

CHAPTER II

LITERATURE REVIEW

Plant cell wall

The most important feature distinguishing the cells of plants from those of animals is the cell wall. In plant, this wall protects the cellular contents and limits cell size. It also has important structural and physiological roles in the life of the plant, being involved in transport, absorption, and secretion. The plant cell wall varies in composition and structure in accordance with developmental stages of different cell types and in response to environmental factors and stresses (Lin, 1991).

In general, a plant's cell wall is composed of several chemical substances, of which cellulose is the most important. Cellulose molecules are united into fibrils; it is called microfibrillated cellulose, which forms the structural framework of the wall. In addition, much more information has been accumulated about the deposition of specific cell wall components with relation to special functions. For example, some cell walls deposit lignin largely in content but it is beneath of cellulose. Lignin serves to harden and stiffen the walls; the epidermal cell walls are impregnated with waxes such as cutin and suberin, which serve to prevent water loss and to provide a mechanical barrier to bacteria, fungi and insects. (Weiner, 1995)

The overall structure of the cell wall is extremely complicated, given the great complexity and variety of the components described above. A number of investigators have attempted to produce models of the whole cell wall. One of the models which is probably possible recently is a model showing a number of networks in cell wall which, when superimposed upon one another, interact further to give rise to the whole complex structure. A number of such networks are outlined in figure 2.1. The result obtained by superimposition of all the networks likely to be found in one cell type will be of enormous complexity. This is because it will encompass not only the

interrelationships between the matrix molecules and cellulose microfibrils, but also the interactions of the matrix components with each other.

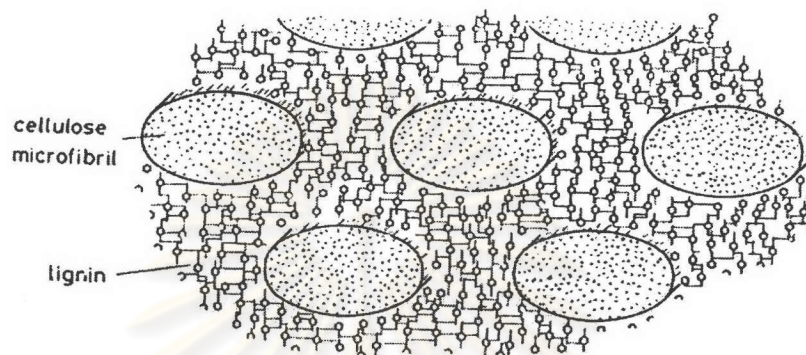


Figure 2.1 : Cell wall model showing the way in which lignin phenolics fill in the spaces between the cellulose microfibrils, thus creating a rigid, impermeable cell wall (Brett and Waldron, 1990)

Cellulose

The cellulose is the first most abundant of organic substance in cell walls of higher plants. It is a carbohydrate material containing carbon (44.2 %), oxygen (49.55 %) and hydrogen (6.3 %). Cellulose is a polymer of glucose molecules condensed and linked together linearly by means of 1,4- β -glycosidic bonds as shown in figure 2.2.

In natural, cellulose exists in three forms which is α , β and γ . α -cellulose has the highest degree of polymerization (DP) and is the chief constituent of lignocellulosic materials. The β and γ forms have much lower DP and are known as hemicellulose (Hebeish et al., 1981).

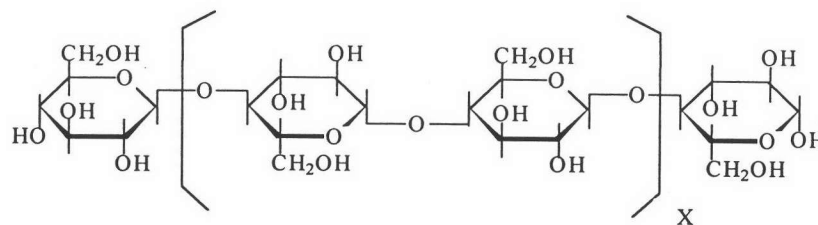


Figure 2.2 : Chemical structure of cellulose (David and Shiraishi, 1991)

Cellulose reacts as a trihydric alcohol with one primary and two secondary hydroxyl groups per glucose unit. In the former, the 2- and 6-hydroxyl groups are usually the most reactive. With cellulose, certain data indicate the preferential reactivity of 2-hydroxyl and other of 6-hydroxyl groups. (Dorfer, 1977 ; Hebeish, 1981). Concerning with trapping concept, the sheet concept also leads to another known reaction of cellulose and that is the formation of reactive cellulose by trapping foreign molecules into the structure via swelling reaction (Figure 2.3).

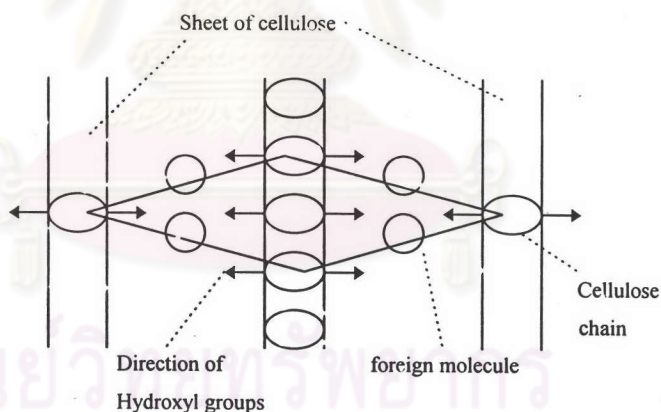


Figure 2.3 : Cellulose sheet trapping foreign molecules (Kennedy, 1985)

Crosslinked-cellulose

Cellulose can be chemically cross-linked by any reagent containing at least two functional groups capable of reacting with alcohol groups. In this reaction with acidic formaldehyde, the methylene ether crosslinks take place predominantly between the secondary hydroxyl groups of cellulose, according to Figure 2.4. However, not all

the formaldehyde is used in linking adjacent chain molecules; some react with two hydroxyl groups in the same chain molecule. (Preston, 1986)

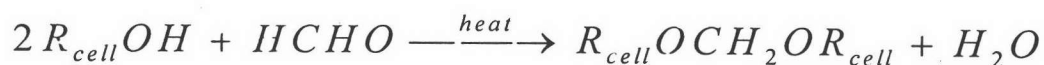


Figure 2.4 : Cross-link reaction between cellulose and formaldehyde

This is to be expected since the crosslinking reaction takes place in highly disorder regions. Beside blocking some of the cellulose hydroxyls, such a change results in a measurable decrease in swellability of the fibre, probably by restricting the freedom of movement of the cellulose molecules while in the aqueous medium. (Hebeish, 1981 ; Preston, 1986).

Cellulosic ion exchanger

Natural cellulose fibers have about 3000 monomers per molecule. Suitable reagents can be made to react with the various functional groups of cellulose to introduce ionic groups into the polymer called cellulosic ion exchangers. These ion exchangers have ion exchanging properties just as do the synthetic resins, but they differ from the latter on a few important points. For example, the cellulose matrix is hydrophilic in contrast to the hydrophobic synthetic resin matrix. As a result of the fibre properties of cellulose, its loose network cross-linked by hydrogen bridges. This leads to rapid exchange and to a higher capacity for large molecules in spite of the smaller absolute exchange capacity of cellulosic exchangers compared with synthetic ion exchange resins. For developing of this ion exchanger for commercial, Serva-cellulose ion exchangers were the first to be manufactured and sold in large quantities, and they consequently contributed to the wide acceptance and successful use of these exchanger types. The large production program for acid and basic types, with their most important properties data, is listed in table 2.1 (Dorfer, 1977).

Table 2.1 : Serva-Cellulose ion exchangers (CE = cation exchanger, AE = anion exchanger)

| Name | Ion exchanging group | Properties | Capacity (meq/g) | Prevailing particle size (μ) |
|-------------------|---|-----------------|------------------|------------------------------------|
| CM-Cellulose | -OCH ₂ COOH | CE, weak acid | 0.62 \pm 1 | 50 - 200 |
| P-Cellulose | -OPO ₃ H ₂ | CE, medium acid | 0.8 - 0.9 | 50 - 200 |
| SE-Cellulose | -OC ₂ H ₄ SO ₃ H | CE, strong acid | 0.2 - 0.3 | 50 - 200 |
| DEAE-Cellulose | -OC ₂ H ₄ N(C ₂ H ₅) ₂ | AE, strong base | 0.4 - 0.55 | 50 - 200 |
| TEAE-Cellulose | -OC ₂ H ₅ N ⁺ Br ⁻ | AE, medium base | 0.55 - 0.75 | 50 - 200 |
| PAB-Cellulose | -OCH ₂ C ₆ H ₄ NH ₂ | AE, weak base | 0.15 - 0.2 | 50 - 200 |
| ECTEOLA-Cellulose | unknow | AE, weak base | 0.3 - 0.4 | 50 - 200 |
| AE-Cellulose | -OC ₂ H ₄ NH ₂ | AE, weak base | 0.33 \pm 0.1 | 50 - 200 |
| BD-Cellulose | -OC ₂ H ₄ N(C ₂ H ₅) ₂ | AE, medium base | 0.8 \pm 0.05 | 50 - 200 |
| GE-Cellulose | -OC ₂ H ₄ NH.C=NH ₂ NH ₂ ⁺ Cl ⁻ | AE, medium base | 0.2 - 0.3 | 50 - 200 |
| BND-Cellulose | -OC ₂ H ₄ N(C ₂ H ₅) ₂ | AE, medium base | 0.8 \pm 0.05 | 50 - 200 |

Source : Dorfer, 1977

Lignin

It commonly has been stated that the plant polymer lignin is the second most abundant organic compound on earth, and that cellulose is the only other organic substance present in the biosphere in large quantities than lignin (Crawford, 1981). Almost plants consist more or less of all three units, namely, guaiacyl, syringyl, and p-hydroxyphenyl moieties (Figure 2.5).

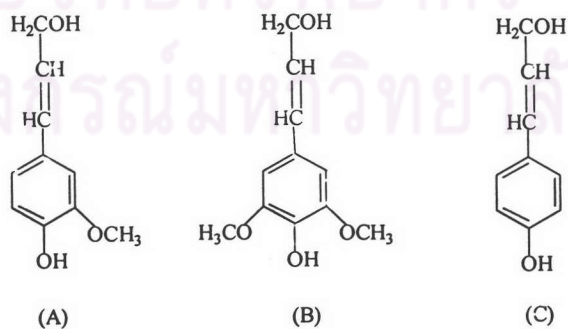


Figure 2.5 : Chemical structure of lignin constituents.

Lignocellulosic materials

The biosphere's ability to produce enormous quantities of lignocellulosic materials is the driving force for life on earth. However, this capability has been exploited by humankind in the development of large lignocellulosic-based industries. Chief among these industries are agriculture, lumbering and paper making. All these industries produce either directly or indirectly astronomical quantities of lignocellulosic waste materials. In Thailand, these wastes often go largely unused natural resources and represent disposal problem such as bark, straw, sawdust, corn cob and bagasse including aquatic weed such as water hyacinth. However, for ecosystem, these agricultural residues are valuable to some extent for soil erosion control and soil nutrient replenishment. In wastewater treatment studies, these wastes have been reported to use in heavy metal ion removal from various industrial wastewaters (Crawford, 1981).

Water hyacinth

Water hyacinth is a common name for a perennial, tropical, aquatic herb, of the family Potedariaceae. This herb has become in the Southern U.S. and in Australia but the native area is in the South Africa.(Weiner, 1995). It is a free floating aquatic flowering plant which has spread throughout the world including Thailand. The free-floating plant body comprises of a shoot that includes branched, stoloniferous, rhizome, with several short internodes, leaves and numerous roots hanging in water (Figure 2.6). Flowers may be blue, violet or white and are usually quite showy. It has a high rate of vegetative growth and multiplication, including a fairly wide ecological amplitude. Therefore, this floating invasive species is probably the most prolific plant species in lake, rivers, and canals of many countries. Growth rates exceed dry biomass production of any terrestrial, salt-water, or freshwater vascular macrophyte (Wolverton and McDonald, 1978). Environmental harm from large water hyacinth populations is degraded water quality and drastic changes in plant and animal communities. Light and oxygen diffusion are severely curtailed by the floating plant (Gopal, 1987), and water movement can be reduced by 40-95 % (Bogart, 1949).

Mechanical controls are used where herbicides are inappropriate but have proved too expensive and too slow to keep pace with water hyacinth growth on a large scale. Several methods such as log booms and barriers, conveyor belts and grapples, toxic sodium arsenite, crusher-boats, blighted worms, and herbicides have been used to eradicate water hyacinth. None of these methods is practical on a large scale. When water hyacinth populations were decreased after herbicide applications, alligator weed expanded (Schmitz et al., 1993).

A computer simulation model was developed to help control personnel determine the best method of control for this species (Akbay et al., 1988). Four biological control agents for this species have been dispersed in Florida. Although they may stress water hyacinth, they don't seem to control or prevent further spread of this rapidly growing pest. The herbicides 2,4-D and diquat are effective controls of water hyacinth, however, only aggressive management reduced water hyacinth in public waters from the third most abundant aquatic plant in 1982 to 50th in 1990 (Schardt and Schmitz, 1990).

Center and Spencer (1981) reported that the leaves of the plant represent 60 to 70% of water hyacinth plant biomass, and the leaf turnover rate can range from 60 to 70%/month. The decomposition of the plants, if a large biomass of the plants are killed at once, can use up all the oxygen in the water. The resulting anoxia from such detritus can enhance the release of phosphorus into the water during decomposition. The additional detrital load that is generated by dense water hyacinth mats is believed to burden these systems with additional nutrient loadings. Consequently, because of the rapid growth rate and high evapotranspiration rate of water hyacinth, populations of this plant species can be a depository for heavy metals and probably for toxic organic compounds, which may pose some risk for an endangered aquatic species. Further study is needed to determine overall ecological effects of water hyacinth invasions on the dynamics of plankton communities (Schmitz et al., 1993)

The root at the edges of water hyacinth mats support many invertebrates (O'Hara, 1967 ; Schram et al., 1987). At least seven fish species are associated with water hyacinth habitat in Florida (Hansen et al., 1971). In contrast, spawning areas for fishes are reduced by water hyacinth mats, and their dead masses shade out benthic

communities and can nearly block the diffusion of oxygen through the water atmosphere interface. Low oxygen concentrations underneath water hyacinth mats can kill fishes (Timmer and Weldon, 1967). Drifting mats of water hyacinth often smother beds of submersed vegetation and overwhelm marginal plants that are important to waterflow (Tabita and Woods, 1962 ; Chesnut and Barman, 1974). In Louisiana, water hyacinth completely eliminated resident fish populations in small lakes (Gowanloch, 1945).

From describe above, it will be concluded that water hyacinth is a lignocellulosic source that enormous in available quantities and low cost. Many of control methods of this species do not seem successfully and may deteriorate regional aquatic's ecological system. It may however, alternative for ideal material by using in heavy metal ions removal from industrial wastewaters.



Figure 2.6 : Water hyacinth (*Eichhornia Crassipes*)

Composition of water hyacinth

The water hyacinth composes of cellulose, lignin and various substances such as pentosan and nutrient trace metals. The proximate composition of this plant tissue shows a fairly high cellulose content but the lignin content is rather low (Table 2.2).

Table 2.2 : Proximate composition of water hyacinth tissues

| Parameter | joedodibroto et al., 1983 | | | Baruah, 1981 | Pranee, 1989 |
|-------------------------------|---------------------------|-------|---------|-----------------|-----------------|
| | Stem | Leaf | Petiole | Shoots | Total |
| % Ash dry wt. | 22.9 | 22.67 | 14.62 | 18.4 | 20-21 |
| % Silica | 1.41 | - | - | - | - |
| % Cold water soluble matter | 29.81 | 10.35 | 15.30 | 15.7 | - |
| % Hot water soluble matter | 24.71 | 11.35 | 16.39 | 17.0 | - |
| 1 % NaOH solubility | 56.59 | 51.67 | 43.77 | 46.8 | - |
| Alcohol-Benzene (1:2) soluble | 13.65 | 4.75 | 6.42 | 10.6 | - |
| % Pentosan | 15.83 | 17.52 | 18.20 | 14.2 | 14-15 |
| % Lignin | 8.67 | 6.02 | 7.42 | 6.7 | 12-13 |
| % Total cellulose | 57.66 | 49.85 | 64.32 | - | 43-44 |

Source : Modified from Gopal, 1987

Water hyacinth for heavy metal removal

It has been reported that water hyacinth tissue contains both nutrient solution and large amount of one or more heavy metals. This plant tissue accumulates from its environment a variety of heavy metals like irons, manganese, zinc, aluminum, cadmium, lead, mercury, nickel, cobalt, strontium, chromium and copper. This result demonstrates the possibility of using the plant for their removal from different kinds

of effluents (Gobal, 1987). The mechanism of heavy metals sorption by lignocellulosic produced from water hyacinth should be ion exchange, adsorption and chelate formation. The main mechanism of sorption is far as to conclude or indicate certainly. However, considering with main composition of lignocellulosic of water hyacinth according to table 2.2, it found that the related mechanism should be ion exchange that can be attributed to the presence of phenolic and hydroxylic groups in which exist the cellulose matrix or in the materials associated with cellulose, such as hemicellulose (Maranon, 1991 ; Haider, et al., 1984). The chelate formation and adsorption mechanism may be caused by lignin and other chelating substances such as alcohols, aldehydes, ketones, acids, phenolic hydroxide and ethers. These compounds can be involved in chemical bonding of adsorption process. (Coupal and Lalancette, 1976 ; Chaney, 1979)

Heavy metal ions in aquatic environment

Metal ions in several river come from natural as well as artificial sources. Metals that are naturally introduced into the river come primarily from such sources as rock weathering, soil erosion, or the dissolution of water-soluble salts. Naturally occurring metals move through aquatic environments independently of human activities, usually without any detrimental effects. However, as the industrialized zone were settled and, the metals added by human activities have affected the water quality of the neighboring river, such the case study of Mississippi River (Garbarino et al., 1995). Some of these metals are essential for proper metabolism in all living organisms yet toxic at high concentrations; other metals currently thought of as non-essential are toxic even at relatively low concentrations.

Heavy metals are transported as either dissolved species in water or as an integral part of suspended sediments. Heavy metals may be volatilized to the atmosphere or stored in riverbed sediments. Toxic heavy metals are taken up by organisms; the metals dissolved in water have the greatest potential of causing the most deleterious effects (see Table 2.2).

For the significance of metals in the environment, the metallic elements can be categorized into two groups. The heavy metals are those having densities five times

greater than water, and the light metals, those having lesser densities. Well-known examples of heavy metallic elements are iron, lead, and copper. Examples of light metals are sodium, magnesium, and potassium. Humans consume metallic elements through both water and food. Some metals such as sodium, potassium, magnesium, calcium, and iron are found in living tissue and are essential to human life-biological anomalies arise when they are depleted or removed. Probably less well known is that currently no less than six other heavy metals including molybdenum, manganese, cobalt, copper, and zinc, have been linked to human growth, development, achievement, and reproduction (Vahrenkamp, 1979; Friberg et al., 1979). Even these metals, however, can become toxic or aesthetically undesirable when their concentrations are too high. Several heavy metals, like cadmium, lead, and mercury, are highly toxic at relatively low concentrations, can accumulate in body tissues over long periods of time, and are nonessential for human health. Table 2.3 lists metals according to their acceptable concentrations of toxicants for marine and estuarine waters.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Table 2.3 : Acceptable concentrations of toxicants for marine and estuarine waters

| Toxicant | Acute criterion ($\mu\text{g/L}$) | Chronic criterion ($\mu\text{g/L}$) | National Guideline 1992 ($\mu\text{g/L}$) |
|--|--|--|--|
| arsenic III arsenic V | 69 | 36.0 | 50.0 (all arsenic) |
| cadmium | 43 | 9.3 | 2.0 |
| chromium | 1100 | 50.0 | 50.0 |
| copper (total) | | 2.9 | 5.0 |
| lead | 140 | 5.6 | 5.0 |
| manganese | | 100.0 | |
| mercury | 2.1 | 0.025 (methyl mercury) | (total; assumes <10% methyl) |
| nickel | 75 | 8.3 | 15.0 |
| selenate inorganic selenite inorganic | 410 | 54.0 | 70.0 (all selenium) |
| silver | 1.0 | | 2.3 |
| thallium | | | 20.0 |
| zinc | 95 | 86.0 | 50.0 |

Source : From USEPA "Quality Criteria for Water" 1986, except for zinc and nickel, 1987 (update) of USEPA and National Guidelines from ANZECC "Australian Water Quality Guidelines for Fresh and Marine waters" 1992.

In the fate of heavy metals concerning, Heavy metals released into the river, by both natural processes and human activities, can be distributed among several different forms within the water environment. Metals can be either transported with the water and suspended sediment or stored within the riverbed bottom sediments. Heavy metals are transported as (1) dissolved species in the water, (2) suspended insoluble chemical solids, or (3) components of the suspended natural sediments. Metals dissolved in the water can exist as hydrated metal ions or as aqueous metal complexes with other organic or inorganic constituents. Water-insoluble inorganic (non-carbon-containing, except for carbonates) chemical solids such as metal hydroxides may be formed, as may organic (carbon-containing) chemical solids, such as those associated with compounds derived from the decay of living organisms. Both

inorganic and organic solids can be transported with the water as individual entities or as chemical coatings on suspended sediments. In addition, mineral components of suspended sediments themselves can contain heavy metals. Heavy-metal solids can also be stored in river-bottom sediments. Suspended sediments and metallic chemical solids are stored in riverbed sediment after they aggregate to form large, denser-than-water particles that settle from the water when the river's flow is not sufficient to keep them in suspension (Garbarino et al., 1995).

Heavy metal removal by using lignocellulosic waste materials.

Randall and Garrett (1974) used bark to remove heavy metal ions from waste solutions. This experiment was investigated using batch and column experiments. Batch experiments showed that all the barks except Douglas-fir were relatively efficient in removing both lead acetate and lead nitrate from solution and red wood could remove significant amounts of Cu, Cd, Ag and Zn ions. In column studies, the results show that the cations Cu, Cd, Zn and Pb ions were efficiently removed by any of the bark substrates and these substrates can be regenerated by using 0.1 N HCl for reuse. After the regenerated substrates were washed with water to remove acid, they had the same capacity for heavy metal ions as fresh material. Thus acid treatment had no apparent effect on the physical appearance of the substrate. For actual wastes, the red wood bark column can remove Pb ion from a lead battery plant to less than 0.05 ppm. In addition, it also completely filtered out the particulate matter present in the waste solution.

Randall, Hautala and McDonald (1978) investigated the binding of heavy metal ions by formaldehyde polymerized peanut skins. Both of batch and column experiments were used. In batch experiment, the results showed that for some metal ions, sorption improved dramatically in acetate solution as compared to nitrate solution. Furthermore, the results indicate that peanut skin should be effective in binding Cd, Cu, Pb and Zn ions and perhaps Ag, Ni and Cr (VI) ions while Ca, Co and Mg ions were not bound well. For effect of metal ion concentration, as the initial metal concentration increased, absolute removal of metal ion from solution would

increase, but percentage removal would decrease. In column experiments, the results showed that all the metals tested were almost completely removed from solution, at least for a short time. Sorption from a solution containing Cd, Cu, Hg, Ni, Pb, Zn ions on a packed column of formaldehyde-treated peanut skin indicated that Hg, Pb and Cu were rapidly and completely bound to the packing, while Cd, Ni and Zn ions were poorly bound until the preferred ions had been removed from solution. The maximum capacity of the substrate was 2.1 meq/g for Pb ion, 3.0 meq/g for Cu ion and 1.3 meq/g for Cd ion. The efficient regenerating acid was nitric acid in the case of Pb ion due to PbCl_2 has limited solubility in water.

Chaney and Hundemann (1979) used peat moss columns to remove cadmium from plating wastewaters and studied on the precipitation / peat sorption system. The results showed clearly that the columns containing peat only : leached less rapidly, were more acidic , and produce effluents generally lower in Cd^{2+} than columns containing peat and CaCO_3 because the dissolved Ca^{2+} could have caused the temporary poorer treatment by interference in Cd^{2+} ions sorption to the peat. In distribution of Cd^{2+} and pH studies, at the end of the leaching trial, the bulk of the Cd^{2+} removal had occurred near the top of the columns. Where CaCO_3 was included, the Cd^{2+} generated even less. The pH of the peat was near 10.5 at the top of the columns ; the base of the peat columns remained acidic (pH 4.5), while that of the peat plus CaCO_3 columns was calcareous (pH 7.6). Exchangeable acidity in the peat consumed substantial amounts of added alkalinity. By the use of the peat columns, ordinarily treated plating effluents could be lowered to $< 3 \mu\text{g/l}$ Cd^{2+} that is to levels no greater than those of domestic wastewater.

Kumar and Dara (1980) used modified barks to remove toxic heavy metal ions. The bark samples chosen for these investigations were Accacia, Bijasal, Laurel and Teak which are most commonly available in India and are also inexpensive. All bark samples were selected and modified with formaldehyde in acid media for investigating their effectiveness in toxic heavy metal ions such as Cu^{2+} , Pb^{2+} , Zn^{2+} , and Cd^{2+} by conducting batch experiments. The results indicate that 76 to 94 % of

Cu^{2+} , 94 to 99 % of Pb^{2+} , 68 to 78 % of Zn^{2+} , and 70 to 90 % of Cd^{2+} could be removed depending upon the nature of the bark used and the predominant anions present in the wastewaters such as sulfate and chloride in the case of Cu^{2+} . From this result, Indian bark samples seem to offer another alternative for removing of heavy metal ions from industrial wastewaters.

Kumar and Dara (1981) studied the binding heavy metal ions with polymerized onion skin. Batch and column experiments conducted with Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Hg^{2+} , and Pb^{2+} . The substrate can be prevented color leaching and the physical characteristics can be improved by treatment with formaldehyde in acid media. In batch experiment results in all cases studied, it can be seen that the final pH is always less than the initial pH because of the metal ions are bound on the substrate while the hydrogen ions are released to the solution. Thus the onion-skin substrate probably acts as an acid-form ion exchanger. Furthermore, it can also be seen that the predominant anion have some effect on the binding of the metal ions, especially acetate anions seem to do better than other anions. In column experiments, the capacities per gram of the onion-skin substrate for Cu^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , and Hg^{2+} were 1.62, 1.35, 1.22, 1.55, 1.3 and 0.82 meq, respectively while the final effluent metal concentrations in ppm for Cu^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} were 0.12, 0.05, 0.25, 0.1, and 1.0 respectively. For competition among other cations, it can be seen that Cu^{2+} , Pb^{2+} , and Hg^{2+} are strongly sorbed as are Cd^{2+} , Zn^{2+} , and Ni^{2+} . From all results, the polymerized onion skin represents another promising and cheap alternative to the expensive commercial ion-exchange resins and seems to possess potential application in wastewater treatment.

Larsen and Schierup (1981) studied the use of barley straw for heavy metals removal from wastewater. Batch and column experiment were also investigated. In batch experiment the efficiency of the barley straw was compared with activated carbon, pine sawdust, and CaCO_3 . The results indicated that one gram of barley straw was able to adsorb amount of Zn^{2+} , Cu^{2+} , Pb^{2+} , Ni^{2+} , and Cd^{2+} ranging from 4.3 to 15.2 mg. One gram of activated carbon adsorbed from 6.2 to 19.5 mg and of the

different metals were precipitated by CaCO_3 . In column experiment the efficiency of the barley straw was not reduced significantly in column experiments. When the barley straw was mixed with CaCO_3 , the efficiency was improved by 10-90 %, a column packed of barley straw and saturated with Cu^{2+} was regenerated with one litre of $\leq 1.0 \text{ N}$. HCl to obtain completely regenerated. Using this regeneration method the same column could be re-used five times. From this studied the use of barley straw in combination with precipitation by CaCO_3 , Na_2CO_3 , NaOH , or $\text{Ca}(\text{OH})_2$ may prove to be suitable, especially for waste water of electroplating industry.

Kumar and Dara (1982) studied the utilization of agricultural wastes for decontaminating industrial/domestic wastewaters from toxic metals. The various agricultural by-products were modified before using for these investigations, including treated bagasse (TBG), treated bark and treated onion skin. Both batch and column experiments were investigated. In batch experiments, treated bagasse is capable of binding mercury, lead, copper, cadmium and nickel effectively while zinc and chromium are bound to a relatively smaller extent. For column experiments, the trends of the metal ion removal by the substrates are similar to those of batch experiments. However, the residual metal ion concentration could be reduced from 220 ppm to 4.1 ppm in the case of bagasse, and to < 0.1 ppm in case of treated laurel bark and techtona bark. Similarly, cadmium could be reduced from 130 ppm to 1.0 ppm in the case of treated laurel bark and techtona bark. The maximum capacities of the various substrates for the heavy metal ions is almost above 1 meq.g^{-1} of the substrate. In addition, the toxic/valuable metal ions can be recovered and the substrates can be repeatedly reused.

Bhargava, Gupta and Varshney (1987) reported that locally available sawdust was found to be a low cost viable adsorbent for removing of the chromium, lead and cadmium in the wastewaters at the low concentration. In the laboratory, batch studies were conducted using different weights of sawdust and stirring it in the different concentration of heavy metal ions as above. It is found that 90 to 99.9 %, 80 to 98.5 %, and 60 to 88 % removals could be affected from the low concentration solutions of

chromium, lead, and cadmium, respectively. However, for higher concentration solutions of these metals, the removals were rather small to the order of 55 to 75 %, 6 to 30 %, and only 0 to 7 %, respectively. Chromium is obviously seen to have more preference for adsorption on the sawdust specially when compared to lead and cadmium. Cadmium has manifested the least affinity for sawdust

Tan and Khan (1988) used waste tea leaves to study the removal of lead, cadmium and zinc. Tea leaves (TL) used in these studies have been previously ground in to granular form by using the sieve of 60-80 mesh size. This experiment was investigated using batch and column techniques. Most of these studies used metal concentration 10-100 times greater than those of natural water level to allow easy determination by atomic absorption spectrophotometry. Batch experiments showed that the metal ions adsorption by tea leaves is pH dependent. The optimum pH range for metal adsorption was pH 6-7 for Zn as well as Cd, and pH 4-7 for Pb. For effect of varying substrate concentration, metal uptake increased with an increase in substrate concentration because the surface area for metal adsorption increased. Linearity was observed only below a certain amount of substrate : 5 mg for 100 µg of Cd and Pb and 10 mg tea leaves for similar amounts of Zn. For effect of ionic strength, the results showed that adsorption capacity of tea leaves decreased with increase in ionic strength because the potassium ions effect a significant change in the adsorption capacity of the tea leaves ; the metal uptake could be suppressed by its ions. Furthermore, the effect of surfactants was also investigated in various types, including cationic, non-ionic and anionic surfactant. In column studies, the results show that 1.8 g substrate can effect close to 100 % removal of up to 100 ppm of Ca, Pb and 50 ppm Zn ions. Lead ions appears to be less sensitive to the change in flow rate than other ions. The affinity for various metal ions toward tea leaves waste is in the order of Pb>Cd>Zn.

Bencheikh-Lehocine (1989) studied the removal of zinc by using peat adsorption. The adsorbent used in this experiment was Sphagnum peat. Batch experiment was investigated where solution of constant zinc concentration and

varying sodium concentration were shaken with peat overnight. The results showed that the removal was not affected by the presence of sodium even at a high concentration of 10 g/l, a level used in the regeneration phase. The efficiency of this peat was 93-96 % which can be confirmed the effectiveness of this substrate. In model studies, it has been found that Langmuir model represents well the removal of zinc in a peat-water system than Freundlich model.

Okieimen and Ongenkpa (1989) studied the removal of solution with melon (*Citrullus vulgaris*) seed husks. This experiment was examined by batch column experiment at 29 °C. The adsorption capacity of melon husks could be enhanced by EDTA modification - a mixture of husks residues and pyridine was heated under reflux for 3 hours. In equilibrium sorption studies, the results showed that the distribution coefficient (D) of the metal ions between the adsorbent phase and the bulk phase showed little variation with the concentration of the metal ions, excepting for Pb(II) ions where the value of D double with five-fold change in the equilibrium condition. The sorption data fitted the Lanmuir isotherm equation and maximum metal-ion binding capacities of 23.3 mg/g husk and 11.4 mg/g husk were predicted for Cd(II) ions respectively. In column experiment studies, the results showed that more than 70 % of the Pb(II) ions adsorbed on the unmodified husk could be removed by dilute nitric acid. (2 % v/v)

Chen et al. (1990) studied copper ions fixation by two types of peat. These used peat were eutrophic and oligotrophic. During fixation of copper ions by both types of raw peat, there exists not only a decrease of pH but also a release of calcium and magnesium. The cupric nitrate fixation by peat seems to incorporate cation exchange and copper complexation ; the fixation of the same equivalent of copper nitrate but no anion was observed what ever the type of peat. These reactions are dependent on copper concentration applied and also influenced by pH. Besides, complexation reactions become essential when free copper concentration is high such as above 6-14 mM. Isotherm of copper (1 and 20 mm.) fixation on two types of peat showed that cation exchange sites are limited whereas complexation site could not be

saturated over free copper concentration ranging between 0 and 15 mM at equilibrium pH ranging between 2.5 and 4.2, 308 and 101 mmol/kg d.w. for eutrophic and oligotrophic peat. The apparent equilibrium constant for ion exchange with acid-treated peat for various metals binding on both peat sites ranged between 1.1 and 10.8 in 15 mM metallic solutions. The apparent affinity in batch conditions for five elements may be compared according to the apparent global equilibrium constants, ranging between 1.1×10^{-6} . The global affinity of peat metal binding decreases as : Pb > Cu > Ca > Mg, Zn for eutrophic peat and Pb > Ca > Cu, Mg, Zn for oligotrophic peat.

Nakajima and Sakaguchi (1990) used plant wastes to investigate the recovery and removal of uranium from non-saline water and seawater. The seven plant wastes used in this experiment were chestnut outer shell, chestnut inner skin, peanut outer shell, peanut inner skin, onion skin, orange peel and grapefruit peel. The results showed that high abilities to adsorb uranium from non-saline water containing 10 mg dm^{-3} of uranium were found in almost of the plant wastes tested, except peanut outer shell. However, the similar results were found only with chestnut residues in seawater because they contain large amounts of tannin compounds which could be and important role in the accumulation of uranium from solutions by polymerization with formaldehyde, their ability to adsorb uranium was increased, except grapefruit peel. These results suggested that some water-soluble components having high affinity to uranium, such as polyphenolic compounds, were fixed by the immobilization. For selective adsorption studies, the heavy metal ions studied in this experiment were Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and UO_2^{2+} . The selective adsorption of heavy metal ions differs with different species of plant wastes. Uranium and copper were more readily adsorbed by all plant wastes tested than other metal ions. Onion skin, orange peel and grapefruit peel adsorbed copper more readily than uranium. Most of the immobilized plant wastes, except the immobilized onion skin and peanut skin, adsorbed uranium more readily than copper. This orange peel and grapefruit peel tends to increase their uranium adsorption selectivities.

Low and Lee (1991) studied cadmium uptake by the moss, *Calymperes delessertii*, Besch. Batch and column experiment conducted with Cd^{2+} ions. The selective moss substrate was ground and digested by using mixture of concentrated nitric and perchloric acids. All analyses were performed in duplicate using a sequential scanning inductively coupled plasma emission spectrometer (Labtest 710-2000). In batch experiment the equilibrium is achieved in about 20 min, indicating the potential of the moss for rapid removal of cadmium in solution. There is a fall in pH after equilibrium, this would suggest that the mechanism of Cd^{2+} ions binding is ion-exchange in nature of moss. For other cations competitive studies, the order of effectiveness of metal competition with Cd^{2+} ion is $Pb > Cu > Zn > Ni$ ions. The effect of ionic strength, indicating that interaction between Cd and site is mainly electrostatic. From the influence of complexing reagents, for metal/ligand mole ratio of greater than one EDTA does not have any significant effect on the sorption process. In addition, the bed depth service time (BDST) model proposed by Hutchins was successfully applied to the system. The result from this study showed that the moss *Calymperes delessertii*, Besch is efficient in removing cadmium from synthetic solutions which contain simply cadmium and a buffer.

Maranon and Sastre (1991) used apple wastes from apple-juice processing to remove heavy metals in packed beds column. The removal/recovery of copper, nickel and zinc ions in packed bed column was investigated, the variables considered being the influence of chemical treatment, particle size and metal concentration in the solutions percolated. The apple waste can be enhanced by mean of chemical modification, treating with phosphorus (V) oxychloride for phosphatation and with epichlorohydrin for xanthation. The results showed that the CEC of original residues were very low values (0.3-0.4 meq/g.) whereas the treated residues were quite increased of CEC values. The xanthated apple residues (CLX-AR) showed CEC values of up to 1.1 meq/g. and the phosphated apple residues (P-AR) of up to 1.6 meq/g. It is obvious that the value of copper exchange were always higher than nickel and zinc. From swelling results, the swelling of P-AR was very lower than unmodified apple residues, being due to the fact that phosphorus (V) oxychloride can also act as a

crosslinking agent. The CLX-AR showed only a slight decrease in swelling value. The chemical treatment effect results showed that the breakthrough capacity or dynamic capacity (DC) was doubled in the residues CLX-AR and five to eight times higher in the residues P-AR, the maximum increase obtain being for the exchange zinc. The breakthrough capacities increased with the dilution of the solution percolated and with the decrease in particle size. The adsorbed metals were completely recovered with three bed-volumes of 0.5 N. HCl for the elution through packed bed column of the P-AR, AR and CLX-AR.

Shukla and Sakhardande (1991) studied the removing of metal ions by using between dyed and undyed cellulosic materials. The cellulosic substrates were used in this study including cotton fibers, bleached bamboo pulp, jute fibers, and sawdust while the dyestuff named CI Reactive Red 31, CI Reactive Orange 13, and CI Reactive Yellow 18 were also used for investigation. Pb^{2+} and Hg^{2+} samples were analyzed by using complexometric method ; titrated with standard EDTA by using Eriochrom black T ad an indicator. While Fe^{2+} and Fe^{3+} samples were determined with standard 0.005 N. $KMnO_4$ in redox reaction method and sodium acetate-potassium thiocyanate method, respectively. The results showed that the control and dyed substrates adsorbed these metal ions to a significant extent. The adsorption of the salts of Pb^{2+} and Hg^{2+} takes place, to a very small extent, on the undyed substrates as compared to the adsorption of the salts of Cu^{2+} , Fe^{2+} and Fe^{3+} . On dyeing, all the substrates showed higher metal adsorption than undyed substrates even in the case of heavy metals like Pb^{2+} and Hg^{2+} . From these results it may be concluded that the dyestuff has a major role to adsorb heavy metal cations due to chelating formation.

Maranon and Sastre (1992) investigated the preconcentration and removal of traces metals from water by apple wastes. The substrate of apple wastes used in this experiment were unmodified apple residues (AR) and phosphated apple residues (P-AR). P-AR is an apple residues which were chemically modified by mean of a phosphatation reaction in order to improve their physico-chemical characteristics. Very dilute synthetic solutions (10 ppb.) of Cu (II) and Ni (II) ions were percolated

through small column filled with both of substrates. The efficiency of the metal retention has been studied at different pH values and different flow rates. It included of some experiment with the same metals chelated by EDTA. In sea water preconcentration, P-AR have also been used for the preconcentration of copper, nickel, cadmium and lead from cantabrian seawater, comparing the results with those obtained the commercial cationic resin Amberlite IR-120. These apple waste packed columns can be regenerated with a small volume of nitric or hydrochloric acid solution.

From metal uptake studies, the results showed that the quantitative retentions of copper and nickel on to P-AR were found for pH values above 2.5, whereas on AR the optimum values of pH were above 3.5 at a flow rate of 10 ml/min. For solution containing 10 ppb of copper or nickel complexed by EDTA at pH 5 ; the results showed very poor retention when the metal ions were forming complexes. In effect of flow rate studies, the maximum flow rate for obtaining quantitative retention of copper and nickel at pH 5 on AR was 20 ml/min ; the retention decreasing to 58 % at a flow rate of 30 ml/min. However, this high flow rate the retention was practically quantitative on P-AR. A synthetic cationic resin, Amberlite IR-120 was also used preconcentrating heavy metal traces from seawater in order to compare result with P-AR resin. The result showed that the concentration of copper was found to be higher when using P-AR but the concentration of nickel, cadmium and lead was lower. However, it is not significant result.

Low, Lee and Lee* (1993) studied the sorption of copper by using dye-treated oil-palm fibres. Only batch experiments were conducted under various conditions, the parameter being effect of pH, initial concentration presence of other metal cations and chelators. The results showed that the dyed-treated sample had a greater sorption capacity for copper ions. Above pH 4 both the fibres which were natural oil-palm fibre (NOPF) and dyed-treated oil-palm fibre (DTOPF) showed comparable sorption capacities. In competitive uptake studies, the affinity of DTOPF is greater than NOPF. The order of sorption decreases as : $Pb > Cu > Cr > Ni$. For effects of chelators the effectiveness of the fibres in removing copper from wastewater must be assessed

critically if strong chelators are present such as Salicylic acid, nitrilotriacetic acid and ethylenediamine tetraacetic acid, depending on range of their $\log K_1$ values. A comparative study of the fibres in removing heavy metals from electroplating wastes was conducted. The results showed that DTOPF could be used in the preliminary stage to remove some of the metals, especially useful for copper.

Tan, Ooi and Lee (1993) used coconut husk fibers (CHF) and palm pressed fibers (PPF) to investigate the removal of Cr (VI) from aqueous solution. This experiment was investigated using batch and column techniques. Batch experimental results showed that two hours contact time was assumed suitable for both CHF and PPF because the adsorption curve shows approaches equilibrium after one hour. The optimum pH range for effective Cr (VI) removal was between 1.5 and 5 for CHF and between 1.5 and 3 for PPF. From the adsorption isotherm, the adsorption capacities of CHF and PPF were estimated to be 29 and 14 mg Cr g⁻¹ substrate at pH 2.05. These results showed that CHF appears to be a better substrate than PPF. In column experimental results, breakthrough curves of various column containing PPF were obtained for various flow rates and bed depths. These results were compared with Hvtchin 's model for adsorption column. This model introduced a bed depth service time (BDST) model which could be used to calculate the effects of varying feed concentrations and flowrates in an adsorption system. The various pack column can be regenerated at least 4 times without affecting the column 's performance by using either 0.05 M. NaOH or 0.1 M. HNO₃ as eluent. It was demonstrated from adsorption-desorption curves. In land fill studies, The results of breakthrough curves of various column containing mixed media of CHF or PPF in soil system showed that both substrate could also be used as barriers in the landfill to enhance the immobilization of Cr (VI) in leachates.

Chawakitchareon et al. (1995) investigated the total capacities for heavy metal removal of acid treated, carboxymethyl, sulphoethyl and crosslink-xanthate resins made from water hyacinth and bagasse. The heavy metals to be studied were copper, nickel and zinc. The experiment was carried out using the

column technique with a 20 cm. Height packed bed of resin. Synthetic wastewater, pH about 5.0, containing heavy metal about 5, 10, 20, 50 mg/l was percolated through the column at a rate of 3 bed volumes/hr. The variables being considered were the influence of chemical treatment and the heavy metal concentration in the wastewater. The experiment results showed that the cation exchange capacities were 0.686-0.809 meq/g, carboxymethyl, sulphoethyl and crosslink-xanthate resins made from water hyacinth, and 0.065-0.086 meq/g and 0.052-0.056 meq/g respectively for acid treated and carboxymethyl resins made from bagasse. The values for copper exchange were always higher than for zinc and nickel for acid treated and carboxymethyl resin. For sulphoethyl and crosslink-xanthate, the values for zinc exchange were always higher than for nickel and copper. The dynamic capacities increased with the dilution of wastewater percolated. The regeneration were completed recovery of metal with 2-3 bed volumes of 0.5 N of each regenerant.



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