UNIVERSITY OF PORT HARCOURT

AGRO WASTES UTILIZATION: THE CHEMIST'S INPUT

An Inaugural Lecture by ONYEWUCHI AKARANTA

INAUGURAL LECTURE SERIES No. 55 4 OCTOBER, 2007

DEDICATION

To Wealth Creation from Wastes and a Pollution Free Environment

The Vice – Chancellor, Sir,

Members of the Governing Council here Present,

Deputy Vice - Chancellors,

Registrar and other Principal Officers,

Provost, College of Health Sciences,

Dean of Graduate School,

Deans of Faculties,

Distinguished Colleagues,

Great Students of Unique Uniport,

Ladies and Gentlemen of the Press,

My Lords Spiritual and Temporal,

Ladies and Gentlemen.

INTRODUCTION

It is with a deep sense of humility that I follow the noble tradition of academia by delivering the 55th Inaugural Lecture of the University of Port Harcourt. Professor C. M. Ojinnaka (FCSN, FICCON), an erudite Professor of Chemistry delivered the first Inaugural Lecture from the Department of Pure and Industrial Chemistry in 1998. I appreciate his contributions

towards the advancement of Chemistry and the support he had given me in my academic pursuit / career.

Mr. Vice-Chancellor, Sir, barely four weeks of your assumption of office in 2005, you concluded my professorial assessment that started in 2002. I am sincerely grateful and proud to announce to you that this is the second inaugural lecture from the Department of Pure and Industrial Chemistry, but the first in Industrial Chemistry discipline.

An inaugural lecture affords one the opportunity to share with the distinguished audience ones academic achievements, concerns and articulate ones expectations in non technical and professional language. Mr Vice –Chancellor, Sir, the topic of this lecture is, **Agro Wastes Utilization: The Chemist's Input**.

Chemistry In Agriculture

Methods of cultivating the soil, harvesting crops, raising livestock have changed with time. Today's agriculture relies on a wide range of fertilizers, fungicides, pesticides, herbicides and hormones. The benefits of using these chemicals in modern agriculture include increase in agricultural produce and reduction in crop losses. Increase in agricultural produce leads to a corresponding increase in agricultural wastes, which have the potentials of causing environmental pollutions. Therefore, the need to research on agricultural wastes utilization culminated to the topic of today's discourse, "Agro Wastes Utilization: The Chemist's Input".

The agricultural commodities of interest include: the fruits and seeds, bulbs, nuts, grains (corn, sorghum, millet, rice), tubers, sugarcane etc. These agricultural commodities produce large volume of collectable wastes during harvesting and processing.

Agro-Wastes Identification

Agricultural wastes could be grouped as follows: crop, animal, lignocellulosic and carbohydrate residues (Detroy and Hesseltine, 1978).

Agricultural	Residues	Potential use of Residues
Produce	Generated	
Corn, Wheat,	Straw, Stalks	Animal feedstuff, Fuel,
Rice	Husks, Cobs	Silica, Furfural, Compost, Chemical Feedstock
Cattle	Animal Waste e.g. Blood, Bone, Dung	Animal glue, Animal Feed Supplement, Methane Production, Activated Carbon, Manure
Sugarcane	Bagasse	Fuel, Furfural, Animal feed Particle Boards, Biopolymers
Fruits and Vegetables	Seeds, Peels, Husks	Animal and Fish Feed, Fuel Compost and Fermentation
Potatoes	Starch Waste Water	Sugars and Alcohols, Single Cell Protein
Oils and Oilseeds	Shells, Husk, Fibres, Sludge, Press Cake	Animal feed, Fertilizers, Fuel, Activated Carbon, Furfural,
Coconut	Coir Dust, Fibres, Shell.	Resins, Pigments, Fillers, Mats, Activated Carbon, Tanning Materials.

Table 1: Residues from the Processing and Harvesting of Some Agricultural Produce.

Table 1 shows a broad range of agricultural residues (wastes) usually produced from harvesting and processing of agricultural commodities. All crops produce collectable residues, however the collection process may increase the cost of utilization. Sugarcane, fruits, grains and nuts are crops that generate significant amount of residues at the processing sites. Bloods and bones from abattoirs and livestock wastes are animal residues of importance.

INDUSTRIAL RAW MATERIALS AND PRODUCTS FROM AGRO-WASTES

A raw material is that primary input which when subjected to some chemical and/or physical processes becomes converted to a valuable product that can be exchanged for money (Fasina, 1985). To a palm oil mill, palm fruit is the raw material, while palm oil, palm kernel and palm fruit fibres are end products. The palm kernel is the raw material for the production of palm kernel oil, which is subsequently used for the production of vegetable oils and soaps. In the same vein, palm fruit fibres are used for the production of furfural (Saad *et al*, 1978). Furfural is a raw material for the production of phenol – furfural resins usually used in the production of some plastic wares. An end product of one industry may become the feedstock (raw material) for another industry.

Industrial raw materials are either of mineral, animal or vegetable origin. Mineral sources include petroleum, ores, and coal, while animal sources are: fats, hides and skins, bloods and bones. Vegetable sources include vegetable oils, timbers, cereals, tubers and nuts. The vegetable sources occupy an important position in the provision of industrial raw materials. This is because they are readily renewable resources. The rapid increasing world population, high demand for industrial raw materials and the realization that the supply of raw materials from mineral sources is finite have given significance to the renew-ability of raw materials.

Although vegetable sources of raw materials are readily renewable, the utilization of agricultural residues as sources of industrial raw materials will help in sustaining the high demand for industrial raw materials and reduce the cost of the end products. It will also reduce the environmental pollutions usually caused by indiscriminate dumping of such wastes. In the University of Port Harcourt, value – added products have been obtained from agricultural wastes through the application of chemical processes.

Crop Residues

These are residues produced mainly during the processing of crops. They include husks, red onion and peanut skins, corn cob, palm fruit fibres etc.

Rice Bran Oil

The production of white rice goes hand in hand with the production of its by-product known as rice bran, the brown skin that covers the rice grain. It is the most valuable "waste" of the rice milling industry due to its high industrial and nutritive potentials. It contains about 15-25% oil. In view of the fact that the vegetable oil industry in developing countries has severe shortage of raw material, rice bran appears to be well on its way to becoming a recognized raw material for the production of vegetable oils and protein based animal feeds (UNIDO, 1985).

Orange Seed and Peel Oils

All seeds contain oils (Ajiwe et al, 1997), but the quantity and the chemical constituents of the oil in any seed determine its commercial value. Orange seed oil has been extracted with feint, a distillery waste liquid containing mainly C₂-C₄ alcohols (Akaranta and Anusiem, 1996). The oil is made up of the following fatty acids: palmitic acid 5.8%, stearic acid 4.0%, oleic acid 56.0% with traces of linoleic acid and has an iodine value of 108. It is a semi-drying oil and has been used in the formulation of surface coatings (Emeledor, 1991). If a fresh orange peel (the epicarp) is squeezed near a flame it ignites. This is due to the presence of some volatile and flammable compounds in the peel. The compounds include: limonene, myecene, alpha-terpineol, aliphatic alcohols and aldehydes (Formacek and Kubeczka, 1982) and are collectively called essential oil. The oil has been extracted using steam distillation aPnd expression methods (Masada, 1976). Orange peel oil is used as fragrance in perfumes and to flavour beverages, ice cream, candy and chewing gum (Nwobi et al, 2006).

Resins

Coconut coir dust (Tuason and Reyes, 1959), red onion skin (Odozi *et al*, 1984) and peanut skin (Stansbury *et al*, 1950) are agricultural wastes known to contain flavonoids. The flavonoids are easily extracted with hot water, dilute alkaline solutions or polar solvents such as acetone and alcohols. The flavonoids are phenolic in nature and for that reason have been used in the production of phenol-aldehyde type of condensation resins.

Wood varnishes have been developed using the condensation products of red onion skin extract and aldehydes (Odozi *et al*, 1985). Excellent oleoresinous varnishes have also been produced from copolymer resins of peanut skin extract, aldehydes and cashewnut shell liquid (Akaranta *et al*. 1994). The adhesive properties of resins obtained by copolymerising red onion skin (Akaranta *et al*, 1996; Odozi and Agiri, 1986; Odozi *et al*, 1986), coconut coir dust (Akaranta and Wankasi, 1996) or peanut skin (Chen, 1982) extracts with aldehydes and synthetic phenols have been reported. The results obtained showed that the resins exhibited adhesive properties that satisfied International Standards Organization (ISO) requirements for exterior grade adhesives.

Antioxidants and Inhibitors

Flavonoids of red onion and peanut skin extracts have been evaluated as antioxidants for vegetable oils and as inhibitors for unwanted polymerisation of some vinyl monomers. The extracts were effective as antioxidants in vegetable oils but at slightly higher concentrations when compared with commercial phenolic antioxidants (Akaranta and Odozi, 1986; Akaranta, 1994). Similar trends have been reported with the extracts when evaluated as inhibitors for the polymerisation of vinyl monomers (Akaranta, 1999).

Dyes and Pigments

It has been reported that red onion skin extract contains polyphenols of the flavonoid type (Odozi *et al*, 1984) which are capable of directing nucleophilic reactions to the ortho and para positions (Akaranta and Odozi, 1985). The extract has been coupled with diazonium salts to give azo dyes of various colours (Akaranta and Efanga, 1997).

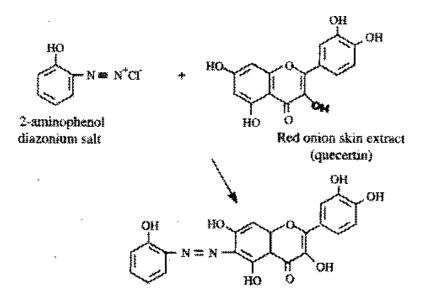


Figure 1: Reaction of Red Onion Skin Extract with a Diazonium Salt

The azo dyes were formed in-situ in cotton fabrics as azoic dyes and applied to polyester fabrics as disperse dyes. They were found to produce not very bright colours on polyester fabrics but brilliant colours on cotton fabrics. The washfastness tests of the azo dyes on both cotton and polyester fabrics were satisfactory. The azo dyes with suitable chelating groups have been used to produce azo-metal complexes suitable for the pigmentation of alkyd resins in paint formulation. (Akaranta, 1996).

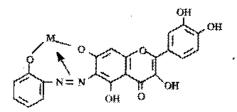


Figure 2: A Red Onion Skin Extract Azo Metal Compound

Tanning Agents

Tannin molecules of vegetable origin have been used since ages for the conversion of hides and skins into leather. The most widely used tannin molecules are the condensed types usually found in minosa, quebracho and mangrove bark extracts. The later part of the 20th century witnessed a shift to the use of synthetic tanning agents based on phenols due to the emergence of petrochemicals, which are readily available sources of synthetic phenols. The ever increasing cost of petrochemicals, particularly phenols, has again stimulated interests in the search for effective, cheap and renewable sources of condensed tannins. Among the renewable sources, the most convenient source to explore is the agricultural wastes. Peanut skin, coconut coir dust and red onion skin extracts and their derivatives have been found to possess good tanning properties (Akaranta, 1999).

Lignocellulosic Residues

They are those agricultural residues that contain cellulose, hemicellulose and lignin as their major components. These include such residues as sugarcane bagasse, orange mesocarp, corn cob, peanut husk, palm fruit fibres, melon seed shell etc.

Particle Boards

The most commonly available type of industrial wood products such as particle boards are made from wood chips obtained from forest thinnings, timber and saw mill wastes. However, the declining potentials of our forest due to deforestation makes it difficult to meet up the rapidly increasing demand for particle boards in future. The situation has been further aggravated by the rapid increase in the population of developing countries. Therefore, in order to meet the raw material requirements for particle board production, agricultural residues appear to be the most attractive and promising source. (Akaranta, 2000). In this regard, corn cob, sugarcane bagasse and peanut husk have been used as sources of lignocellulosic materials for chips, while red onion and peanut skins have been used as sources of phenols for adhesives in the production of particle boards (Odozi *et al*, 1986). Performance evaluation results of the boards showed that boards produced using agricultural residues were superior to the commercial grade boards made from wood chips and usually bonded with modified urea-formaldehyde resin adhesives.

Jute stick which is obtained as an agricultural residue from jute cultivation has three major components: α cellulose 41%, pentosan 22% and lignin 23%. Lignin recovered from the spent liquor of soda pulping of jute stick has been used for the production of lignin – phenol formaldehyde resins. The resins were then used as adhesives to produce particle boards from jute stick chips (Roy *et al*, 1989).

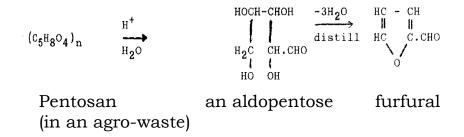
Activated Carbons

Dyes and pigments in some industrial effluents are often discharged into receiving rivers and their high degree of colour is easily detectable and detracts the aesthetic value of a river. The removal of these dyes and pigments from such effluents in an economic manner is still posing some challenges, even though a number of adsorption techniques have been developed for their removal from effluents (Robinson *et al*, 2001).

In order to reduce the cost of treating industrial effluents, coconut shell, an agricultural residue has been converted into decolourising carbons and successfully used to remove dyes and pigments from effluents (Singh and Raman, 1976). Palm Kernel shell has also been used for the production of activated carbons suitable for the removal of dyes from solutions (Odozi and Akaranta, 1986). Granular Activated carbons (GACs) have been produced from other agricultural residues (Johns and Marshall, 1994). The GACs are capable of qualitatively removing metal ions from effluents. Therefore, it is now possible to produce from agricultural residues activated carbons that are capable of removing dyes, pigments and metal ions from industrial effluents.

Furfural

Pentosan containing agricultural residues yield furfural upon treatment with mineral acids.



Corn cob, rice and peanut husks are lignocellulosic residues that readily yield furfural when subjected to acid hydrolysis (Dunlop, 1966). Saad *et al* (1978) optimised the conditions for the formation of furfural by acid hydrolysis of palm fruit fibres. The pentosan containing agricultural wastes can be pulled together and used for the commercial production of furfural. The industrial uses of furfural have been reviewed (Kovaly, 1982).

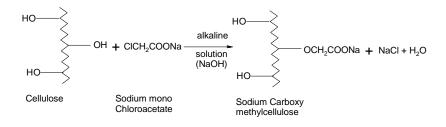
Animal Feeds

One of the major problems in the utilization of lignocellolusic residues for animal feed production is the difficulty usually encountered when digesting such residues using chemical and/or biochemical processes. Mild pre-treatment of such residues with steam, acid or alkali helps in loosening the crystalline lignocellulosic structures, thus improving the utilization of the treated substrate by micro-organisms, with an increase in the nutritive value of the residues (Gupta *et al*, 1986). Agricultural residues might provide greater portion of animal feed supply if the problem of making such residues more digestible for animals is overcome.

Alkali treatment has shown promise in making crop and wood residues more digestible for animals. In addition to its effect on digestibility, when ammonia is used for pretreatment, it provides nitrogen for microbial protein synthesis and effectively inhibits spoilage of the feed during storage (Fontenot, 1980).

Carboxymethylated Cellulose

Cellulose isolated from orange mesocarp, a lignocellulosic residue, has been carboxymethylated to a degree of substitution of 0.45-0.63 and used in the formulation of drilling mud (Akaranta and Osuji, 1997).



Cellulose has little tendency to swell in water, but the introduction of carboxymethyl groups into cellulose molecule through the reaction between alkali cellulose and sodium monochloroacetate to produce carbxymethyl cellulose (CMC), increases the tendency of cellulose to swell in water. Carboxymethylated cellulose, the sodium form, swells in cold water to give a highly viscous gel.

Carboxy methylated cellulose has applications in surface coatings, pharmaceutical, detergent and cosmetic industries. The use of cellulose isolated from agricultural residues for the production of carboxymethylated products would reduce the rate of exploitation of established sources of cellulose. It will also have a direct cost reduction effect on the products. Corn cob, rice and peanut husks have been used as sources of cellulose for the production of carboxymethylated cellulose and related products (Akaranta, 1996).

Carbohydrate Residues

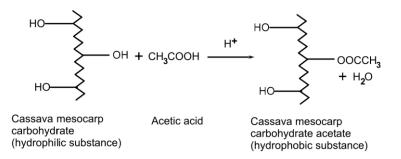
Cassava, which contains mainly carbohydrates, is leading the way in the international drive to promote the use of bio-fuels to supplement and reduce world dependence on fossil fuel as source of energy. Food and Agricultural Organization (FAO) recent findings indicate that with the price of petroleum running at \$ 60 or higher per barrel, it is quite profitable to convert cassava into bio-fuel for use separately or as a mixture with fossil fuel for energy (FAO 2007).

The presidential initiative on cassava has increased the level of cassava production in Nigeria leading to a corresponding increase in cassava residues to the point that cassava is fast becoming an agricultural commodity with the highest volume of wastes in Nigeria.

Cassava peel, the mesocarp, which is a major residue emanating from the processing of cassava tubers has been used to raise pigs, sheep and goats (Montilla, 1977; Adebowale, 1985; Fetuga and Tewe, 1985; Tewe 1987). The results obtained by using such an agricultural waste in feeding livestocks were not very encouraging due to its high hydrocyanic acid content (Conn, 1979). Fermented cassava peel has been reported as a good poultry feed when formulated (Ofuya and Obilor, 1993).

Similarly, carbohydrate residues obtained during the conversion of cassava pulp into the edible form "garri" has been carboxymethylated to give carboxymethylated starch (CMS) and subsequently used in the formulation of latex emulsion paints (Odozi *et al*, 1986).

Cassava mesocarp carbohydrate and its chemically modified form have been used as fillers in low density polyethylene to produce plastic films that are biodegradable (Akaranta and Oku, 1997).



The modification of the cassava mesocarp carbohydrate to its acetate form made it hydrophobic and therefore more compatible with the polyethylene. Such biodegradable plastic films are environment friendly.

Carbohydrate residues are the major raw materials for the production of biopolymers and single cell protein (Shipman and Fan, 1978).

Animal Residues

accumulation animal residues The of causes severe environmental pollution. The utilization of the residues other than as manure has proceeded mainly through biological and thermochemical processes. The biochemical process produces primarily sugars and alcohols. while the anaerobic fermentation produces methane.

The thermochemical process involves dehydration and hydrocarbonation to yield char (carbon), oil and gaseous fuels. The greatest handicap of the thermochemical process is the large amount of moisture that needs to be removed to make the process feasible.

Dried animal blood, which is sometimes used as organic fertilizer, contains about 12% nitrogen with traces of phosphorous, iron, copper and other minerals. It is often mixed with superphosphates and used as compound fertilizer (Divakaran, 1982). The nutritive value of animal bloods from abattoirs has been reported (Neelakantan, 1975) and used primarily as a source of protein (Halliday, 1975).

Blood char is a form of activated carbon from animal blood. It serves as an adsorbent, capable of adsorbing gases many times its volume. Blood char selectively adsorbs colouring matters from solutions under specified conditions and is thus used as industrial decolourant, particularly in the sugar industry, and in gas masks (Mattson and Mark, 1971; Smisek and Cerry, 1977).

Animal blood has been used for the production of blood albumin (Divakaran, 1982). It is usually obtained from coagulated animal blood. Commercially available blood albumin usually called dried blood serum is a cheap substitute for egg albumin powder. Blood albumin is often used to obtain lighter coloured protein finishes for leather and gives high lustre without altering the breathing property, unlike synthetic resin finishes that block the pores in leather. Blood albumin is soluble in water and in suitable concentrations provides highly tacky solutions that give firm adhesive properties. The substrate joints that are bonded with blood albumin based adhesives can be made water resistant by heat or formaldehyde treatment.

AGRO-WASTES IN EFFLUENTS TREATMENT

The input of metal ions from effluents, particularly from processes, has been of much concern industrial to environmental protection agencies because of the possible ecological consequences of discharging such effluents into receiving waters. Metal poisoning from wastewater occurred in Minamata Bay in Japan in 1953 when a factory using mercury compounds as raw materials discharged its effluents into the surrounding river. This resulted in the death of many people who consumed fish from the river (Ui,1992). Environmental protection agencies such as Federal Environmental Protection Agency (FEPA) and United States Environmental Protection Agency (USEPA) have put in a lot of efforts to set the limits of various toxic metals in effluents before they are discharged into the receiving environment.

Industrial effluents treatment systems employ a variety of physical and / or chemical methods in treatment plants. (Azbar *et al* 2004). The methods include chemical precipitation, electro deposition, cementation, ultra filtration or reverse osmosis, ion exchange and activated carbon adsorption. Cation exchange resins are particularly effective in removing metal ions and other positively charged species from aqueous solutions. Activated carbons are finding increased use as metal ions scavengers because of the high cost of cation exchange resins derived from petroleum resources. The need for effective and economic removal of toxic/valuable heavy metal ions and organic pollutants in industrial effluents has resulted in a search for unconventional methods and materials that might be useful in industrial effluents treatment (Kumar and Dara, 1981).

Agricultural residues, especially those from widely grown commodity crops, are quite inexpensive and have been shown to possess natural adsorbent properties (Waiss *et al*, 1973; Young *et al*, 1973, Waiss and Friedman, 1972). The adsorbent properties of the unmodified agricultural residues are due to the presence of carboxylic, phenolic and hydroxyl groups in the substrates. However, the sorption capacities of agricultural residues can be enhanced by chemical modifications.

Alkali Treated Agricultural Residues

Azab and Peterson (1989) reported that alkali treated peanut hull removed 99% cadmium ion from solution in column applications. This is an improvement over the untreated peanut hull which removed 68% cadmium ion. Akali treatment of crystalline lignocellulosic agricultural residues helps in loosening the crystalline structures thus improving the exchange capacities of the treated substrates. The results obtained with the alkali treated peanut hull in the uptake of cadmium ion is an indication that other agricultural residues with similar chemical compositions as peanut hull would be expected to show improved exchange capacities when treated with alkalis. Hence increasing the number of agricultural residues, that can effectively remove metal ions from industrial effluents.

Polymerised Agricultural Residues

Using polymerised agricultural residues in effluents treatment, Kumar and Dara (1981) reported that formaldehyde polymerized onion skin is highly effective for binding heavy metal ions from aqueous solutions. The exchange capacity of the substrate for a number of the metal ions studied was well above 1 meq/g. Similarly, Randall et al (1978) reported that formaldehyde polymerised peanut skin can quantitatively remove lead, copper, mercury and cadmium from industrial effluents. The function of formaldehyde in the process is to form a high molecular weight compound with the tannin molecules in the peanut skin. This prevents the tannin molecules from leaching out of the substrate. When the substrate is sulphonated, the tannin molecules provide the base for the introduction of sulphonic acid groups into the tannin aromatic nuclei. The sulphonic acid and the hydroxyl groups are responsible for the enhanced exchange capacities of formaldehyde polymerized and sulphonated agricultural residues.

Odozi and Emelike (1985) reported that polymerised red onion skin tannin/corn cob powder produced good cation exchange resins for the removal of heavy metal ions from aqueous solutions. The ion exchange capacity of the corncob based resins was above 1 meq/g, a value in keeping with commercial ion exchange resins. Therefore resins derived by polymerising tannin molecules and corncob can serve as effective substitutes for commercial cation exchange resins. The corn cob serves to produce the furfural which is then polymerises with the red onion skin tannin molecules to form the resins.

The batch experiments carried out using the corn cob hydroxylate - red onion skin tannin resins showed that the final pH is always less than the initial pH. Accordingly, it was concluded that the corn-cob-red onion skin product acts as an acidic ion - exchanger since H⁺ ions are released into the solution as the metal ions are bound to the substrate. Thus, the equilibrium attained corresponds to a solution of lower pH than that of the original test solution. Similar observation was reported by Randall et al (1975) while using formaldehyde polymerised peanut skin tannin resins to remove copper ions from aqueous solutions. However, for the metal salts of acetate anion, no reasonable lowering of pH was observed owing to the buffering effect of the acetate ion. As expected for benzene sulphonic acid cation exchangers, the ion exchange process of various divalent metal ions from their solutions onto the

substrate is in the following decreasing order: $Pb^{2+} > Cd^{2+} = Ni^{2+} > Zn^{2+} > Ca^{2+} > Hg^{2+} > Mn^{2+}$. Some of the metal ions studied showed an unusual ion exchange pattern. This may be due to the extent of dissociation of their salts and probably due to the degree of stability of the high molecular weight formed between the metal ion and the tannin molecules of the red onion skin (Odozi and Emelike, 1985).

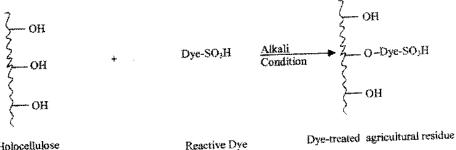
Composite Polymerised Agricultural Residues

Most studies on the use of agricultural residues in the treatment of industrial effluents have treated each agricultural residue type as an independent entity. As a result many agricultural residue concentrations are deemed too small to support commercial waste conversion processes. However, if agricultural residues from dissimilar sources are combined the problem may be overcome. To this end, Odozi *et al* (1985) developed composite resins of corncob, sawdust, red onion skin and formaldehyde with excellent exchange capacities for metal ions in effluents.

The use of composite polymerised agricultural residues in the treatment of industrial effluents will lead to the development of a number of cheap and effective value – added products for the removal of toxic metal ions and organic pollutants in effluents.

Dye Treated Agricultural Residues

Rice husks treated with different reactive dyes were effective in removing various metal ions in both batch and column processes (Suemitsu *et al*, 1986). Coconut pollens treated with reactive dyes have been reported to show similar enhanced removal of metal ions from industrial effluents (Agiri *et al*, 2006). Low *et al* (1993) studied the effect of pH, initial concentrations, presence of other metal ions and chelating agents on the exchange capacity and efficiency of dye – treated oil palm fibres in removing metal ions from electroplating effluents. The results showed that reacting oil palm fibres with reactive dyes has a pronounced effect on metal ion sorption properties of the substrate.



Holocellulose (in an agricultural residue)

Figure 3: A Schematic Representation of a Dye – Treated Agricultural Residue

The sulphonic acid group in the dye molecule is largely responsible for the removal of metal ions from the effluents.

Other Chemically Modified Agricultural Residues

Okieimen and Okundaye (1989), reported the use of thiolated corn cob in the removal of significant quantities of cadmium and copper ions from aqueous solutions. The results showed that the metal ion binding capacity of corn cob was significantly improved by the incorporated thiol groups. Similarly, EDTA – modified groundnut husk has been used for the removal of cadmium and lead metal ions from solutions (Okieimen *et al*, 1991). However, the binding capacity of the EDTA – modified groundnut husk was lower than those for commercially available cation exchange resins.

Roberts and Rowland (1973) reported the removal of mercury ion from aqueous solutions using nitrogen – containing chemically modified cotton linters. In order to improve the physical stability of soyabean hull and sugar beet fibre, Lazzlo and Dintzis (1994) crosslinked each of the agricultural residues with epichlorohydrin to produce high binding resins for calcium ion. Apple wastes treated with phosphorous oxychloride showed improved efficiency in removing heavy metal ions from solutions (Maranon and Sastre, 1991).

Granular Activated Carbons from Agricultural Residues

Granular activated carbons (GACs) are usually used for the removal of organics from effluents. Presently, they are also being used as metal ions scavengers because of the high cost of cation exchange resins derived from petroleum resources. GACs are usually produced from coals (Mdoe and Mkayula, 1996). Since petroleum and coals are non-renewable resources and being depleted worldwide, there is the need to use renewable resources such as agricultural residues as cheaper alternatives to the non-renewable resources. Periasamy *et al* (1991) carbonised peanut shells and found the resultant activated carbons to be more efficient in removing mercury and chromium (VI) ions from effluents than commercially available activated carbons.

Palm kernel shell has been successfully carbonised and the resultant product used for the adsorption of dyestuffs from aqueous solutions (Odozi and Akaranta, 1986). The effects of carbonisation (activation) temperatures and oxidation conditions were compared with respect to the adsorptive properties of the resultant carbons. The adsorptive capacity of the carbons increased with increase in activation temperature from 600[°]C to 1000[°]C and the nitric acid oxidized carbons exhibited better adsorption properties than those oxidized with potassium permanganate. Yield of the activated carbons decreased when activation temperature is increased beyond 800[°]C. An activation temperature of 800[°]C was found to be the optimum temperature for the production of high yield and effective activated carbon from palm kernel shell.

RECOMMENDATIONS

It is customary on an occasion of this nature to make some recommendations based on one's experiences and research findings. From the studies so far carried out on agrowastes utilization, it is clear that agricultural wastes can play important roles as sources of industrial raw materials and in the treatment of industrial effluents.

- In this era of rising cost of petroleum and its products, the use of renewable resources such as agricultural wastes as sources of industrial raw materials for the production of some industrial products is recommended.
- ii) Indiscriminate discharge of industrial and domestic wastes into the receiving environment has been implicated as the major source of the high concentrations of some heavy metal ions in our ecosystem. The Federal and State Governments should device means of controlling the indiscriminate discharge of untreated industrial and domestic wastes

into our environment. The guidelines are in place but the political will to enforce them is lacking.

- iii) As a result of the proven effectiveness of some chemically modified agro-wastes products for the removal of heavy metal ions from industrial wastewaters, I, therefore, recommend such products for inplant cost effective treatment of effluents before their discharge into the environment.
- iv) A post graduate programme in Environmental Science in the University of Port Harcourt should be introduced. This will enhance further research in agricultural and industrial wastes utilization and disposal. These wastes pollute the environment if not utilized or properly disposed of.
- An Intellectual Property Right Unit should be established in the University of Port Harcourt for the patenting of innovative research outputs.

vi) The volume of our yearly publications is an indication that we are carrying out researches in the University of Port Harcourt, but we do not have records of how much money is spent on research. The University should have records of the amount of money that is spent on research yearly. Parents and guardians sponsor research projects at the undergraduate and graduate levels, and there is no record of the amount of money spent.

CONCLUDING REMARKS

Mr. Vice – Chancellor, Sir, the three main functions of an academic are: Teaching, Research and Service to the Community.

In the past twenty-five years, I have taught a number of students in this University. A few of my former students are in this audience as lecturers in various institutions of higher education in Nigeria. In the next few years some of them will be privileged to deliver their inaugural lectures as they are witnessing today.

My research activities, the production of value added products from agro and industrial wastes, constitute the main subject of this lecture. In the course of my research work, I have published a number of journal articles, supervised one doctoral and over fifteen master's graduates. I am currently supervising three doctoral and two master's students.

In the area of community service, I have served as Head of Department in addition to serving in various committees at departmental, faculty and university levels. Outside of the University, I have contributed my quota in various ways in my local community, professional bodies and the church.

Mr. Vice-chancellor Sir, I am proud to say that I have paid my dues in the three main functions of an academic and if any one wants to create wealth from wastes let him consult an Industrial Chemist.

Distinguished ladies and gentlemen, I thank you all for listening.

Onyewuchi Akaranta.

Professor of Industrial Chemistry

REFERENCES

- Adebowale, E.A (1985), Non –conventional Feed Resources in Nigeria, *Nig. Food J.* 3, 181 -189.
- Agiri, G.O., Akaranta, O. and Ajayi, I.O. (2006), Studies on Dyed Coconut (Cocos nucifera) Pollens for Removal of Cu(II) and Zn(II) Ions form Aqueous Solution. *African Journal of Biotechnol*. 6(7), 929-932.
- Ajiwe, V. I. E, Okeke, C. A., Nnabuike, B., Ogunleye, G. A., and Elebo, E. (1997) Applications of Oil Extracted from African Star Apple, Horse Eye Bean and African Pear Seeds, *Bioresource Technol* 59, 259 – 261.
- Akaranta O., Nwaneri, O. and Nworgu, S., (1994) Oleoresinous Wood Varnishes from Modified Extracts of Red Onion and Peanut skins. J. Appl. Sci. Manufact. Technol. 1, 41 -49.
- Akaranta, O. (1994), Food Waste Extracts as Antioxidants for Rubber Seed Oil, J. Appl. Sci. Manufact. Technol., 1, 33-44.
- Akaranta, O. (1996), Raw Materials for Surface Coatings from Agricultural Wastes, *Surface Coatings International*, 79(4) 152 -154.
- Akaranta, O. (1999) Agro Based Raw Materials in Nigeria for the Chemical Industry, Timi Hyacinth Enterprises, Lagos.

- Akaranta, O. (2000) Production of Particle Boards from Bioresources., *Bioresource Technol.*, 75, 87-89.
- Akaranta, O. and Efanga, D. E. (1997) Dyeability of Textile Fibres with Azo Compounds Prepared by Coupling Red Onion Skin Extract with Diazornum salts, *J. Natn. Sci. Coun. Sri Lanka*, 25(2), 121 -126.
- Akaranta, O. and Odozi, T. O. (1986), Antioxidant Properties of Red Onion Skin Tannin Extract, *Agricultural Wastes*, 18,299-303.
- Akaranta, O. and Oku, G. (1997), Some Properties of Cassava Mesocarp Carbohydrates – low Density Polyethylene Blends, *Carbohydrates Polymers* 34, 403-405.
- Akaranta, O. and Osuji. L. C. (1997), Carboxymethylation of Orange Mesocarp Cellulose and its Utilization in Drilling Mud formulation, *Cellu. Chem. Technol.* 31, 193-198.
- Akaranta, O. and Wankasi, D. (1996), Effects of Kaolin Clay on the Bond Quality of Coconut Coir Dust Tannin – Formaldehyde Based Wood Adhesives, J. Natn. Sci. Coun. Sri lanka, 24 (2), 127 -132.
- Akaranta, O. Donbebe, W., and Odozi, T. O. (1996), Plywood Adhesives Based on Red Onion Skin Extract Modified with Cashewnut Shell Liquid *Bioresource Technol.*, 56, 279 -280.

- Akaranta, O. and Anusiem, A.C. I. (1996), A Bioresource Solvent for Extraction of Seed Oils, *Industrial Crops and Products*, 5, 273 – 277.
- Azab, M.S and Peterson, P.J. (1989), The Removal of Cadmium form Water by the Use of Biological Sorbents, *Water Science and Technol.*, 21, 1705-6.
- Azbar, N., Yonar, T., and Kestioglu, K. (2004), Comparison of Various Advanced Oxidation Processes and Chemical Treatment Methods of Effluents, *Chemosphere*, 55(1), 35-43.
- Chen. C.M. (1982), Effects Formaldehyde Concentration on the Bond Quality of Peanut Hull Extract Copolymer Resins. *Ind*. *Eng. Chem. Prod. Res. Dev.* 21, 450-456.
- Conn, E.E.(1979) Cyanogenic Glycosides. In Biochemistry of Nutrition, Vol. 27. A. Neuberger and T. H. Jukes, eds., University Park Press, Baltimore, p. 21.
- Detroy, R. W., and Hesseltine, C. W. (1978), Availability and Utilization of Agricultural and Agro-industrial Wastes; *Process Biochemistry* 9, 2 -5.
- Divakaran, S. (1982), "Animal Blood Processing and Utilisation", FAO *Agricultural Services Bulletin* No. 32, Rome.
- Dunlop, A. P. (1966), *Othmer Encyclopedia of Chemical Technology* 2nd ed. Vol. 6. Interscience Publishers, New York. p243.

- Emeledor, A. (1991) "Studies on the Film Forming Properties of Epoxidised Vegetable Oils," M.Sc Thesis, University of Port Harcourt, Nigeria.
- FAO (2007), Consensus at the 66th Meeting of the Committee on Commodity Problems held at the Food and Agricultural Organizations of the United Nations in Rome from April, 23 -25.
- Fasina, A. K. (1985), Industrial Raw Materials, *The Nigerian Banker*, 5(2), 6-8.
- Fetuga, B.L and Tewe, O.O. (1985). Potentials of Agro-Industrial By –Products and Crop Residues as Animal Feeds, *Nig. Food J.* 3, 136-142.
- Fontenot, J. P. (1980) In *Upgrading Residues and Byproducts for Animals* J.T. Huber ed., CRC Press, Boca, Raton p17.
- Formacek, V. and Kubeczka, K. H. (1982), Essential Oils Analysis by Capillary Gas Chromatography and Carbon – 13 NMR Spectroscopy, John Wiley and Sons, New York.
- Gupta, V. K., Prasad, K.S. Bakshi, M.P.S and Langar, P.N. (1986), Improving the Utilization of Agricultural Residues for Animal Feeds. *Agricultural Wastes*, 16, 161–7.

- Halliday, D. (1975), Animal Blood as a Source of Protein. *Process Biochemistry*, 4, 11-13.
- Johns, M. M. and Marshall, W. E. (1994) Abstract of Paper, Am. Soc. Agron. Annual Meeting.
- Kovaly, K.A. (1982), Chemicals from Biomass, *Chemtech*, 8, 486-488.
- Kumar, P. and Dara, S.S. (1981), Binding Heavy Metal Ions with Polymerized Onion Skin, *Journal of Polymer Science*, 19, 397-402.
- Lazzlo, J. A. and Dintzis, F. R. (1994), Crop Residues as Ionexchange Materials: Treatment of Soyabean Hull and Sugar beef Fibre (pulp) with Epichlorohydrin to Improve Cation Exchange Capacity and Physical Stability., *Journal of Applied Polymer Science*, 52, 531-8.
- Low, K.S., Lee, C.K and Lee, K.P. (1993), Sorption of Copper by Dye-Treated Oil Palm Fibres, *Bioresource Technol.*, 44, 109-112.
- Maranon, E. and Sastre, H. (1991), Heavy Metal Removal in Packed Beds Using Apple Wastes; *Bioresource Technol.*, 38, 1-6.
- Masada, Y. (1976), *Analysis of Essential Oil by Gas Chromatography and Mass Spectrometry*, John Wiley and Sons, New York.

- Mattson, J.S. and Mark, H.B.Jr. (1971). Activated Carbon: Surface Chemistry and Adsorption from Solution, Marcel Dekker, New York.
- Mdoe, J. E.G. and Mkayula, L.L. (1996)., Adsorption of Gold on Activated Carbons Prepared from Some Tanzanian Carbonaceous Agrowastes and Bituminous Coals, *Bulletin of Chemical Society of Ethiopia*, 10(1), 21 -32.
- Montilla, J.J (1977), *Cassava in the Nutrition of Broilers* In Cassava as Animal Feed., B. Nestel and M. Graham eds., IDRC, Ottawa; p.43.
- Neelakantan, S. (1975), Nutritive Evaluation of Animal Bloods, *J. Food Sci. Technol.* 12, 287-293.
- Nwobi, B. E., Ofoegbu, O. and Adesina, O. B. (2006) Extraction and Qualitative Assessment of African Sweet Orange Seed Oil. *African Journal of Food, Agriculture, Nutrition and Development*, 6 (2), 2 -11.
- Odozi T. O. and Akaranta, O. (1986), Activated Carbons from Palm Kernel shell: Studies on Adsorption of Dyestuff from Aqueous Solutions, *Nig. J. Appl. Sci.* 4, 85 – 90.
- Odozi, T. O. Akaranta, O. and Ejike, P.N (1986) Particle Boards from Agricultural Wastes, *Agricultural Wastes* 16, 237 -240.
- Odozi, T. O. Dore, R. O. Akaranta, O. and Hart, A. E. (1986), Using Carboxymethylated Cassava Wastes as

Thickeners in Latex Paints, *Carbohydrate Polymers* 6, 249 -256.

- Odozi, T. O., Akaranta, O. and Ogban, I.. U (1985) Development of Wood Varnishes from Palm Fruit Fibre Hydroxylate and Red Onion Skin Tannin Extract *J. Oil and Colour Chemists' Assoc.* (JOCCA), 68(4), 94 -97.
- Odozi, T. O., Okeke, S. and Lartey, R. B. (1985), Studies on Binding Metal Ions with Polymerized Corn Cob and a Composite Resin with Sawdust and Red Onion Skin, *Agricultural Wastes*, 17, 13 -21.
- Odozi, T.O. and Agiri, G. O. (1986); Wood Adhesives from Modified Red Onion Skin Tannin Extract. *Agricultural Wastes*, 17, 59-62.
- Odozi, T.O. and Emelike, R (1985), The Sorption of Heavy Metals with Corn Cob Hydroxylate-Red Onion Skin Resins, *Journal of Applied Polymer Science*, 30, 2715-19.
- Odozi, T.O., Akaranta, O. and Agiri, G.O. (1984), Some chemical Features of Red Onion Skin (Allium Cepa) Extract: A Tanning Material *J. of Leather Res.* 2(1), 10 -16.
- Ofuya, C.O. and Obilor, S.N (1993), The Suitability of Fermented Cassava Peel as Poultry Feedstuff. *Bioresource Technol.* 44, 101–107.

- Okieimen, F.E, and Okundaye, J.N (1989), Removal of Cadmiun and Copper Ions form Aqueous Solutions with Thiolated Maize (Zea Mays) Cob Meal, *Biological Wastes*, 30, 225-30.
- Okieimen, F.E., Okundia, E.U and Ogbeifun, D.E. (1991), Sorption of Cadmium and Lead Ions on Modified Groundnut (Arachis Hypogea) Husks. *Journal of Chemical Technol. Biotech* 51, 97-103.
- Periasamy, K., Srinivasan, K, and Murgan, P.K. (1991), Studies of Chromium (VI) Removal by Activated Groundnut Husk Carbon, *Indian Journal of Environmental Health*, 33, 433-9.
- Randall J.M., Reuter, F.W. and Waiss, A.C. (1975), Removal of Cupric Ion from Solution by Contact with Peanut Skins, *Journal of Applied Polymer Science* 19, 1563-71.
- Randall, J.M., Hautala, E. and McDonald, G. (1978), Binding of Heavy Metal Ions by Formadehyde Polyemerized Peanut Skin, *Journal of Applied Polymer Science*, 22, 379-87.
- Roberts, E.J and Rowland, S.P. (1973), Removal of Mercury from Aqueous Solutions by Nitrogen Containing Chemically Modified Cotton Linters, *Environmental Science and Technol*. 7, 552-3.
- Robinson, T., McMullan, G., Marchant, R., and Nigam, P. (2001), Remediation of Dyes in Textile Effluent: A

Critical Review on Current Treatment Technologies with a Proposed Alternative. *Bioresource Technol.*, 77(3), 247 -255.

- Roy, A. K. Sardar, D. and Sen, S. K. (1989) Jute, stick lignin –
 Based Adhesives for particle boards. *Biological Wastes*, 27, 63 -68.
- Saad, S. M. Naser, A. M. El-zimarity, M. T., and Abdel Meged, H.F(1978), 2 – Furfuraldhyde (Furfural) Formation from Local By – products and its Utilization in the Field of Surface Coatings, *Journal of Oil and Colour Chemist's Assoc.*, 61, 43 -49,
- Shipman, R.H. and Fan. L.T (1978), Carbohydrate Residues for the Production of Biopolymers and Single Cell Protein, *Process Biochemistry* 8, 19-21.
- Singh, J. and Raman, S. K. (1976) Activated Carbon from Coconut Shell for the Removal of dyes from effluents. *Indian J. Technol.*, 14, 145–149.
- Smisek, M. and Cerry, S. (1977), Activated Carbon; Manufacture, Properties and Applications, Elsevier, New York.
- Stansbury, M. F., Field, E. T., and Guthrie, J. D. (1950), Tannin and Related Pigments in Red Skins of Peanuts; *Journal of American Oil Chemist's Society (JAOCS)*, 27, 317, 319-322.

- Suemitsu, R., Uenishi, R., Akashi, I. and Nakano, M. (1986), The Use of Dyestuff Treated Rice Hulls for Removal of Heavy Metals form Waste Water, *Journal Polymer Science* 31, 75-83.
- Tewe, O.O. (1987), Cassava Peel Utilization in Poultry Diets, In Root Crops and the African Food Crisis, E.R. Terry, M.D. Okoroda and O.B. Arene, eds., IDRC, Ottawa, p150.
- Tuason, A. M; and Reyes, A. T. (1959) Water Soluble Extract from Coconut Husk and its Application in Leather Technology, *Philippine J. Sci.* 88, 253 – 256.
- Ui, J. (1992), *Industrial Pollution in Japan*, United Nations University Press, Tokyo.
- UNIDO Publication (1985), Rice Bran: *An Under-utilized Raw Material*, New York, p3.
- Waiss A.C. and Friedman, M. (1972), Mercury Uptake by Selected Agricultural Products and By-Products, *Environmental Science and Technol.* 6(5), 457-8.
- Waiss, A.C., Wiley, M.E., Kuhnle, J.A., Potter, A.L. and McCready, R.M. (1973), Adsorption of Mercuric Cation by Tannins in Agricultural Residues, *Journal of Environmental Quality*, 2, 369-71.
- Young, R.N., McDonald, G. and Randall, J. M. (1979), Effects of Light Metal Ions on the Sorption of Heavy Metal Ions on Natural Polymers, *Journal of Applied Polymer Science*, 23, 1027-35.