1967; Anderson and Maier, 1979; Snoeyink et al., 1974; Giddey et al., 1975; Anderson and Maier, 1979; Boening et al., 1980) colour removal in texile operations, (Kennedy et al., 1673; Snyder and Alspaugh, 1974; Hodges and Alspaugh, 1975) Kraft paper industry waste decolorization (Sanks, 1973) and for protecting ion exchange demineralizer resins from organic fouling (Abrams, 1969; Oehme and Martinola, 1973).

Carbonaceous adsorbents are a recent addition to the inventory of synthetic adsorbents. These materials are manufactured by partial pyrolysis of appropriate beaded polymer matrices, yielding black spherical particles of chemical composition intermediate between those of activated carbon and polymeric adsorbents (Rohm and Haas Co., 1977). (Walter and Weber, 1985).

2.6 Activated Carbons

Activated carbon is a microporous carbonaceous material which is produced from various raw-materials, such as peat, wood, lignite, anthracite, fruit pits or shells. The raw materials are converted into activated carbon using steam (temperature above 900 C) or acid (temperature above 450 C). The activation process creates pores in the carbon, whose surface area may exceed 1500 m^2/g. It is by far the most important adsorptive media due to its wide range of pore sizes.

Activated carbons are produce with a wide range of properties and physical forms, which leads to their use in numerous applications. For example, their high internal surface area and pore volume are pertinent to their being employed as adsorbents, catalysts, or catalyst supports in gas and liquid phase processes for purification and chemical recovery (Derbyshire et al., 1978).

Activated carbons are commonly fabricated in the form of fine powders and larger sized granules, pellets, or extrudates. However, activated carbons can also be produce as fibres, mesocarbon microbeads, foams and aerogels, and in the form of flexible or rigid solids. The form, as well as other properties, helps to determine the suitability for a specific application. Rates of adsorption or reaction can be orders of magnitude higher for activated carbons with narrow dimensions (e.g., powders and fibers with diameters in the range 10 to 50 µm) than for granular carbons (0.5 to 4.0 mm): in the former case, most of the adsorptive surface is readily accessible, and there is much less dependence on intragranular diffusion (Figure 2.1) (Radovic, 1985).

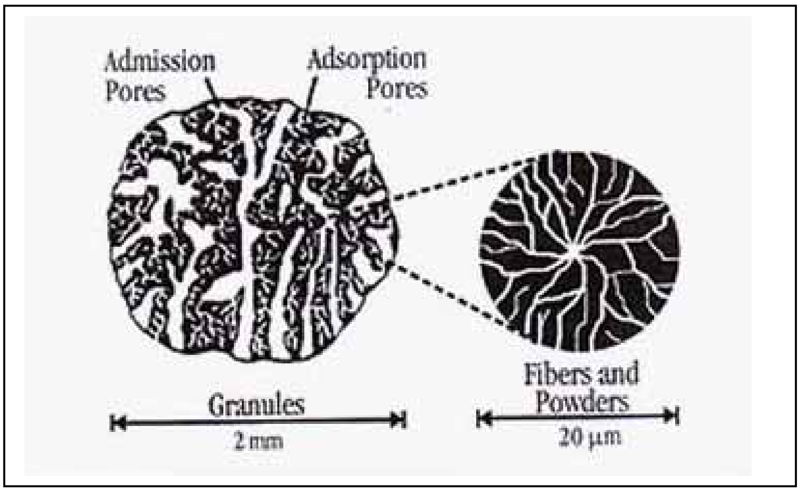

Figure 2.1: Schematics showing internal structure of AC forms.

The adsorption affinity of the internal surface (V/d Waals adhesion forces) together with the pore size distribution (cohesion forces), constitute an activated carbon's purification capability. Physical adsorption forces are not always sufficient to adsorb a component, and in these circumstances, the internal surface may be used as a carrier for an active component, or chemical compound.

2.6.1 Formation and Manufacture of Activated Carbon

The modern manufacturing process basically involves the following steps: raw material preparation, low-temperature carbonization, and activation. The conditions are carefully controlled to achieve the desired pore structure and mechanical strength. The raw materials for activated carbon are carbonaceous matters such as wood, peat, coals, petroleum coke, bones, coconut shell, and fruit nuts. Anthracite and bituminous coals have been the major sources. Starting with the initial pores present in the raw material, more pores, with desired size distributions, are created by the so-called activation process. Two standard activation methods are used: gas and chemical. After initial treatment and pelletizing, gas activation first involves carbonization at 400-500 ºC to eliminate the bulk of the volatile matter, and then partial gasification at 800-1000 ºC to develop the porosity and surface area. A mild oxidizing gas such as CO_2 and steam, or flue gas, is used in the gasification step because the intrinsic surface reaction rate is much slower than the pore diffusion rate, thereby ensuring the uniform development of pores throughout the pellet. The activation process is usually performed in fixed beds, but in recent years fluidized beds have also been used. The activated carbon created by the activation process is used primarily for gas and vapour adsorption processes. The other activation process that is also used commercially depends on the action of inorganic additives to degrade and dehydrate the cellulosic materials and, simultaneously, to prevent shrinkage during carbonization. This is called chemical activation, usually used for lignin-based precursors such as sawdust. No pre-carbonization step is required. Lignin, usually the raw material that is blended with activators such as phosphoric acid, zinc chloride, potassium sulphide, or potassium thiocyanate, is carbonized at temperatures between 500 to 900 ºC. The remaining chemicals are removed from the carbon by acid or water wash. The product, usually in powder form, is used for aqueous or gas phase purposes. The inorganic material contained in activated carbon is measured as ash content, generally in the range between 2 and 10%. Beside granulated activated carbon (GAC), powdered activated carbon (PAC) is also used commercially (for example, for dioxin removal from incinerators by injection of PAC (Yang et al., 2001).

Although the process for manufacturing activated carbon has been largely empirical, a considerable understanding of the fundamental processes is now available. During carbonization of the precursor raw material, condensation of polynuclear aromatic compounds and breakage of side-chain groups occur, resulting in a carbon residue. In the meantime, cross-linking reactions occur that inhibit the development of a pre-graphite structure. Hence activated carbon is referred to as non-graphitizing, as opposed to graphitizing. The graphitizing type applies to pitches derived from petroleum, coal tar, and aromatic hydrocarbons, which form an intermediate liquid crystal phase called mesophase. Carbonization alone is not adequate to develop large porosity, hence activation by gasification is needed. The resulting activated carbon can be described by various models. The most representative model is a twisted network of defective hexagonal carbon layer planes, cross-linked by aliphatic bridging groups. The layer planes consist of single layers or layers of two, three or four with variable interlayer spacing s that typically range from 0.34 to 0.8 nm. The size of the layer planes varies but is typically about 5 nm wide. Simple functional group (e.g., C–OH, C=O), as well as heteroatoms (mainly oxygen and hydrogen) , are incorporated in the network (Yang et al., 2001).

2.6.2 Pore Structure and Standard Tests for Activated Carbon

Activated carbon are characterized by a large surface area between 300 ~ 4000 m^2/g, as measured by the BET method, and are the largest among all sorbents. Commercial grades of activated carbon are designated for either gas phase or liquid phase, depending on its application. A majority of the pore volume is from pores or near or larger than 30 Å in diameter for liquid-phase carbons, whereas the pores of gas-phase carbons is due to the large size of many dissolved adsorbates and the slower diffusion in liquid than in gas for molecules of the same size.

A polymodal pore-size distribution is generally found in activated carbon. The pore structure may be pictured as having many small pores branching off from larger ones, which are open through the entire particle. The larger pores are called feeder or transport pores; the smaller ones, which may be dead-end, are called adsorption pores. The cumulative pore-volume distribution of the fine pores for a typical gas-phase activated carbon is shown, along with four other sorbents, in Figure 2.2. The larger pores are mostly submicrometer in size, and their total volume amounts to a fraction of that found in the fine pores. The micropore structures of activated carbons can be determined by a variety of adsorption methods (Yang et al., 2001).

Testing of activated carbons involves measurements of bulk density, absolute density (or helium density), particle density, particle size distribution, pressure drop across packed beds, and mechanical strength. Standardized ASTM tests are available for these measurements. Details of these tests are available from ASTM. The mechanical strength is defined by the abrasion number, which is a measure of the change of the mean particle size, expressed as a percentage, of a sample after 3 min of vigorous agitation with smooth steel balls. In addition, numerous adsorption tests are used for the characterization of the adsorbents properties of commercial carbons. The effectiveness of activated carbon is usually specified by the amount of a certain test chemical it can adsorb under standardized conditions. For gas-phase applications, CCl_4 is commonly used, whereas for aqueous-phase or liquid-phase applications, iodine and molasses are used (Yang et al., 2001).

2.7 Influence of the adsorbate type

The type of adsorbent can influence the equilibrium adsorption capacity in two ways:

1. The total pore volume of the adsorbent.

   Adsorption occurs by condensation of the adsorbate in the adsorbents pores. A larger total pore volume will therefore result in a higher maximum amount of adsorbate being adsorbed. This maximum adsorption capacity, however, can only be obtained if the gas/air flow is totally saturated with the adsorbate.

2. The pore size distribution of the adsorbent.

   According to IUPAC:

   - Micropores : below 1 nm radius
   - Mesopores : 1-25 nm radius
   - Macropores : radius > 25 nm

The actual adsorption occurs almost only in the micropores. The macropores will determine the accessibility of the adsorbent, while the mesopores influence the transport of the adsorbate from the gas phase to the micropores. An adsorbent with a high activation degree, and therefore a high total pore volume, will possess a high maximum adsorption capacity.

At low adsorbate concentrations adsorption occurs almost only I the smallest micropores, possessing the highest adsorption energy. The higher the activation degree of adsorbent, the larger the average pore diameter and the lower the content of very small micropores. This means that the adsorbent with the highest activation degree will possess the lowest equilibrium adsorption capacity at low adsorbate concentrations. This concentration influence on the equilibrium adsorption capacity implies that carbons with a high activation degree are less suitable for air purification purpose. This effect will be enhanced by adsorbent density. This applies particularly in the air purification field, where the adsorbent is used on a volume basis, the volume adsorption capacity (grams adsorbed per 100 ml activated carbon) instead of the weight adsorption capacity is the relevant parameter.

2.8 General Adsorption Properties

The unique surface property of activated carbon, in contrast to the other major sorbents, is that its surface is nonpolar or only slightly polar as a result of the surface oxide groups and inorganic impurities. This unique property gives activated carbon the following advantages:

1. It is the only commercial sorbent used to perform separation and purification processes without requiring prior stringent moisture removal, such as is needed in air purification. For the same reason, it is also widely used as a sorbent for processes treating aqueous solutions.
2. Because of it’s large, accessible internal surface (and large pore volume, shown in figure 2.2), it adsorbs more nonpolar and weakly polar organic

molecules than other sorbents do. For example, the amount of methane adsorbed by activated carbon at 1 atmosphere (atm) and room temperature is approximately twice that adsorbed by an equal weight of molecular sieve 5A (Figure 2.3).

3. The heat of adsorption, or bond strength, is generally lower on activated carbon than on other sorbents. This is because only non-specific; van der Waals forces are available as the main forces for adsorption. Consequently, stripping of the adsorbed molecules is relatively easier and results in relatively lower energy requirements for regeneration of the sorbent (Yang et al., 2001).

2.9 Surface Chemistry and Its effects on Adsorption

Activated carbon can be represented by a model of a twisted network of defective hexagonal carbon layer planes (typically 5 nm wide), which are cross-linked by aliphatic bridging groups. Heteroatoms are incorporated into the network and are also bound to the periphery of the planes. The heteroatoms bound to the surfaces assume the character of the functional groups typically found in aromatic compounds, and react in similar ways with many reagents. These surface groups play a key role in the surface chemistry of activated carbon. They are particularly important for adsorption in aqueous solutions and the catalytic properties of carbon.

The surface groups shown in Figure 2.4 are acidic groups. Concentration of these groups can be created or increased by oxidation with oxygen at elevated temperatures (or by aging at mile temperatures) or with liquid oxidants,