CHAPTER 2
THEORY AND LITERATURE REVIEWS

2.1 Activated carbon

Activated carbon, a microcrystalline, nongraphitic form of carbon, is processed in such a way that internal surface area and porosity are developed, and hence, exhibiting a large capacity for adsorbing chemicals from gases or liquids. Activated carbons are characterized by a large specific surface area of 300-2,500 $m^2 g^{-1}$, and large distribution of pore sizes. It has a very complex structure, with pore sizes ranging from micropores (<20 Å diameter pore) to macropores (>200 Å diameter pore), and has a variety of functional surface groups as shown in Table 2.1 and Figure 2.1 (Ismadji et al., 2005). Activated carbon is distinguished from elemental carbon by the removal of all non-carbon impurities and the oxidation of the carbon surface (Mattson and Mark, 1971).

Activated carbon consists of 3 types, such as powder, granular, and fibrous according to its size and shape, and each type has its specific applications. The activated carbon surface is non-polar which results in an affinity for non-polar adsorbents such as organics. Adsorption is a surface phenomenon in which an adsorbate is held onto the surface of the activated carbon by Van der Waal's forces and saturation is represented by an equilibrium point. These forces are physical in nature, which means that the process is reversible (using heat, pressure, etc.) Activated carbon is also capable of chemisorptions, whereby a chemical reaction occurs at the carbon interface changes the state of the adsorbate.

2.2 Raw materials for the production of activated carbon

Activated carbons are produced from a wide variety of carbonaceous materials, including wood and agriculture by-products and any other inexpensive materials with high carbon content (Vernersson et al., 2002). The properties of manufactured activated carbon depend on the type and properties of the raw material used. Raw materials for activated carbon are chosen depending on their purity, price, potential extent of activation, and stability of supply. The most frequently used precursors are hard coal, brown coal, wood, coconut shells and some polymers. Some agricultural by-products such as fruit stones and various nut shells can be used as raw material. They are well suited for activated carbon manufacture due to their pyrolytic

transformation into porous coke which produces an economically justifiable yield. Suitable adsorbent properties (adsorption capacity, hardness, and granularity) require the use of mechanically stable cokes with a small fraction of macropores (Heschel and Klose, 1995). Some examples of source materials that have been reported for the production of activated carbon are tabulated as shown in Table 2.2.

Inexpensive materials with high carbon and low inorganic (i.e. low ash) contents are preferred as a raw material for the production of activated carbon. High density of the precursor and sufficient volatile content are of considerable importance. Evolution of volatiles during pyrolysis results in a porous character, while high density contributes to enhanced structural strength of the carbon, essential to withstand excessive particle crumble during use. Conventional raw materials in order of their importance as activated carbon production capacity, characteristics and market are: wood, coal, lignite, coconut shell, peat and others. A comparison of the properties of activated carbon derived from the various types of raw material is given in Table 2.3.

2.3 Production of activated carbon

Activated carbon can be produced by activating the carbonized materials under different conditions that the activating agents, e.g. steam, carbon dioxide, nitrogen gas, etc., react with the carbon. Figure 2.2 shows a flow diagram for activated carbon production. There are basically two methods for preparing activated carbons: physical and chemical activations.

2.3.1 Physical activation

Physical activation is usually carried out in two steps: carbonization and activation.

2.3.1.1 Carbonization

Carbonization of the raw material is basically a heat treatment of raw materials in an inert atmosphere at a temperature below 700 °C. During carbonization most of the non carbon elements, hydrogen and oxygen are firstly removed in gaseous by pyrolytic decomposition of the staring material, and the freed atoms of elementary carbon are grouped into organized crystallographic formations known as elementary graphitic crystallites. The mutual arrangement of the crystallites is irregular, so that free interstices remain between them and apparently as the result of deposition and decomposition of tarry substances.

2.3.1.2 Activation

The activation is carried out to enlarge the diameter of the pores which are created during the carbonization process, thus resulting in the formation of a well-developed and readily accessible pore structure with very large internal surface area. Activation in the presence of steam, carbon dioxide, and/or air is often conducted at temperatures between 800 and 1000 °C. Several types of oven can be used in the manufacture of activated carbon such as rotary kiln, fluidized bed and furnaces. The porous structure is created due to the elimination of volatile matter during the carbonization step and the carbon on the char is removed by reaction with steam or CO_2 during the activation step (Hayashi et al., 2002).

2.3.2 Chemical activation

In chemical activation, the raw material is impregnated with an activation reagent and heated in an inert atmosphere. The carbonization step and the activation step proceed simultaneously. By dehydration and oxidation reactions of the chemicals, the pores are developed. Chemical activation is usually carried out at temperature ranging from 400-600°C. These temperatures are lower than those needed for activation with gaseous agents (physical activation). Zinc chloride and phosphoric acid are often used as activation reagents (Toles et al., 1996). Recently, alkali hydroxide compounds such as potassium hydroxide and sodium hydroxide have been used in order to prepare activated carbons with high specific surface area (Lillo-Ródenas et al., 2001). During chemical activation the chemistry of pyrolysis is changed and a different macromolecular system is established with enhanced porosity. The activation agent also changes the chemical nature of cellulose substrate by dehydration, which decomposes the organic substances by the action of heat and prevents the tar formation. Upon carbonization, the formation of tar is restricted with the formation of solid carbon, and this prevents somewhat the contraction of the particle. After carbonization, most of the chemical is still in the particle, and the intense washing produces the porosity.

The physical and chemical activation technologies are currently being used to treat a variety of materials to activated carbon. There are certain factors that may limit the applicability and effectiveness on activated carbon as summarized in Table 2.4. Some examples of source materials that have been reported for the production of activated carbon are provided in Table 2.5. When compared the two modes of activation, chemical activation involves carbonizing the parent material after

impregnation with common chemicals that act as dehydrating agents such as sodium chloride, zinc chloride and some acid such as phosphoric acid. This process normally takes place at a temperature lower than that used in the physical activation process. Literature demonstrates that zinc chloride activation provided the highest level of iodine number. However, phosphoric acid activation yielded the highest surface area. On the contrary, physical activation takes place at a much longer activation time than required in the chemical activation process. Therefore, there is always a high energy cost regarding the use of physical activation.

2.4 Activated carbon from eucalyptus

Eucalyptus by-products have lately been employed for the production of activated carbon. Table 2.6 illustrates the condition of activated carbon derived from eucalyptus trees which shows that the properties of activated carbon from eucalyptus are generally satisfactory, e.g. the surface area of greater than 1,000 m^2g^{-1}. The high iodine number indicated that the resulting activated carbon was constituted of a large number of micropore. On the other hand, methylene blue number was quite low which demonstrated a low level of mesopore. When compared with activated carbon derived from other raw materials (as summarized in Table 2.5), eucalyptus was always found to give a higher level of micropore. In addition, the yield of carbon from eucalyptus was generally quite high when compared with other raw materials. It should be noted that, in all cases, the physical activation was chosen for the production of activated carbon from eucalyptus.

2.5 Phosphoric acid activation

Phosphoric acid has been mostly used for the activation of lignocellulosic materials, which have not been carbonized previously. When compared to zinc chloride, phosphoric acid is more environmentally preferable as phosphate is much less toxic than zinc chloride. Moreover, the carbons obtained using zinc chloride cannot be used in pharmaceutical and food industries as it may contaminate the product (Srinivasakannan and Bakar 2004). Martin-Gullon, et al. (2004) reported that the phosphoric acid carbons could be obtained at low temperatures (450–600°C) and the resulting product presented a wide opened micropore structure with an important contribution of mesopores. The ratio of impregnation of phosphoric acid, or the weight ratio of phosphoric acid to precursor, appeared to be significant in controlling

the properties of the carbon and this ratio was often found to be in the range of 1 to4 (Derbyshire et al., 1995). Phosphoric acid activation has been applied on a wide variety of cellulosic precursors such as cotton stalk (Girgis and Ishak, 1999), sugar cane bagasse (Castro et al.,2000), grain sorghum (Diao et al., 2002), peanut hull (Girgis et al., 2002), and *Arundo donax* cane (Vernersson et al., 2002). Summary of the previous works on the production of activated carbon with phosphoric acid activation was given in Table 2.7.

2.6 Adsorption theory

Rigorous theory on adsorption can be found in sorption and biosorption (Volesky, 2003). A repeat of fundamental adsorption theory is not an intention of this work, however, some significant adsorption backgrounds are given below to facilitate the understanding of the subsequent work in this report.

2.6.1 Mechanism of adsorption onto the porous adsorbent

For the adsorption of a solute onto the porous surface of an adsorbent, there are essentially four stages in the adsorption process, as shown in Figure 2.3 and briefly described below:

(1) Transport of molecules from the bulk of solution to the exterior surface of the adsorbent;

(2) Movement of molecules across the interface and adsorption onto external surface sites;

(3) Migration of molecules with in the pores of the adsorbent, and

(4) Interaction of molecules with the available sites on the interior surfaces, bounding the pore and capillary spaces of the adsorbent.

2.6.2 Type of adsorption

The process of adsorption occurs in both steady-state and unsteady-state conditions. The primary force driving the interaction between the adsorbate and the adsorbent is the electrostatic attraction and repulsion between molecules of the adsorbate and the adsorbent. These driving forces can be either physical or chemical. Table 2.8 illustrates some differences between physical and chemical adsorptions.

2.6.2.1 Physical adsorption

Physical adsorption is a result of intermolecular forces that interact between the adsorbate and the adsorbent. These physical electrostatic forces include

the Van der Waals force, consisting of weak attraction and repulsion through dipole-dipole interactions and dispersing interactions, and hydrogen bonding. Dipole-dipole interactions are the result of polar compounds orienting themselves so that their charges result in a lower combined free energy. Dispersing interactions are the result of attractive forces between electrons and nuclei of molecular systems. Hydrogen bonding is a special case of dipole-dipole interaction in which the hydrogen atom in molecule has a partial positive charge, attracting another atom or molecule with a partial negative charge. Physical adsorption is a readily reversible reaction and includes both mono- and multilayer coverage. Because physical adsorption does not involve the sharing of electrons, it generally has low adsorption energy, and is not site specific.

2.6.2.2 Chemical adsorption

Chemical adsorption, like physical adsorption, is also based upon electrostatic forces but it is often stronger (approaching the adsorption energies of chemical bonds). The transfer of electrons and the formation of chemical bonds between the adsorbate and the adsorbent produce chemical adsorption. It may be an irreversible reaction with high adsorption energies. Chemical adsorption involves mono layer coverage, and is a site specific reaction, occurring at specific functional group locations. Functional groups are distinctive arrangements of atoms in organic compounds that give compound its specific chemical and physical properties.

2.6.3 Adsorption equation

Adsorption isotherm is the relationship between adsorption capacity and concentration of the remaining adsorbate at constant temperature. Generally, adsorption isotherms can be mathematically presented in several forms, but the two most commonly employed isotherms are Langmuir and Freundlich equations.

2.6.3.1 Langmuir equation

The Langmuir isotherm is based on the assumption that the sorbent has limited sorption sites, therefore q_{eq} cannot increase continually with increasing C_{eq}. The relationship of this model is as follows:

$$q_{eq} = \frac{q_m b C_{eq}}{1 + b C_{eq}} \tag{2.1}$$

where q_{eq} is equilibrium amount (mmol/g) of adsorbed per unit mass of adsorbent at relative pressure P/Po; q_m represents the total number of surface sites per mass of sorbent; and b is the Langmuir constant or capacity factor (Langmuir, 1918).

The assumptions for Langmuir isotherms are: (i) there is only a monolayer of adsorbate on the adsorbent surface; (ii) adsorption is localized on adsorbate-adsorbate interaction; (iii) adsorbent surface is uniform with the same affinity for all binding sites; and (iv) the sorption reaction can be represented as a coordination reaction with 1:1 stoichiometry. The Langmuir equation is used for homogeneous surfaces. The Langmuir isotherm has a capacity term (q_m) in its definition, and once the concentration of adsorbed species reaches this capacity term, no further adsorption takes place (Langmuir, 1918).

2.6.3.2 Freundlich equation

Freundlich isotherm is the mathematical model used to describe the adsorption process. The Freundlich equation is an empirical equation based on the assumption that the sorption occurs in multiple sites of the adsorbent. The relationship of this model is as follows (Freundlich, 1906):

$$C_s = K_F \cdot C_w^{1/n} \tag{2.2}$$

where K_F is the Freundlich constant or capacity factor (e.g., $(mol\,kg^{-1})\,(mol\,L^{-1})^{-n}$); and n is the Freundlich exponent.

The Freundlich equation is based on the following assumptions: (i) there are many layers (multilayer) of adsorbate on the adsorbent surface; and (ii) adsorbent surfaces are heterogeneous surface (Freundlich, 1906). If this isotherm does not match the experimental data, the assumption behind Freundlich isotherm might not hold true. Nevertheless, there is no total capacity term in the Freundlish isotherm equation, so there is no upper limit on adsorption. This condition is less likely to be true for any specific case, and hence, Freundlich isotherm is often used for a specific range of concentration of adsorbate, which is most of the time at the low concentration range.

2.7 Adsorption of heavy metals

Activated carbon could be applied to the removal of heavy metals. Heavy metals or metallic compounds are used during the manufacturing of variety of products. The industries discussed include coating, smelting and refining of metals, paint, ink and associated products, iron and steel manufacturing, photographic industry, leather tanning and finishing, wood preserving and battery manufacturing.

Waste streams from each of these industries have their own unique characteristics. However, they also contain a number of common metals, such as aluminium, arsenic, cadmium, chromium, copper, lead, nickel, silver and zinc. Factors capable of influencing this removal of heavy metals are described below.

2.7.1 pH

pH may influence the removal of heavy metals by changing the number of positive charged protons in the heavy metal solution. This can then compete with the metal for the active sites on the surface of adsorbent. Other major effect that pH could exert on the system is the solubility of heavy metals which generally depends significantly on the pH level. Normally, pH of wastewater was vary value depend on type of wastewater such as battery manufacturing is acidic pH. Overall, the optimal pH for the adsorption system strongly depends on the heavy metal and adsorbent surface chemistries. The optimum pH for the maximum uptake for each adsorption system must be experimentally determined. Literature on the effects of pH was given in Table 2.9 whereas the brief description on the effect of pH are given below:

- At a lower pH range (< 3) the surface of activated carbon takes up the H^+ ions from the solution and hence, increasing the acidity of the sorbent surface.

- At moderate pH values (3-6), linked H^+ is released from the active sites and adsorbed amount of metal ions is generally found to increase.

- The increasing pH (>6), the percentage adsorption decreases substantially, due to the possession of active sites on activated carbon with hydroxyl groups, and therefore the surface becomes fully deprotonated and negatively charged.

2.7.2 Adsorption kinetics

Table 2.10 summarizes literature reviews on the kinetic models of various adsorption systems. Most kinetics experiments demonstrated that the first order kinetic model could be employed satisfactorily in describing the adsorption at high initial concentration, whilst the second order was suited for the case with low initial concentration. It is interesting to note that the rate constants for both first and second order kinetics became higher with initial concentration and temperature of metal solution.

2.7.3 Adsorption isotherm

The distribution of metal ions between the liquid and the solid phases can be described by several mathematical model equations such as the standard Langmuir and Freundlich isotherm models as described earlier. Literature reviews on the adsorption isotherm (Table 2.11) revealed that heavy metal adsorption on activated carbon could generally be fitted to Langmuir isotherm. This suggests that the uptake of heavy metals takes place as a monolayer adsorption.

2.8 Adsorption in column experiment

The adsorption process continues, however, till equilibrium between the solute concentration in solution, and the solute adsorbed per unit weight of the adsorbent is reached. This equilibrium established is static in nature, as it does not change further with time. In dynamic column adsorption, solution continuously enters and leaves the column, so that the complete equilibrium is never established at any stage between the solute in solution and the amount adsorbed. Equilibrium has to be continuously established, as each time, it meets the fresh concentrations, and hence, equilibrium in column mode is termed as dynamic equilibrium. Additional information on the efficiency of the treated adsorbent in the column mode has been gathered in order to ascertain the practical applicability of the adsorbent for real industrial wastewaters. A fixed-bed column adsorption system is one of the most well-known application processes. The advantages of this method are continuous flow operation, virtually unlimited scaled-up, and no need for solid/liquid separation. It is also possible to carry out in situ generation and washing (Volesky, 2003). The fixed bed column operation allows more efficient utilization of the sorptive capacity than the batch process. Examples of fixed-bed applications are carbon adsorption column for treatment of phenolic wastes (Gupta et al., 2000), removal nickel by waste of tea factory (Malkoc and Nuhoglu, 2006), immobilized activated sludge in packed bed system for adsorption of phenol (Aksu and GÖnen, 2004), etc. The shape of the breakthrough curve and the time for the breakthrough appearance are the predominant factors for determining the operation and the dynamic response of the sorption column. The general position of the breakthrough curve along the volume/time axis depends on the capacity of the column with respect to bed height, the feed concentration and flow rate (Kumar and Bandyopadhyay, 2006).

2.8.1 Data analysis

The quantities of metal to be removed from solution in a fixed-bed was expressed in terms of C/C_0 where C and C_0 are effluent and influent concentrations. These were a function of time or volume of the effluent for a given bed height, giving a breakthrough curve as the final effluent concentration reached that of influence (Guibal et al., 1995). The maximum column capacity, q_{total} (mmol), for a given feed concentration and flow rate is equal to the area under the plot of the adsorbed Cu(II) and Pb(II) concentration C_{ad} ($C_{ad} = C_0 - C$) (mmol L^{-1}) versus time (min) and is calculated from Eq. (2.3):

$$q_{tatal} = \frac{QA}{1000} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} C_{ad} dt \qquad (2.3)$$

where t_{total} is the total flow time (min); Q is volumetric flow rate (ml min^{-1}) and A the area under the breakthrough curve.

The bed capacity (q_{column}), the weight of Cu(II) and Pb(II) adsorbed per unit dry weight of adsorbent (mmol $^{g-1}$) in the column, is calculated from:

$$q_{column} = \frac{q_{total}}{X} \qquad (2.4)$$

where X is the total dry weight of activated carbon in column (g).

The total amount of Cu(II) and Pb(II) entering the column (m_{total}) is calculated from Eq. (2.5)

$$m_{total} = \frac{C_0 Q t_{total}}{1000} \qquad (2.5)$$

The total removal percentage of Cu(II) and Pb(II) is the ratio of the maximum capacity of the column (q_{total}) to the total amount of Cu(II) and Pb(II) entering the column (m_{total}).

$$\text{Total removal}(\%) = \left(\frac{q_{total}}{m_{total}} \right) \times 100 \qquad (2.6)$$

2.9 Desorption study

For an effective recovery process, adsorbed metal ions should be easily desorbed under suitable conditions. Commonly used organic solvents such as benzene or chlorine containing solvents have not been recommended because they are carcinogenic which might adversely affect health and environmental states. In addition, to increase the efficiency of the removal of metals from the surface of these

porous substances, it is often that considerable volumes of solvents are used in the extraction process. This therefore leads to other environmental problems. Different processes have been proposed for the desorption of heavy metal molecules from the loaded activated carbon. Examples of the most related research are given below.

Kazi et al., 2001:

The objective of this work was to extract and oxidize Cr-Cu-As out of sludges composed of chromium as CrO_3, 47%; copper as CuO, 18%; arsenic as As_2O_5, 37%. The sludges were generated from wood preservative process and must be purified before disposed of as waste. Extraction and oxidation included three steps;

1. Extracted chromium and arsenic by NaOCl (5.25%)

    temp. 70-100°C

    time 0.25-3 h

    reagent-sludge ratio(R:S) 25-250

2. Extracted copper by H_3PO_4 (2.5%)

    reagent-sludge ratio(R:S) 25-250

    H_3PO_4 conc. 0-5%

3. Oxidation of leachate by NaOCl (5.25%), 100°C, 1h for conversion Cr^{3+} to Cr^{6+}

    leachate-reagent ratio(L:R) 2-20

Conclusion

Optimum conditions for removal of 90%Cr, 80%As and 97%Cu were:

1. 100°C, 2 h, R:S = 100

2. R:S = 100, H_3PO_4 conc. 2.5%

3. L:R = 12

This work did not intend to separate and recover each of the metal from the mixture of the metals and therefore did not report any success in the recovery for each metal.

Kakitani et al., 2006:

This work seemed to be the extension of the previous work mentioned above as it focused on the extraction of Cr-Cu-As from contaminated wood (chromium as

CrO_3, 45-51%; copper as CuO, 17-21%; arsenic as As_2O_5, 30-38%). A two steps extraction by solvents was employed with different conditions as follows;

1. 1st Oxalic acid (1N, 75°C, 1h) for extraction chromium and arsenic,

    2nd Sulfuric acid (1N, 75°C, 1-3h) for extraction copper and remaining arsenic

2. 1st Oxalic acid (1N, 75°C, 1h) for extraction chromium and arsenic,

    2nd Phosphoric acid (1N, 75°C, 1-3h) for extraction copper and remaining arsenic,

3. 1st Citric acid (1N, 75°C, 1h) for extraction copper and arsenic,

    2nd Sulfuric acid (1N, 75°C, 1-3h) for extraction chromium and remaining arsenic,

4. 1st Citric acid (1N, 75°C, 1h) for extraction copper and arsenic,

    2nd Phosphoric acid (1N, 75°C, 1-3h) for extraction chromium and remaining arsenic,

5. 1st Citric acid (1N, 75°C, 1h) for extraction copper and arsenic,

    2nd H_2O_2/NaOH (3%/1%, 75°C, 1-3h) for extraction chromium and remaining arsenic,

6. 1st Oxalic acid (1N, 75°C, 1h) for extraction chromium and arsenic,

    2nd Ammonia water(10%, 75°C, 1-3h) for extraction copper and remaining arsenic,

7. 1st Citric acid (1N, 75°C, 1h) for extraction chromium and arsenic,

    2nd Sodium-oxalate solution (pH 11.2 and 3.2, 75°C, 1-3h) for extraction copper and remaining arsenic,

Conclusion

% removal of heavy metals from each method could be summarized as shown below:

1. 100% As, 91.6% Cu, 88.0% Cr
2. 98.0% As, 74.9% Cu, 77.1% Cr
3. 100% As, 87.7% Cu, 90.0% Cr
4. 100% As, 99.1% Cu, 95.7% Cr
5. 97.3% As, 85.7% Cu, 95.6% Cr
6. 100% As, 74.4% Cu, 93.3% Cr
7. 100% As, 61.4% Cu, 81.2% Cr

With regard to those two literatures mentioned above, researchers did not concentrate on the recovery a single of each metal. They concentrated only on the

separation of heavy metals from the waste wood in order to prevent the diffusion of toxins into the atmosphere (as in the case of incineration) or into the soil and groundwater (as in the case of landfill).

Park et al., 2006:

This work focused on the leaching of Cu-Ni-Co from artificial matte composing of 24.95%Cu, 35.05%Ni, 4.05%Co, 11.45%Fe, and 24.5%S. Matte was mixture of molten metallic sulfides and produced from Pacific Ocean nodules. The leaching process employed $FeCl_3$ and HCl as leaching reagents where the extraction was done at 300 rpm of shaking rate. Ranges of concentration and temperature examined in this work were:

$FeCl_3$ conc. 0.5- 2.0 M

HCl conc. 0.1- 0.5 M

temp. 30-90 °C

Conclusion

1. The extraction of all metals increased with an increase in $FeCl_3$ conc. where 0.1 M $FeCl_3$ was sufficient for extraction.

2. The extraction of all metals increased with an increase in temperature.

3. Optimum conditions for removal of 99.5% Cu, 93.2% Ni, 85.2% Co were 1.5M $FeCl_3$, 0.3 M HCl, 90°C and 7 h

Researchers did not concentrate on the recovery a single metal species. Ferric chloride solutions could rapidly leach metals from sulfide minerals, but this process was unselective. Fe in the resulting solution could therefore be rejected as precipitate. Other metals in the resulting solution must then be separated by ion exchange resin or chemical precipitation if the recovery of the metals is of concern.

The choice of choosing desorption methods mainly depends on the interaction between the adsorbate and adsorbent. From the literature reviews on the recovery of heavy metals, citric, sulfuric and phosphoric acids were found to be able to extract some of the metals such as copper. Research could be directed towards the determination of suitable extracting conditions which could selectively extract metal species from the mixtures. The regenerated metal from the spent activated carbon can be used as raw material for other process where feasible. Note that, at presently, about 30% of the total Cu is produced from low-grade ores using copper selective oxide

based reagents by the hydrometallurgical solvent extraction process (Cox, 2004). Therefore, the regeneration of Cu from the waste mixture could substitute this requirement and provides viable alternation for Thai industry.

Table 2.1 Porous structure of activated carbon

	Macropores	Mesopores	Micropores
Diameter pores	more than 20 nm	20-200 nm	less than 20 nm
Specific surface area	less than 0.5 m^2 g^{-1}	20-100 m^2 g^{-1}	300-2,500 m^2 g^{-1}
Volumes of pores	0.2-0.8 cm^3 g^{-1}	0.1 -0.5 cm^3 g^{-1}	0.2-0.6 cm^3 g^{-1}
Transportation	-	-	adsorption proceeds using the mechanism of volume filling

Table 2.2 Source materials for activated carbon

Raw material	References
Almond shells	Ferro-García et al., 1988
Arundo donax cane	Vernersson et al., 2002
Bagasse, and coconut shell	Sirichote et al., 2002
Bituminous coal	Linares-Solano et al., 2002
Coal	Paajanen et al., 1997
Coconut shells	Paajanen et al., 1997
Coffee bean husks	Baquero et al., 2003
Coirpith	Kadirvelu and Namasivayam, 2003
Corncob	Bosinco et al., 1996;
Hazelnut shell	Cimino et al., 2000
Kraft lignin	Montané et al., 2005
Olive stones	Ferro-García et al., 1988
Palm shells	Guo et al., 2005
Peach pulp	Arslanoğlu et al., 2005
Peach stones	Ferro-García et al., 1988
Peat	Paajanen et al., 1997
Pecan shell	Bansode et al., 2003
Pericarp of rubber fruit	Sirichote et al., 2002
Rice Hulls	Teker and Imamoğlu, 1999
Solid wastes	Nakagawa et al., 2004
White oak	Jagtoyen and Derbyshire, 1998
Yellow poplar	Jagtoyen and Derbyshire, 1998

Table 2.3 Characteristics of various conventional raw materials used for making activated carbon (Streat et al., 1995)

Raw material	Carbon (%)	Volatile (%)	Density (g cm^{-3})	Ash (%)	Texture of activated carbon
Softwood	40–45	55–60	0.4–0.5	0.3–1.1	Soft, large pore volume
Hardwood	40–42	55–60	0.55–0.8	0.3–1.2	Soft, large pore volume
Lignin	35–40	58–60	0.3–0.4	–	Soft, large pore volume
Nut shells	40–45	55–60	1.40	–	Hard, large micropore volume
Lignite	55–70	25–40	1.0–1.35	5–6	Hard, small pore volume
Soft coal	65–80	25–30	1.25–1.50	2.12	Medium hard, medium pore volume
Petroleum	70–85	15–20	1.35	0.5–0.7	Medium hard, medium pore volume
Semi hard	70–75	1–15	1.45	5–15	Hard, large pore volume
Hard coal	85–95	5–10	1.5–2.0	2-15	Hard, large pore volume

Table 2.4 Advantages and disadvantages of physical and chemical activations

	Chemical activation	Physical activation
Advantages	- performed in one stage process (Redriguez-Reinoso, 1997) - lower temperatures of activation (Redriguez-Reinoso, 1997; Martin-Gullon, 2004; Maciá-Agulló, 2004) - higher yields carbon products (Castro et al., 2000; Diao et al., 2002; Daifullah et al., 2004) - easily recover chemicals (Philip, 1996) - high surface area (Diao et al., 2002) - reduced the energy costs in activated carbon production (Castro et al., 2000) - good development of the porous structure (Redriguez-Reinoso, 1997; Maciá-Agulló, 2004) - recovery of these chemicals from the products (Montané, 2005)	- no contaminant of chemical (Laine and Yunes, 1992)
Disadvantages	- contaminated with hazardous chemicals i.e zinc chloride (Girgis et al., 2002; Daifullah, 2004) - impurities coming from the activating agent, which may affect the chemical properties of the activated carbon (Gómez-Serrano et al., 2005)	- performed in one stage, or two stage process (Hayashi et al., 2002) - carbonized at high temperature (El-Hendawy, 2001) - used water steam or carbon dioxide (Hayashi et al., 2002) - low yield (Kim et al., 2001) - lack of homogeneity of the product (Kim et al., 2001)

Table 2.5 Summary of recent works on the conversion of agricultural based-raw materials to activated carbon

Type of raw material	Method of activation	Type of chemical	Impregnation ratio	Condition					Properties of activated carbon			Ref.
				Carbonization		Activation			Iodine number (mg g⁻¹)	Methylene blue (mg g⁻¹)	Surface area (m² g⁻¹)	
				Temp. (°C)	Time (h)	Gas or Steam	Temp. (°C)	Time (min)				
Waste rubber	chemical	70 wt% ZnCl$_2$	1:145	400	30	N$_2$ at 100 mL s^{-1}	500	120	352	-	237	Barame, 1999
Sugar cane and bagasse	chemical	mixed 28-60 wt% H$_3$PO$_4$	1:1.5	-	-	-	500	60	746	258	1132	Castro et al., 2000
Walnut shell	chemical	3 M of ZnCl$_2$	1:3	-	-	-	375	60	1297	-	-	Kim et al., 2001
Plam shell	chemical	NaCl	1:3	-	-	-	800	60	486	-	386	Khuysangaain, 2001
Coconut shell	chemical	NaCl	1:3	-	-	-	800	60	532	-	492	Khuysangaain, 2001
Durian rind	chemical	NaCl	1:3	-	-	-	800	60	567	-	-	Nithasanacharukul, 2001

Table 2.5 Summary of recent works on the conversion of agricultural based-raw materials to activated carbon (continued)

| Type of raw material | Method of activation | Condition | | | | | | | Properties of activated carbon | | | References |
| | | Type of chemical | Impregnation ratio | Carbonization | | Activation | | | Iodine number (mg g⁻¹) | Methylene blue (mg g⁻¹) | Surface area (m² g⁻¹) | |
				Temp. (°C)	Time (h)	Gas or Steam	Temp. (°C)	Time (min)				
Cashew nut shell	chemical	NaCl	1:3	-	-	-	800	60	532	-	-	Nithasanacharuki 2001
Arundo donax cane	chemical	mixed 32–60 wt% H$_3$PO$_4$	1:2	-	-	-	500	60	-	-	1114	Vernersson et al., 2002
Coffee grounds	chemical	-	-	-	-	-	600	45	640	440		Namane et al., 2005
Pistachio shells	physical	-	-	450 at 5 °C min⁻¹ & steam at 3 cm³ min⁻¹	90	steam at 3 cm³ min⁻¹	830	120	-	-	821	Wu et al., 2005
Palm-oil shells	physical	-	-	-	-	air at 0.72 nl min⁻¹	750	120	620	177	559	Vitidsant et al., 1999

Table 2.5 Summary of recent works on the conversion of agricultural based-raw material to activated carbon (continued)

Type of raw material	Method of activation	Condition							Properties of activated carbon			References
		Type of chemical	Impregnation ratio	Carbonization		Activation			Iodine number (mg g^{-1})	Methylene blue (mg g^{-1})	Surface area (m^2 g^{-1})	
				Temp. (°C)	Time (h)	Gas or Steam	Temp. (°C)	Time (min)				
Bagasse pith	physical	-	-	200	120	steam of 5 ml min^{-1} & heated at 10 °C min^{-1}	400	60	-	-	536	Krishnan and Anirudhan, 2002
Bagasses	physical	-	-	450 at 5 °C min^{-1} & steam at 5 cm^3 min^{-1}	120	steam at 5 cm^3 min^{-1} & heated 5 °C min^{-1}	840	120	-	-	607	Juang et al., 2002
Pinewood	physical	-	-	550 at 5 °C min^{-1} & steam at 3cm^3 min^{-1}	240	steam at 3 cm^3 min^{-1}	900	240	1067	-	-	Tseng et al., 2003

Table 2.6 Eucalyptus-based activated carbon obtained from other reports

Description	Bello et al. (2002)	Jindaphunphairoth (2000)	Tancredi et al. (1996)	Arriagada et al. (1994)
Raw material	*Eucalyptus globules* wood	*Eucalyptus camaldulensis Dehnh.* wood	*Eucalyptus globulus* sawdust	*Eucalyptus globulus* wood
Carbonization	$870^{\circ}C$ for 2 h with N_2 and a heating rate of 4 $^{\circ}C$ min^{-1}	$450^{\circ}C$ and 45 min	$800^{\circ}C$ for 2 h with N_2 and a heating rate of 10 $^{\circ}C$ min^{-1}	$450^{\circ}C$ for 2 h
Activation	$600^{\circ}C$ for 30 min	$900^{\circ}C$ for 2.5 h	$800^{\circ}C$ for 1 h	$900^{\circ}C$ for 4.5 h
Activating agent	Carbon dioxide	Steam	Steam	Steam
% Yield	-	33	23	23
Iodine number (mg g^{-1})	-	1,233	-	968
Methylene blue number (mg g^{-1})	-	242	-	311
BET surface area (m^2 g^{-1})	-	1,076	1,190	1,193

Table 2.7 Phosphoric acid-derived activated carbon obtained from other reports

Description	Girgis and Ishak (1999)	Castro et al. (2000)	Diao et al. (2002)	Girgis et al. (2002)	Vernersson et al. (2002)	Daifullah et al. (2004)
Raw material	Cotton stalk	Sugar cane bagasse	Grain sorghum	Peanut hull	*Arundo donax* cane	Rice husk
Carbonization	-	-	300 °C for 15 min with N_2	-	-	-
Activation	500°C for 2 h	500 °C for 1 h & heating rate of 3 °C min^{-1}	500°C for 15 min	500°C for 3 h	500°C for 1 h & heating rate of 3 °C min^{-1}	500°C for 2.5 h & heating rate of 10 °C min^{-1}
Impregnation ratio	1:1.6 with 65% acid by weight	1:1.5 with mixed 28-60% acid by weight	1:0.76 with 15% acid by weight	1:1 with 85% acid by weight	1:2 with mixed 32-60% acid by weight	1:0.7 with 85% acid by weight
% Yield	-	-	29	22	-	-
Iodine number (mg g^{-1})	-	746	-	-	-	-
Methylene blue number (mg g^{-1})	-	283	-	384	-	-
BET surface area (m^2 g^{-1})	1,032	1,132	1,522	1,177	1,333	376

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Table 2.8 Distinction between physical and chemical adsorptions

Physical adsorption	Chemical adsorption
- Low heat of adsorption (<2 or 3 times latent heat of evaporation)	- High heat of adsorption (>2 or 3 times latent heat of evaporation)
- Non specific	- Highly specific
- Monolayer or multilayer	- Monolayer only
- No dissociation of adsorbed species	- May involve dissociation
- Only significant at relatively low temperatures	- Possible over a wide range of temperatures
- Rapid, non-activated, reversible	- Activated, may be slow and irreversible
- No electron transfer although polarization of sorbate may occur	- Electron transfer leading to bond formation between sorbate and surface
- Weak attraction	- Stronger attraction
- Reversible reaction	- Irreversible reaction

Table 2.9 Effects of pH on various adsorption systems

Adsorbent	Heavy metals	pH Studies	Condition			Optimum pH	References
			Temp. (°C)	Agitation rate (rpm)	Time (h)		
Sago waste	Cu, Pb	2-6	25±5	150±5	24	5, 4.5	Quek, 1998
ACs pretreated with NaCl	Cu, Pb, Ni	2-10	20±1	-	12	5	Faur-Brasquet, 2002
ACs pretreated with citric acid	Cu	3-11	25	-	48	3-4	Chen, 2003
ACs pretreated with CO_2 and H_2SO_4	Ni	2-7	25	-	48	5	Hasar et al, 2003
Hazelnut shell ACs	Cr	1-8	30	200		1	Kobya, 2004
ACs from apricot stone	Cu, Pb	1-6	25	200	48	4, 3	Kobya, 2005
ACs pretreated with tannic acid	Cu	2-7	-	-	-	5.4	Ücer, 2006
CTAB modified carbon	Pb	1-10	30	160		5.5	Nadeem, 2006

Table 2.10 Literature reviews on the kinetic model of various adsorption systems

Adsorbent	Heavy metals	Initial concentration (mg L^{-1})	Condition Temp. (°C)	Condition Agitation rate (rpm)	Condition Time (h)	Kinetic model	Rate Constant	References
Sago waste	Cu	50 &100	25±5	150±5	24	Second order	-	Quek et al., 1998
Sago waste	Pb	50 & 100	25±5	150±5	24	Second order	-	Quek et al., 1998
ACs	Mn, Fe, Ni, Cu	200	30	140	-	First order	$k_1 = 0.017, 0.0209, 0.0308, 0.0395$ h^{-1}	Uzun et al., 2000
ACs from waste walnut shell	Cu	50, 100, 200, & 300	-	-	-	First order	$k_1 = 0.016, 0.036, 0.060, 0.080$ min^{-1}	Kim et al., 2001
Steam activated sulphurised carbon	Cd	50, 100, 150, 250, & 400	30	200	-	Second order	$k_2 = 7.88\times10^{-3}, 4.74\times10^{-3}, 3.40\times10^{-3}, 2.33\times10^{-3}, 1.64\times10^{-3}$ g mg^{-1}.min^{-1}	Krishnan et al., 2003
Steam activated sulphurised carbon	Cd	250	30, 40, 50, & 60	200	-	Second order	$k_2 = 2.33\times10^{-3}, 2.8\times10^{-3}, 3.58\times10^{-3}, 4.46\times10^{-3}$ g mg^{-1}.min^{-1}	Krishnan et al., 2003
CTAB modified carbon	Pb	30	30	160	-	Second order	$k_2 = 0.0087$ g mg^{-1}.min^{-1}	Nadeem et al., 2006

Table 2.11 Reviews on the adsorption isotherm of various adsorption systems

Adsorbent	Heavy metals	Variation	Condition			Isotherm	References
			Temp. (°C)	Agitation rate (rpm)	Time (h)		
Sago waste	Cu, Pb	pH 2-6	25±5	150±5	24	Langmuir q_m = 12.42, & 46.64 mg g^{-1} b = 0.069, & 0.246 (mg L^{-1})$^{-1}$	Quek et al., 1998
ACs	Cu	Initial conc. 100-300 mg/L	30	140 -	0.5	Freundlich K_F = 2.394 mg g^{-1} 1/n = 0.38	Uzun et al., 2000
ACs from waste walnut shell	Cu	Initial conc. 50-300 mg L^{-1}		-	-	Freundlich K_F = 1.66 mg g^{-1} 1/n = 2.79	Kim et al., 2001
ACs pretreated with 1 M citric acid	Cu	pH 3-11	25	-	48	Langmuir q_m = 14.92 mg g^{-1} b = 0.08 (mg L^{-1})$^{-1}$	Chen et al., 2003
ACs pretreated with CO_2	Ni	Initial conc. 25-250 mg L^{-1}	20	100	-	Langmuir q_m = 30.769 mg g^{-1} b = 0.025 (mg L^{-1})$^{-1}$	Hasar, 2003
ACs pretreated with H_2SO_4	Ni	Initial conc. 25-250 mg L^{-1}	20	100	-	Langmuir q_m = 37.175 mg g^{-1} b = 0.091 (mg L^{-1})$^{-1}$	Hasar, 2003

Table 2.11 Reviews on the adsorption isotherm of various adsorption systems (continued)

| Adsorbent	Heavy metals	Variation	Condition			Isotherm	References
			Temp.(°C)	Agitation rate (rpm)	Time (h)		
Steam activated sulphurised carbon	Cd	Initial conc. 50-1000 mg L^{-1}	30, 40, 50, & 60	200	-	Langmuir q_m = 149.93±5.44, 163.32±7.16, 172.81±4.17, & 190.48±12.07 mg g^{-1} b = 0.161±0.015, 0.213±0.077, 0.317±0.028, & 0.421±0.046 (mg L^{-1})$^{-1}$	Krishnan et al., 2003
ACs pretreated with HNO$_3$	Cu	Dosage 0.01-2.5 g	25	-	48	Langmuir q_m = 15.34 mg g^{-1} b = 0.23 (mg L^{-1})$^{-1}$	Chen and Wu, 2004
Rice husk ash	Pb, Hg	Dosage 2 g Initial conc. 40 mg L^{-1}	15	-	0.5	Langmuir q_m = 12.346, & 9.32 mg g^{-1} b = 0.3250, & 0.0115 (mg L^{-1})$^{-1}$	Feng et al., 2004
Rice husk ash	Pb, Hg	Dosage 2 g Initial conc. 40 mg L^{-1}	30	-	0.5	Langmuir q_m = 12.61, & 6.72 mg g^{-1} b = 0.163, & 0.018 (mg L^{-1})$^{-1}$	Feng et al., 2004
GAC pretreated with tannic acid	Cu, Fe, Cd, Zn, Mn	Dosage 0.02-2.0 g	-	-	-	Langmuir q_m = 2.73, 2.8, 2.46, 1.8, 1.73 mg g^{-1} b = 4.76, 0.88, 1.67, 1.29, 0.72 (mg L^{-1})$^{-1}$	Ücer et al., 2006
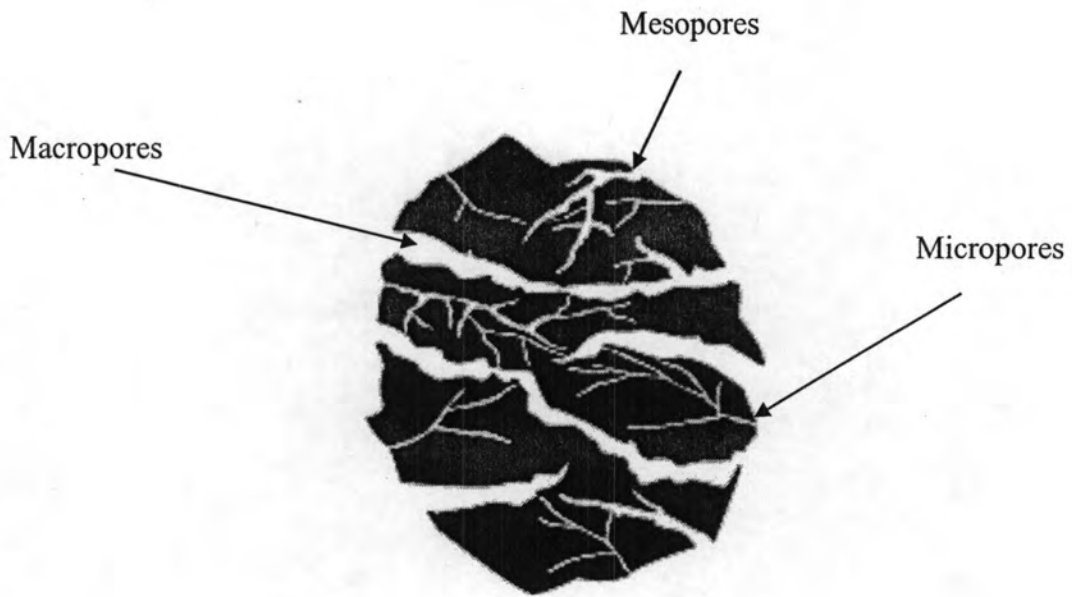
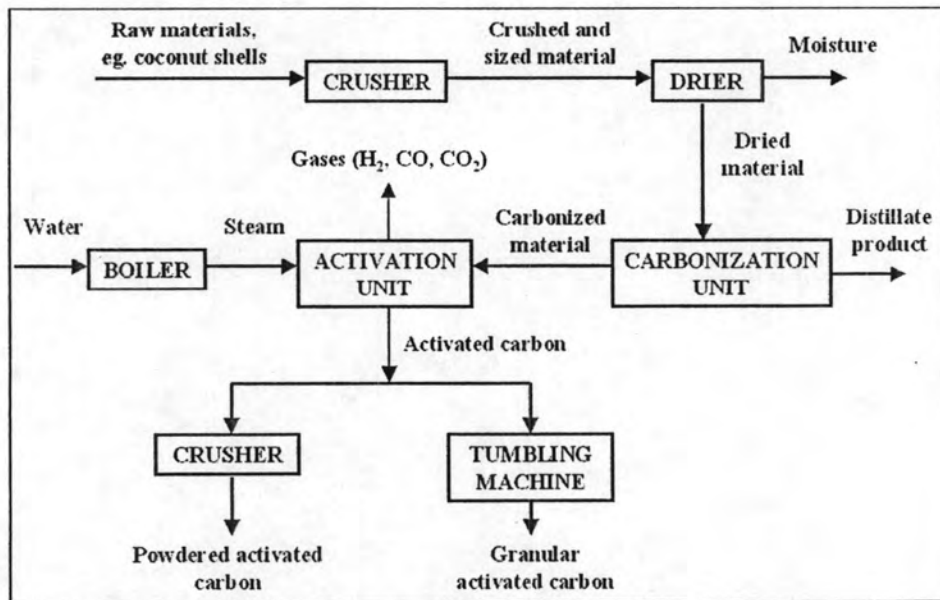Figure 2.1 Structure of activated carbon

Figure 2.2 Flow diagrams for activated carbon production (Lartey and Acquah, 1999)
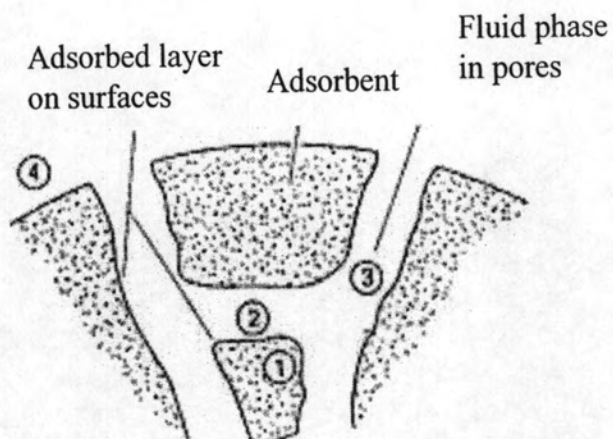
Figure 2.3 Adsorption operations with solid-particle sorbents
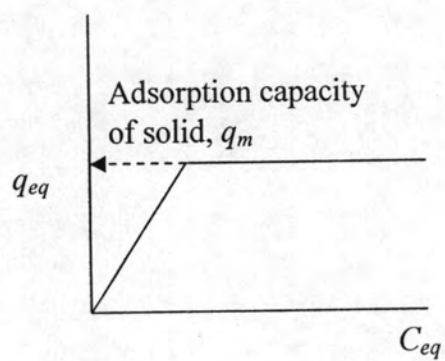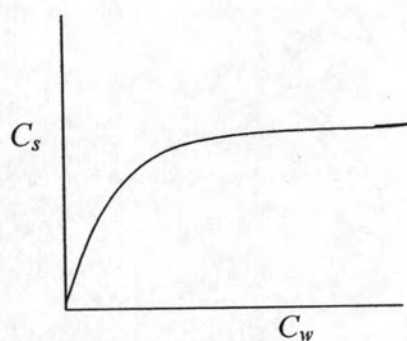

Figure 2.4 Langmuir adsorption isotherm

Figure 2.5 Freundlich adsorption isotherm