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*Contents*  
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### Physical Sciences

<table>
<thead>
<tr>
<th>Title</th>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Transfer Rates and Column Heights in Reactive Extraction Processes</td>
<td>M. T. Saeed, R. Khanam and M. Y. Shaheen</td>
<td>1</td>
</tr>
<tr>
<td>Humidity Effect on the Disintegrant Property of $\alpha$-Cellulose and the Implication for Dissolution Rates in Paracetamol Tablets</td>
<td>M. U. Uhumwangho and R. S. Okor</td>
<td>8</td>
</tr>
<tr>
<td>Proximate, Mineral and Phytate Profiles of Some Selected Spices Found in Nigeria</td>
<td>E. I. Adeyeye and E. D. Fagbohun</td>
<td>14</td>
</tr>
<tr>
<td>Effects of Exposures to Cement Dust and Powder on Workers in Cement Distribution/Retail Outlets in Benin City, Nigeria</td>
<td>I. F. Obuekwe and L. I. Okoh</td>
<td>23</td>
</tr>
<tr>
<td>Determination and Seasonal Variation of Heavy Metals in Algae and Sediments in Sewers from Industrial Areas in Lagos State, Nigeria</td>
<td>O. R. Awofolu</td>
<td>28</td>
</tr>
</tbody>
</table>

### Short Communication

<table>
<thead>
<tr>
<th>Title</th>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screening of Fused Pyrimidines as Antimicrobial Agents: Inhibitory Activities of Some Tetrahydrobenzothieno-Pyrimidines</td>
<td>M. M. H. Bhuiyan and M. Fakruddin</td>
<td>37</td>
</tr>
</tbody>
</table>

### Biological Sciences

<table>
<thead>
<tr>
<th>Title</th>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Determination of Trace Metals in Silver Cat Fish ($Chryssichthys nigrodigitatus$) Associated with Water and Soil Sediments from Beach-Line Fish Ponds</td>
<td>O. O. Ayejuyo, O. G. Raimi and O. R. Moisili</td>
<td>39</td>
</tr>
<tr>
<td>Studies on the Lipolytic Enzymes of Carica papaya Seed Powder</td>
<td>M. A. Javed, M. Naeem and R. Amjad</td>
<td>47</td>
</tr>
<tr>
<td>Characterisation of Amidohydrolytic Activity of Bacillus megaterium in Submerged Fermentation</td>
<td>Q. Syed, N. Bashir and M. A. Kashmiri</td>
<td>51</td>
</tr>
</tbody>
</table>
Short Communications

Mechanism of Monocarpic Senescence of *Momordica dioica*: Source - Sink Regulation by Reproductive Organs
A. Ghosh

Status of Grain Smut *Sphacelothea sorghi* and Long Smut *Tolyposporium ehrenbergii* of Sorghum in Sindh and Balochistan, Pakistan
A. A. Hakro and A. Khan

Technology

The Dyeability Potential of Cellulosic Fibres Using African Yellow Wood (*Enantia chlorantha*)
A. O. Adetuyi, A. V. Popoola, L. Lajide and M. O. Oladimeji

The Effect of Local Materials (Fillers) on the Crosslink Density, Hardness, Resilience and Hysteresis of Natural Rubber
B. F. Adeosun and O. Olaofe

Preparation and Characterisation of Alkyd Resins Using Crude and Refined Rubber Seed Oil
E. U. Ikhudoria and F. E. Okieimen

Erratum
Mass Transfer Rates and Column Heights in Reactive Extraction Processes

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Abstract. A mathematical model, which is based on the simultaneous interfacial chemical reactions and diffusion processes, is developed for the extraction of zinc ions from sulphate solution by di(2-ethylhexyl) phosphoric acid in n-heptane diluent. Actual column heights were compared with the predicted ones, using the design algorithm based on chemical kinetics. The experimental values of mass transfer coefficients could be varied and were in the range of industrial interest. Using the physicochemical data, hydrodynamics, mass transfer coefficient parameters and reaction kinetics pertaining to the system, it was possible to predict the interfacial flux and column height from first principles with a reasonable degree of accuracy.

Keywords: interfacial flux, reactive extraction, chemical kinetics, zinc/DEHPA, spray column

Introduction

Continuous counter current contactors are usually designed assuming interfacial equilibrium. In the case of mass transfer with interfacial chemical reaction, this assumption is only valid if the chemical reaction is very fast with respect to the mass transfer rate (Chapman et al., 1975). In hydrometallurgical processing, the use of liquid-liquid extraction systems are already very popular. The successful application of such related extraction processes has encouraged fundamental research on the extraction equilibria and kinetics leading to development of mathematical models for the solvent extraction of metals. The kinetics of these systems is generally controlled by a combination of diffusion and chemical rate factors and a properly developed model could become a design equation having practical significance. If all the parameters relating to the system, namely physicochemical, hydrodynamics, mass transfer, and the reaction kinetics are known, it would be possible to design extraction column from first principles.

In this paper a mathematical model is developed for interfacial flux, which is based on simultaneous interfacial chemical reactions and diffusion processes. An attempt has also been made to predict the column height from first principles. The system comprises the extraction of zinc ions from acidic aqueous phase by di(2-ethylhexyl) phosphoric acid (DEHPA) in n-heptane diluent. In order to check the validity of the model for design purposes, the predicted values are compared with actual heights.

Model formulation. In a column for continuous extraction in aqueous phase, with interfacial chemical reactions, the mass balance of zinc ions over a differential height δh for unsteady state operation may be given as follows (Saeed and Jamil, 1998a):

\[
\frac{\partial C_{za}}{\partial t} (1-\phi_D) = \frac{L_c}{S} \frac{\partial C_{za}}{\partial h} + E_{ax,c} (1-\phi_D) \frac{\partial^2 C_{za}}{\partial h^2} - R_{za} (1-\phi_D) \quad (1)
\]

The first term on the right hand side of equation (1) accounts for convection, the second term for axial mixing and the third one represents the overall rate of interfacial transfer. The term on the left hand side represents the variation of zinc concentration with time.

A similar differential mass balance equation can be derived for metals in the dispersed organic phase (Saeed and Jamil, 1998a):

\[
\frac{\partial C_{zo}}{\partial t} \phi_D = \frac{L_{ol}}{S} \frac{\partial C_{zo}}{\partial h} + E_{ax,d} \phi_D \frac{\partial^2 C_{zo}}{\partial h^2} + R_{za} \phi_D \quad (2)
\]

Under steady state conditions, assuming constant flow rates and neglecting backmixing, equations (1) and (2) reduce to:

\[
L_c \frac{dC_{za}}{dh} = R_{za} S (1-\phi_D) \quad (3)
\]

and

\[
L_{ol} \frac{dC_{zo}}{dh} = R_{za} \phi_D \quad (4)
\]

which on integration give the contactor height:

\[
H_c = \int_1^2 \frac{dC_{zo}}{R_{za} \phi_D} \quad (5)
\]

and

\[
H_c = \int_1^2 \frac{dC_{za}}{R_{za} \phi_D} \quad (6)
\]

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Introduction

The polymer α-cellulose is that part of cellulosic materials which is insoluble in 17.5% w/w solution of sodium hydroxide at 20 °C (Seymour, 1971). This property distinguishes it from β- and γ-celluloses. It is obtained from wood pulp (Nitz, 1994) or more recently from agricultural wastes such as maize cob, rice husk or groundnut shell (Okhamafe et al., 1991). It has potential in tablet formulations as a disintegrant and a direct compression base (Okhamafe et al., 1992). The polymer is readily hydrated being capable of absorbing approximately 4 and a 1/2 times its own weight of water (Okhamafe et al., 1991). This swelling ability is its greatest asset as a disintegrant in tablet formulations. Swelling of the α-cellulose inside the tablet causes localized stress, which leads to tablet rupture. The hydrophilic swelling property of α-cellulose has also been exploited in controlled drug release from matrices which are non-disintegrating tablets (Okor et al., 1992).

The previous studies (Nitz, 1994; Okor et al., 1992; Okhamafe et al., 1992; 1991) on the applicability of α-cellulose in tableting relate to freshly made tablets only, with no consideration for ageing effects. Therefore, information on its long-term performance under different conditions of storage is rare in the literature. In the tropics, high humidities prevail throughout the year. Hence, in the present study, humidity effect on the particle structure and disintegrant property of α-cellulose was investigated.

α-Cellulose powder. The polymer α-cellulose was used as the test disintegrant. It was obtained locally as a fine white powder of irregular shaped particles from an agricultural waste, maize cob, by sodium hydroxide and sodium sulphite digestion process already described in detail elsewhere (Okhamafe et al., 1991). It is readily hydrated and swells in water and other aqueous fluids. Maize starch (BP grade) was also used as disintegrant in a comparative study. Magnesium stearate (BDH) was used as lubricant. Paracetamol powder (pharmaceutical grade) was used as the test drug. It was selected for the study because it forms poorly disintegrating tablets on its own (i.e., without a disintegrant).

Granulation and tableting. Paracetamol granules were formed by wet granulation technique using starch mucilage (20% w/w) as the binder fluid and dried on a tray in a hot air oven (Kottermann, Germany) to moisture content, 1.3 ± 0.2% w/w. The lubricant (1% w/w) and the disintegrant (5% w/w) were added to the granules and compressed with a single punch machine (Manesty, Type F1) to form flat faced tablets of diameter 12.5 mm, thickness 3.38 mm, and weight 550 mg. The compression load was 27.5 (arbitrary unit on the load scale) and held on the tablet for 30 sec for consolidation before releasing the load.

Evaluation of the tablets. Storage tests. Twenty tablets, freshly made, were stored in each of the three chambers of different relative humidities (RH) of 1%, 78% and 100% for various time intervals up to a maximum of 2 weeks. Humidity effect on the particle structure of α-cellulose was determined by photomicroscopy. Tablets exposed to RH of 1% and 78% disintegrated very fast, within a minute, similar to the fresh samples. In contrast, tablets exposed to RH 100% for ≥ 24 h failed to disintegrate within 60 min even though the tablets became softer. Tablet dissolution rate was also markedly impaired in this set of tablets. Exposure of the α-cellulose powder to RH 100% for 24 h caused the particles to gel, which accounted for the impairment of its disintegrant property.

Keywords: α-cellulose, disintegrant property, gel formation, humidity effect
Proximate, Mineral and Phytate Profiles of Some Selected Spices Found in Nigeria

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Abstract. The proximate, mineral and phytate (phy) compositions, as well as the calculations for fatty acid, metabolisable energy, phy:Zn, Ca:phy and [Ca] [phy]/[Zn] were determined in 13 spices (S₁₁ - S₁₃) used as seasoning agents in Nigeria. The mean values of various parameters for proximate composition (g/100 g) were: moisture (3.61±3.56), dry matter (96.39±9.56), crude fat (5.46±10.02), crude fibre (27.0±17.34), crude protein (13.78±9.84), ash (4.57±2.22) and carbohydrates (45.58±22.25). Fatty acids were noted to be 4.37±8.02 (g/100 g) and energy was 1211.23±317.64 (kJ/100 g). Significant differences (P < 0.05) existed in moisture, dry matter, fat, fibre, crude protein and fatty acid levels. Minerals (mg/100 g) included: Na (183.08±14.19), K (1621.54±170.39), Ca (505.38±463.24), Mg (243.08±235.74), Zn (434.92±945.86), Fe (72.5±92.38) and P (740±264.64), while Pb, Cu and Co, were not detected. The relationships between Na and K as well as between Ca and P were mostly within the desirable range with the respective ratios of Na/K (0.59±0.87) and Ca/P (2.20±3.32). Significant differences existed among the levels of Na, K, Ca, Mg, Zn, Fe, Na/K and Ca/P. The [Ca] [phy]/[Zn] had an overall mean value of 1.45±1.74 showing that the bioavailability of zinc in the spices may be low (except in S₁₁, S₁₂ and S₁₃) due to the high phytate content of the spices.

Keywords: spices, chemical composition, metabolisable energy, phytate levels

Introduction

Broadly speaking, spices are aromatic vegetable products of tropical origin that are used, in a pulverised state, primarily for seasoning or garnishing foods and beverages. They are characterised by pungency, strong odour, and sweet or bitter taste. Included in this category are hard or hardened parts of plants such as pepper, cinnamon, cloves, ginger, cardamom, turmeric, nutmeg and mace, all spices, and vanilla. In ancient times, they were valued as basic components of incense, embalming preservatives, ointments, perfumes, antidotes against poison, cosmetics and medicines, and were little used in food. It was only in the first century AD that spices found their way into the kitchen (Kochhar, 1986). Spices cannot be classed as foods since they are used in foods at levels that yield no significant nutritive value, but impart certain aroma and flavour to the food. The importance of spices in our daily diet is as follows (Kochhar, 1986): (1) to give an agreeable flavour and aroma (piquancy or tang) to otherwise monotonous or insipid food, particularly in the tropics where it consists mainly of starchy grains or roots, thereby adding greatly to the pleasure of eating; (2) to stimulate appetite and increase the flow of gastric juices, for which reason they are often termed as food ‘accessories’ or ‘adjuncts’; (3) to camouflage or disguise the slightly unpleasant taste of many dried meats; and (4) to increase the rate of perspiration, thus having a cooling effect on the body.

The spices analysed in this work have been variously described (Akinadewo, 2001; Gill, 1992; McGraw-Hill Encyclopedia of Science and Technology, 1987; Kochhar, 1986; Shaw, 1973). Despite the wide utilization of spices, little work has been reported on their nutritional composition. Most works have been concentrated on tropical chillies (Adeyeye and Otokiti, 1999; Fagbemi and Oshodi, 1993; Bamgbose et al., 1991; Keshinro and Ketiku, 1981). Other works on spices include: isolation of vitamin C in paprika in 1937 (Kochhar, 1986), proximate and mineral composition of black pepper (Piper guineense) (Udosen, 1995) and the determination of calcium, zinc, phytate, phy:Zn, Ca:phy and [Ca] [phy]/[Zn] molar ratios in bell and cherry peppers, okro, tomato, onion and sugarnut (Adeyeye et al., 2000).

The importance of a foodstuff as a source of dietary zinc depends upon both the total zinc content and the level of other constituents in the diet that affect zinc bioavailability. Phytic acid (myoinositol 1, 2, 3, 4, 5, 6-hexakis dihydrogen phosphate), a compound found only in plant foods, may reduce the bioavailability of dietary zinc by forming insoluble mineral chelates at the physiological pH (Oberleas, 1983). The formation of the chelates depends on relative levels of both zinc and phytic acid (Davies and Olpin, 1979). Conse-
Introduction

Cement can cause ill health on inhalation, and skin and eye contacts. Risk and extent, or severity of injury obtained, depends on the duration and level of exposure, as well as individual sensitivity. Thousands of labourers working at cement distribution outlets are exposed to the product in various forms, ranging from dry cement powder, cement dust, wet cement, and concrete everyday, being absolutely ignorant of the underlying health hazards and consequences of their occupation. Cement dust, released and inhaled during bag handling and bag ‘dumping’, can irritate the skin causing xerosis, which may result in scaling, itchiness, burning and redness (Yang et al., 1996). Irritant contact dermatitis, as well as allergic dermatitis may develop. When cement is trapped, against the skin, it may take several months to heal and may involve hospitalization and skin grafts. The most hazardous effects of cement dust are on the lungs. In the short term, such exposures irritate the mucous membrane of the nose and throat causing choking, as well as difficulty in breathing (Al-Neami et al., 2001; Yang et al., 1996). Cement has also been classified as a carcinogen due to its silica content.

Incidences of occupational health hazards amongst workers have been reported (Mwaiselage et al., 2004; Alvear-Galindo and Mendez-Ramirez, 1999; Ng et al., 1992). Workers in small-scale enterprises make up the second largest employment sector in developing countries. They confront very high social and health risks with poor working conditions, employment insecurity and minimum health care. Most of the workers even do not know that they are being exposed to numerous health risks. Reports show that more than 70% of workers at small-scale enterprises hardly know and believe that they are exposed to certain occupational health hazards (Fell et al., 2003). The minimal occupational exposure standard for cement dust has been suggested to be 10 mg/m$^3$ total inhalable dust and 4 mg/m$^3$ total respirable dust. However, in developing countries, these standards are hardly maintained, particularly in small-scale enterprises. Therefore, workers at these sites are exposed to greater risks of developing job-related diseases (Al Neami et al., 2001; Leffler and Milton, 1999; Yang et al., 1993).

It has been reported that cement-related pneumocosis, e.g., silicosis, is attributed to the presence of silica in inhaled cement dust (Mengesha and Bekele, 1998; Ng and Lee, 1995). This is usually due to occupational exposure and inhalation of airborne crystalline silica. Silicosis is a disabling dust-related disease of the lungs. Even materials containing small amounts of crystalline silica may be hazardous if exposed to, in ways that produce high dust concentration, such as ‘bag
Determination and Seasonal Variation of Heavy Metals in Algae and Sediments in Sewers from Industrial Areas in Lagos State, Nigeria

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Abstract. The level of heavy metals (Cd, Pb, Cu and Zn) in algae and sediments in sewers from industrial areas was determined by atomic absorption spectrophotometry (AAS). In order to evaluate the metal load of the sewers, as a result of discharged effluents, algae and sediments were collected from three major industrial areas in Lagos, Nigeria during the two main seasons (rainy and dry). Using total digestion, the mean concentration of Cd, Pb, Cu and Zn in algae at Oshodi/Isolo industrial area for the two seasons respectively ranged from 0.04-0.15 µg/g, 0.32-1.86 µg/g, 0.42-1.52 µg/g and 0.10-1.80 µg/g, while those in sediments ranged from not detectable (ND)-0.10 µg/g, 0.12-1.32 µg/g, 0.21-2.65 µg/g and 0.18-1.74 µg/g, respectively. At Iganmu industrial area, the range in algae was ND-0.21 µg/g, 0.20-1.84 µg/g, 0.17-1.90 µg/g and 0.05-1.87 µg/g, while those in sediments was 0.04-0.50 µg/g, 0.22-1.85 µg/g, 0.15-1.78 µg/g and 0.48-2.86 µg/g in the same metal order. The range in algae at Ikeja industrial area was 0.05-0.18 µg/g, 0.08-0.82 µg/g, 0.51-1.40 µg/g and 0.24-2.80 µg/g, while the sediments recorded a range of 0.04-0.60 µg/g, 0.16-0.90 µg/g, 0.24-3.5 µg/g and 0.23-2.84 µg/g, in the respective metal order. Levels of the metals were higher in most samples during the dry season and there were significant differences in the metal concentrations from industrial and residential areas.

Keywords: heavy metals, sewer, algae, sediment, atomic absorption spectrophotometry (AAS)

Introduction

The concept of ‘save environment’ is rapidly gaining vast attention in many developing countries of the world, especially in Africa and South East Asia. However, one of the major impediments to the realization of this concept is due, partly, to inadequate and ineffective monitoring of proper waste treatment and disposal by industries and to non-compliance of waste treatment legislations by the industries where such exist. Most of these industries still consider waste treatment as a profit reduction venture. These scenarios exist in Lagos State, the industrial nerve center and former capital of Nigeria, where over 60% of the industries are located. A sizeable percentage of these industries are the chemical and allied industries. Trace metals, such as Cd, Pb, Cu and Zn, are the common pollutants. These are widely distributed in the environment with sources mainly from the weathering of minerals and soils (O’Neil, 1993; Merian, 1991). However, there has been a greater input to the amount of these metals in the environment as a result of human activities. These inputs are mostly from industrial discharges, domestic effluents, urban runoffs and atmospheric deposition.

Some of these metals, especially Cd, Pb, Zn and Hg, have been found to be harmful even in small quantities (Borgmann, 1983; Tyler, 1981), hence usually monitored for health purposes. Cadmium is one of the most toxic elements with reported carcinogenic effects in humans (Goering et al., 1994). It accumulates mainly in the kidney and liver, and its high concentration has been found to cause chronic kidney dysfunction. It induces cell injury and death by interfering with calcium regulation in biological systems. Copper is among some of the heavy metals that are essential to life but could be toxic at elevated levels. It is toxic at low concentration in water and is known to cause brain damage in mammals (DWAF, 1996). Provisional health-based guideline value of 2 mg/l for copper was proposed and concentration above 5 mg/l can give rise to problems of taste (IPCS, 1998). United States Environmental Protection Agency classified lead as potentially hazardous and toxic to most forms of life (USEPA, 1986). It has been found to be responsible for quite a number of ailments in humans, e.g., chronic neurological disorder, especially in foetus and children. Although Zn has been found to have low toxicity to man, yet prolonged consumption of large doses can result in some health complications such as fatigue, dizziness, and neutropenia (Hess and Schmid, 2002). Health-based guideline value was not derived for zinc, however, drinking water containing zinc at levels above 3 mg/l may not be acceptable to consumers (WHO, 1996).

The determination and evaluation of environmental metal burden have been carried out by using potable water (Garcia et al., 1999; Gulson et al., 1997; Holynska et al., 1996), fresh
Short Communication

Screening of Fused Pyrimidines as Antimicrobial Agents: Inhibitory Activities of Some Tetrahydrobenzothieno-Pyrimidines

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(received April 7, 2004; revised September 30, 2004; accepted October 10, 2004)

Abstract. Seven synthetic tetrahydrobenzothieno fused pyrimidine derivatives were investigated for their antibacterial and antifungal activities. Their comparative ability to inhibit growth of bacterial species Bacillus subtilis, B. megaterium, Staphylococcus aureus, Salmonella typhi and Escherichia coli in comparison with the commercial antibiotic brand Ampicillin, and of fungal species Verticillium sp., Fusarium solane, Aspergillus sp., and Penicillium sp., in comparison with the commercial antifungal brand Nystatin is reported.

Keywords: fused pyrimidines, thienopyrimidines, antimicrobial activity

Pyrimidine derivatives, which constitute a partial structure of the purine base and many biologically active compounds, are involved widely in living organisms and have attracted much attention from the view point of medicinal chemistry. The soporific and hypnotic barbiturates and a number of antibacterial and antimalarial drugs also contain pyrimidine rings (Burger, 1960). Some of thienopyrimidine derivatives are reported as potential chemotherapeutic agents (Ram et al., 1981). In a programme to obtain new potent antimicrobial agents, the synthesis of some tetrahydrobenzothieno fused pyrimidine derivatives has been reported earlier (Rahman et al., 2000). The present work describes their antimicrobial activity.

Compounds for antimicrobial screening. Seven compounds studied for the purpose were: 4-amino-5,6,7,8-tetrahydrobenzothieno[2,3-d]pyrimidine (1), m.p. 226-227 °C; 8,9,10,11-tetrahydrobenzothieno[3,2-c]imidazo[1,2-c] pyrimidine (2), m.p.187-190 °C; 4-amino-2-phenyl-5,6,7,8-tetrahydrobenzothieno[2,3-d]pyrimidine (3), m.p. 224-225 °C; 5-phenyl-8,9,10,11-tetrahydrobenzothieno[3,2-c]imidazo[1,2-c] pyrimidine (4), m.p. 183-185 °C; 5,6,7,8-tetrahydrobenzothieno[2,3-d] pyrimidine-2,4 (1H,3H)-dithione (5), m.p. 250 °C (decomposed); 4-amino-5,6,7,8-tetrahydrobenzothieno[2,3-d] pyrimidin-2(1H)-thione (6), m.p. 228-230 °C; and 3-tosyl-5,6,7,8-tetrahydrobenzothieno[2,3-d]pyrimidine-4(3H)-one (7), m.p. 110-112 °C (Fig. 1).

Antimicrobial activity trials. The fused pyrimidine compounds (1-7) were screened for antibacterial activity (Table 1) against three gram-positive bacteria, Bacillus subtilis, B. megaterium, Staphylococcus aureus and two gram-negative bacteria Salmonella typhi and Escherichia coli using disc diffusion method (Bauer et al., 1966). These compounds (1-7) were also screened for antifungal activity (Table 2) against four phytopathogenic fungi, Verticillium sp., Fusarium solane, Aspergillus sp., and Penicillium sp., using poisoned food technique (Grover and Moore, 1962). Commercial antibacterial and antifungal brands, respectively, Ampicillin and Nystatin were also tested under similar conditions for comparison.

Compound (5) showed the highest antibacterial activity against B. subtilis, Staph. aureus, Salm. typhi and E. coli. Compound (1) showed the highest activity against B. megaterium. The other compounds also showed weak to moderate activity against all the tested bacteria. The antibacterial activities of

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Introduction

The advancement in technology and the growth in population have led to high levels of industrialization and urbanization which in turn have led to environmental pollution arising from the indiscriminate discharge of industrial effluents. These effluents may contain most common heavy metals, such as Hg, Zn, Cu, Co, Sb, Cd, Pb and Cr (Ibok et al., 1989). It has been pointed out that industrial manufacturers may endanger public health by discharging toxic substances, including heavy metals into water, which may cause taste and odour problems, contaminating irrigated food crops, and killing fishes and other natural life in rivers (Oni, 1987). Water pollution by heavy metals has become a health hazard in recent years (Sastry and Tyaji, 1982), while human activities have increased the quantity and distribution of heavy metals in the atmosphere, on land, in rivers, lakes, and the seas (Warren, 1981). The extent of this widespread, but generally diffused contamination, has caused a great concern about its possible effects on plants, animals and human beings. Heavy metals are common components of natural waters, though some are essential for living organisms, these may be toxic when present beyond tolerant limits (Lehniger et al., 1993; Volesky, 1990). Generally, these metals remain for a long time in seafoods, and through a series of reaction mechanisms accumulate in them. These are subsequently transported in large concentrations through the food chain to animals or human beings when consumed.

Description of site. The beach-line fishponds in Lagos, Nigeria are constructed in such a way that the Ojo river is allowed to flow freely in and out of the ponds. The ponds have been in existence for more than 10 years and the harvested fish are sold to the nearby consumers. The river is open to the sea at the south-east (Bar-beach) and also at the south-west (Ceme-beach) through Badagry, Lagos. Human activities such as dumping of refuse, sewage discharge, excavation of soil and the discharge of industrial waste into the river have increased over the years. The data of this work will be helpful in determining the level of pollutants entering into the ponds through this river.

Materials and Methods

Description of the ponds. The ponds are square-shaped, each with a dimension of approximately 20 by 20 m by 1.3 m deep.

Sampling. Collection of fish. Fish samples of the same species were collected from three ponds (P1, P2 and P3) by hand-net. Later, each specimen was cut into three parts, head, trunk and tail, with a plastic knife and then stored at 4 °C prior to analysis.

Collection of water. The water samples were collected in plastic containers, acidified with 0.01N HNO₃ for preservation.

Determination of Trace Metals in Silver Cat Fish (*Chryssichthys nigrodigitatus*) Associated with Water and Soil Sediments from Beach-Line Fish Ponds

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Abstract. Levels of cadmium, lead, zinc, copper and chromium were determined in the head, middle and tail regions of the silver cat fish (*Chryssichthys nigrodigitatus*). Water and sediments from three neighbouring man-made fresh water ponds were also analyzed using atomic absorption spectrophotometer. The mean concentration of these metals were found to be more in the soil, followed by the water and then the fish. The highest concentrations of zinc between 33.05-33.19 µg/ml and 39.72-40.13 µg/g, were found in the water and soil, respectively. Chromium concentration in water and soil ranged from 0.220-0.254 µg/ml and 0.335-0.347 µg/g, respectively. In the fish parts, zinc and chromium were found to be more in the head with values ranging from 19.05-19.23 µg/g and 0.210-0.215 µg/g, respectively. Cadmium, copper and lead were found to be more in the middle region, having values ranging from 0.260-0.261 µg/g, 4.60-4.62 µg/g and 0.320-0.321 µg/g, respectively. All metals investigated were consistently low in the fish tail. There was no significant difference in the mean concentration of all the metals in the three ponds at p ≤ 0.05, while the distribution of the metals in the fish parts and between the fish and the water was significantly different at p ≤ 0.05.

Keywords: trace metals, silver cat fish, soil sediments, atomic absorption spectrophotometer, *Chryssichthys nigrodigitatus*
Development of a High Yielding Wheat Variety “Bahawalpur-97” for Southern Punjab, Pakistan

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Abstract. Studies were conducted to develop and release new improved wheat (Triticum aestivum L) varieties that can yield better and resist the diseases. On the basis of performance under field conditions, a line, MLT’S’ (Metaltail)= ORE F1 158/FDI/KI/BB/3/Nac, was selected from the Bread Wheat Observation Nursery MRA (1985-86), received through the courtesy of CIMMYT (Mexico) and given the No. V-7222. This line was tested/evaluated in 36 yield trials at different locations in Preliminary and Advanced Yield Trials (1986-89), Micro Wheat Yield Trials (1989-90) and National Uniform Wheat Yield Trials (1990-91 and 1991-92). On the average of 36 yield trials, Bahawalpur-97 gave 2.14, 5.94 and 1.22% higher yield than Inq-91, Pwz-94 and Pb-96, respectively. Its production technology was also developed. Its best sowing time was November to December. It gave maximum yield when NPK @ 125-100-50 kg/ha was applied. It was resistant to all foliar diseases. Its yield potential was 7200 kg/ha. This variety was approved and released by the Punjab Seed Council, Lahore, as a general-purpose variety for Southern Punjab in the name of “Bahawalpur-97” during 1998.

Keywords: wheat variety, disease resistance, Southern Punjab

Introduction

Wheat is the staple food in most countries of the world. The ever growing population pressure keeps the wheat breeders busy to develop sustainable new and better wheat varieties. Among the most widely cultivated crops in the Punjab, in terms of area and production, wheat ranks the highest covering more than 15 million acres. Inspite of the biggest cereal crop, yield per acre is low, only slightly more than one ton per hectare. Consequently, a huge amount of foreign exchange is being spent on its import every year. Research efforts have resulted in increasing the yield per hectare from 849 kg (APCOM, 1987) to 2300 kg in 1997. Dwarf gene has resulted in the green revolution in the world. Genetic yield improvement is almost non-significant. On the other hand, the removal of agronomic plant constraints, better response to fertilizer and resistance against foliar diseases has resulted in a jump in the yield.

Southern Punjab of Pakistan, although cotton zone, contributes about 44% to the total wheat production of the province. Cotton, being the major crop of the region, has a long stay in the field. So, about 80% of the wheat crop is being planted under late conditions. This cropping pattern demands wheat varieties that are of medium duration and can be successfully grown after the harvest of cotton. At present, wheat variety Inqlab-91 is covering maximum area under normal and late sowing. There is a need therefore for a high yielding, widely adapted, disease resistant variety, which can fetch more area under wheat cultivation and increase genetic diversity in the wheat fields.

The new wheat strain V-7222 developed at the Regional Agricultural Research Institute, Bahawalpur has a potential to share the only adapted wheat variety Inqlab-91(Inq-9) for sowing after cotton harvest in Southern Punjab. Furthermore, the strain carries blood of the world famous cross “Metaltail”, which will be a new addition to the existing wheat genetic make up in the country. The cross “Metaltail” is famous for its high yield potential and resistance to foliar diseases. Therefore, the new variety V-7222 has the high yield potential and resistance to foliar diseases. It has more tillers compared to Inq-91. The food products prepared from this variety have better dietary qualities. Its ‘bhoosa’ (chopped wheat shaft) is cream-white in colour and is liked by the animals as fodder.

Materials and Methods

On the basis of performance under filed conditions, a line, MLT’S’ (Metaltail) = ORE F1 158/FDI/KI/BB/3/Nac was selected from the Bread Wheat Observation Nursery MRA (1985-86), received through the courtesy of CIMMYT (Mexico) and given the No. V-7222 (Bahawalpur-97; Bwp-97). This line, having desirable traits, was evaluated in Preliminary Yield Trials (1986-87), Advanced Yield Trials...
Studies on the Lipolytic Enzymes of *Carica papaya* Seed Powder

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(accepted October 25, 2004)

**Abstract.** The lipolytic enzymes (lipase and phospholipase) extracted from the defatted seeds of *Carica papaya* showed optimum activity at 40 °C and pH 7 in aqueous media. *n*-Heptane was found to be the most satisfactory solvent to maximize activities of lipase and phospholipase. The activity of lipase extracted from germinated seeds increased with the stage of seed development, but the phospholipase activity was noted to decrease.

**Keywords:** *Carica papaya*, lipase/phospholipase activity, pH/temperature optima, triglycerides

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**Introduction**

The enzymatic studies of lipase and phospholipase of *Carica papaya* have been carried out using different temperatures, pH, aqueous media and organic solvents. The objective was to establish optimum conditions for the hydrolysis of simple triglycerides and phosphoglycerides by lipase and phospholipase so that these conditions can be applied both in the laboratory and industry.

*Carica papaya* (papaya) locally known as “papita”, of the family Caricaceae is used as a common fruit in the Indo-Pakistan sub-continent and also in other countries of the world. The medicinal usefulness of the papaya fruit is well-established for different ailments (Kirtikar and Basu, 1984; Nadkami, 1982), especially in the treatment of digestive system due to the presence of enzymes. Enzymes *in vivo* play an important role both in the synthesis and metabolism of a number of organic compounds in the animal and plant kingdoms. Review of the literature reveals that *C. papaya* has been studied for its papain, latex, lipase catalyst, flavonoids, proteolytic activity, sugar content, chitinase, cysteine proteinases, pectinesterase and lipids (Caro *et al.*, 2000; Rahkimov, 2000; Mangos *et al.*, 1999; Nguyen and Thanh, 1999; Askari and Qadri, 1998; Esperanza *et al.*, 1998; Albert and Philippe, 1997; Fayyaz *et al.*, 1993; Raie *et al.*, 1992; Azarkan *et al.*, 1977), respectively, but studies related to the lipase and phospholipase of *C. papaya* seeds have not been previously reported. In the present studies, these enzymes have been extracted from mature and germinated seeds to determine their optimum activities on purified triglycerides of olive oil and egg lecithin, respectively, under different conditions. Such type of investigations have also been carried out on corn, wheat grains, oat grains and castor bean (Berner and Hammond, 1972; Banu and Serban, 1970; Ory 1969; Ferrigan and Geddes, 1958). The different research groups have conducted similar studies on the lipolytic enzymes of different species (Blain *et al.*, 1976).

**Materials and Methods**

**Extraction of lipase and phospholipase.** The dried seeds of *papaya* obtained from the fruit available in the local market, were ground to a fine powder and defatted in a Soxhlet extractor with diethylether. The defatted seed powder (50 g) was suspended in 200 ml citrate buffer (citric acid 0.1 M and disodium hydrogen phosphate 0.2 M) of pH 7 for 1 h at 40 °C. The supernatant containing enzymes was obtained by centrifugation (Karl Kolb, Germany) for 15 min at 12,000 rpm. The extract was diluted to 200 ml with citrate buffer and utilized to study the enzyme activities under different conditions (Blain *et al.*, 1976).

**Preparation of substrates and determination of enzyme activities.** Olive oil (origin: Italy, local market) was taken and its triglycerides were separated and purified by thin layer chromatography. The triglycerides (1 g) were emulsified by blending with 10% gum acacia suspension (aqueous medium) to determine lipase activity, whereas 10% egg lecithin (BDH, England) emulsion was used as substrate for the phospholipase activity (Javed *et al.*, 1999). Hydrolysis of the two substrates by enzymes (lipase and phospholipase), extracted from mature seeds under different parameters, is described below:

**Effect of pH.** The enzyme extract (15 ml) was incubated at 40 °C for 1 h in the presence of substrates (triglycerides or lecithin emulsion), separately with citrate buffer (pH 7) and calcium chloride (0.1 M). The released fatty acids, after extraction with 5 ml hexane:chloroform (1:1 v/v), were treated with...
Penicillin amidohydrolase is the enzyme that cleaves the acyl side chain of penicillin. This enzyme is used widely in pharmaceutical industries for the production of 6-aminopenicillanic acid (6-APA), which is processed further during the manufacturing of various clinically important semi-synthetic penicillins (Bruggink et al., 1998). Penicillin amidohydrolase catalyzes the hydrolysis of penicillin to 6-APA, which is widely distributed among bacteria, fungi and actinomycetes (Bernard et al., 2002; Babu and Panda, 1991). Bacteria, like *Escherichia coli* and *Bacillus megaterium*, are known to produce penicillin amidohydrolase. The penicillin amidohydrolase activity of *B. megaterium* in the fermentation broth has been reported by Son et al. (1982) and Fumian et al. (1996) in the range of 11.0 and 45.0 iu/ml, respectively. Most of the reported work has been on the intracellular penicillin amidohydrolase activity of *E. coli*, despite the fact that it involves expensive cell disruption for the enzyme recovery (Isebel et al., 1994; Sudhakaran et al., 1991). Therefore, the present work deals with the optimization of cultural conditions in shake flasks for the production of extra-cellular penicillin amidohydrolase by the selected strain of *B. megaterium* 5B.

**Materials and Methods**

**Microorganism.** The strain of *B. megaterium* 5B was provided by the Pakistan Type Culture Collection (PTCC), Biotechnology and Food Research Centre, PCSIR Laboratories Complex, Lahore, Pakistan. The cultures were maintained on nutrient agar slants at 4 °C and revived after every 2 weeks.

**Fermentation technique.** The 20 h old vegetative inoculum was developed in 250 ml flasks containing 25 ml of nutrient medium (g/l): yeast extract, 2.0; peptone, 5.0; sodium chloride 5.0 (Oxoid). Fermentation was carried out at 37 °C for 24 h in shake flasks. The fermentation medium consisted of (g/l): glucose, 2.0; polypeptone, 5; yeast extract, 5; K$_2$HPO$_4$, 1; MgSO$_4$. 7H$_2$O, 0.2; and benzyl penicillin, 0.1 at pH 7.0 (Sunaga et al., 1976). The inoculum was transferred aseptically into 25 ml fermentation medium in 250 ml shake flasks at the rate of 3% v/v. After optimization of carbon source, glucose was replaced by sucrose at the rate of 0.3% (w/v) in the fermentation medium for further studies.

**Assay of penicillin amidohydrolase.** The penicillin amidohydrolase activity was determined by measuring 6-APA liberated from benzyl penicillin according to the ninhydrin method (Nam and Ryu, 1979). One unit of penicillin amidohydrolase activity was defined as the enzyme that formed 1 µmole of 6-APA per min under the procedure conditions.

**Determination of cell mass.** Cell mass was obtained from the culture broth by centrifugation at 10,000 rpm and dried at 105 °C to constant mass (Kim et al., 1981).

**Standard solutions.** Phosphate buffer (0.5 mol/l, pH 7.0). Phosphate buffer was prepared by mixing 24.3 g potassium dihydrogen phosphate and 56.0 g di-potassium hydrogen phosphate in 1 litre of distilled water. Lower or higher pH values were obtained by adding hydrochloric acid (5 mol/l) or sodium hydroxide (5 mol/l).
**Mechanism of Monocarpic Senescence of *Momordica dioica*: Source-Sink Regulation by Reproductive Organs**

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(received February 25, 2003; revised September 13, 2004; accepted November 20, 2004)

**Abstract.** Average chlorophyll levels of male (♂) plants alongwith defruited plants of *Momordica dioica* were higher than female (♀) plants or monoecious plants. The order of senescence was as follows: ♀ > monoecious > ♂ > defruited. Protein content in the leaves and dry weight of aerial plant parts remained higher in ♂ as compared to defruited, ♀ and monoecious plants. Evidently, the absence of fruit was noted to delay senescence.

**Keywords:** chlorophyll, defruited plant, monoecious, protein, dry weight, *Momordica dioica*

Most of the Cucurbitaceous plants are annuals and monoecious. In a strict sense, however, not all fruit bearing Cucurbitaceous plants are monoecious annuals showing monocarpic senescence. *Momordica dioica* seems to provide useful evidences for the determination of whole plant senescence in annuals. Though most of these plants are hermaphrodite, yet some are unisexual (dioecious). So, except a few, Cucurbitaceous members are monoecious. Due to peculiar male-female differentiation of *M. dioica*, it was selected for the study of mechanism of monocarpic senescence. *Momordica* has 3 types of plants (♂, ♀ and ♂ plants) developed from the same lot of seeds in the same field under normal conditions. This paper aims at separating the role of male and female flowers in relation to their combined effect (monoecious plants) during correlative senescence of this plant.

Certified seeds of *M. dioica* were procured from Bhubaneswar, Government of Orissa, India. Seeds were surface sterilized in 0.1 % *HgCl*₂ for 1 min and then washed well in running water. *M. dioica* seeds were sown in the field in lines on the ridges (80 cm apart) at the advent of winter (November). Soil was moist lateritic, previously mixed with rotted farmyard manure. Watering was done as and when required. All the experiments were conducted in a net-house to avoid damage from pests. It was noted on seed germination that few plants were bisexual, some produced only male flowers, while maximum number of plants produced fruits. Twenty plants were defruited through excision of fruits. For the determination of senescence and source-sink relationship, chlorophyll and protein levels of leaves as well as dry weight of the aerial plant parts were determined at the plant age of 240 days.

Chlorophyll was extracted from 50 mg randomized samples of leaves with chilled acetone (-4 °C) and the values were determined at 660 nm in a Spectrochem spectrophotometer according to Arnon (1949). After removing chlorophyll, the leave samples were washed 3 times with trichloroacetic acid (18 %) and the residue dissolved in 1 ml of 0.5 M NaOH at 85 °C for 1 h. After removing the tissue debris, protein was determined with Folin-phenol reagent (Lowry *et al.*, 1951). For the determination of dry weight, the aerial plant parts were oven dried at 80 °C for 12 h. Each determination was done on 3 replicates and the entire experiment was repeated at least thrice. All the data were statistically analysed by taking the source of variance as days, replication and error. The critical difference (CD) values were calculated at the significant level *P* = 0.05 (Panse and Sukhatme, 1967).

The female plants senesced earlier than the male plants. The chlorophyll level (Table 1) of defruited and male plants remained higher than those of female and monoecious plants indicating the senescence pattern as follows: female > monoecious > male > defruited. Maximum deferment of senescence in both defruited and male plants may possibly be due to the absence of fruits, which may be the initiator of the senescence signal. The senescence signal developed in the fruits and migrated downwards for the induction of leaf senescence as reported earlier (Ghosh, 2002; Ghosh and Biswas, 1995; Ghosh and Biswas, 1995).

**Table 1.** The levels of chlorophyll, protein and dry weight of plants at the plant age of 240 days (just prior to harvest)

<table>
<thead>
<tr>
<th>Plant category</th>
<th>Chlorophyll (mg/g FW)</th>
<th>Protein (mg/g FW)</th>
<th>Dry weight (g/plant)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Male (♂)</td>
<td>1.04</td>
<td>41.10</td>
<td>32.20</td>
</tr>
<tr>
<td>Defruited</td>
<td>1.07</td>
<td>40.80</td>
<td>32.00</td>
</tr>
<tr>
<td>Female (♀)</td>
<td>0.67</td>
<td>22.40</td>
<td>30.10</td>
</tr>
<tr>
<td>Monoecious</td>
<td>0.84</td>
<td>20.10</td>
<td>31.00</td>
</tr>
<tr>
<td>CD at 5 %</td>
<td>0.15</td>
<td>4.25</td>
<td>00.66</td>
</tr>
</tbody>
</table>

CD: critical difference; FW: fresh weight
Sorghum (*Sorghum vulgare*) is cultivated for grain, forage and juice in the drier climate regions of Pakistan, on limited acreage because of its low yield and susceptibility to diseases. Davies (1978) reported that sorghum is grown in 55% semi-arid tropical countries of the world. Sorghum crop in Pakistan occupies a major position in Rawalpindi, Sargodha, Multan, Bahawalpur, D.I. Khan, Sukkur, Hyderabad and Sibi Divisions (Hafiz, 1986). Sattar and Hafiz (1952) reported that the grain smut *Sphacelotheca sorghi* and the long smut *Tolyposporium ehrenbergii* cause considerable loss in the production of sorghum in all sorghum growing areas of Pakistan. Reed (1923) recorded grain smut in USA and other sorghum growing countries. Hafiz (1958) reported that the long smut disease of sorghum caused appreciable loss in the districts D.G. Khan, Muzaffargarh, Sukkur, Jacobabad, Larkana, Nawabshah and Khairpur. Kamal and Mughal (1968) and Hakro *et al.* (1990) reported that grain smut is more prevalent in all sorghum growing areas of Sindh. In Sindh and Balochistan provinces of Pakistan the old/susceptible varieties are still being grown for grain and fodder. An extensive survey of sorghum crop was thus carried out to determine the latest position of the prevalence and distribution of the sorghum smut diseases (grain smut and long smut) in Sindh and Balochistan as no recent studies had been conducted in these two provinces.

An extensive survey was carried out during 2002 to determine the incidence and distribution of sorghum smut diseases in Sindh and Balochistan. The prevalence of grain smut and long smut, in the farmers’ fields in the two provinces, was recorded for their incidence and intensity on the head count basis according to the procedure of Rodenhiser and Holton (1945). Diseased and healthy heads were counted at three random localities of each field in one square metre area. It was observed that the grain smut and long smut were prevalent in all sorghum growing areas of Sindh and Balochistan. Sorghum grain smut and long smut data and the infection level at individual sites are presented in Table 1.

Out of the 22 sites of sorghum crop fields visited, the lowest grain smut (0.5%) was recorded at Piyaro Goth and the highest (20.5%) was recorded at Khairpur. In the remaining 20 sites, i.e., Dadu, Mehar, Nasirabad, Larkana, Kamber, Shahdadkot, Jacobabad, Thull, Kandhkot, Lakhi, Jehan Khan, Sukkur, Rohri, Ghotki, Mirpurmathelo, Ubaro, Daherki, and Karoondhi in Sindh, and Nasirabad and Usta Mohammad in Balochistan, grain smut was recorded from 2 to 20%. The lowest (0.1%) and highest (8.9%) infections of long smut were recorded at Piyaro Goth and Daherki, respectively. The long smut infection ranged from 0.2 to 8.1% at Dadu, Mehar, Nasirabad, Larkana, Kamber, Shahdadkot, Jacobabad, Thull, Kandhkot, Lakhi, Jehan Khan, Sukkur, Rohri, Ghotki, Mirpurmathelo, Ubaro, Daherki, and Karoondhi in Sindh, and Nasirabad and Usta Mohammad in Balochistan, grain smut was recorded from 2 to 20%. The lowest (0.1%) and highest (8.9%) infections of long smut were recorded at Piyaro Goth and Daherki, respectively. The long smut infection ranged from 0.2 to 8.1% at Dadu, Mehar, Nasirabad, Larkana, Kamber, Shahdadkot, Jacobabad, Thull, Kandhkot, Lakhi, Jehan Khan, Sukkur, Rohri, Ghotki, Mirpurmathelo, Ubaro, Khairpur and Karoondhi in Sindh, and Nasirabad and Usta Mohammad in Balochistan. These results are comparable with the earlier reports (Hakro *et al.*, 1990; Hafiz, 1986;
The Dyeability Potential of Cellulosic Fibres Using African Yellow Wood 
(*Enantia chlorantha*)

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(received January 29, 2004; revised August 31, 2004; accepted September 2, 2004)

Abstract. The dye from African yellow tree, *Enantia chlorantha*, extracted by solvent extraction using acetone at a solute-solvent ratio of 1:25 was studied for its dyeability potential on cellulosic fibres. A golden yellow dye having a melting point ca 146-149 °C with 6.2% recovery was obtained. The dye was soluble in hydroxyl organic solvents. The cellulosic fibre has a greater dye uptake (26.0-23.2 mg/g) when dyed at a temperature of 80 °C than at 60 °C (22.0-21.6 mg/g). Its optimum dye-uptake, at both the temperatures, was achieved 90 min after the commencement of dyeing. However, the dyeability potential of the dye on unmordanted cellulosic fibres showed less substantivity as revealed by its low mean fastness ratings of 1.5 and 1.0 to washing and light, respectively. The tensile properties of the dyed cellulosic fibres, nevertheless, were greatly enhanced.

Keywords: Enantia dye, dye-uptake, *Enantia chlorantha*, African yellow wood

Introduction
African yellow wood, *Enantia chlorantha* (locally called, oso pupa/yaru), family Annonaceae, recognised by its bright yellow slash and conspicuous black fruits, is a fairly sized forest tree usually grown in dense shade (Dalziel, 1955). It is found in Southern Nigeria, West Cameroun, Gabon, Angola and Zaire. The wood is yellow, uniform throughout, fairly fine-grained, splitting easily and rather soft, turning brown after long exposure. It is used locally for house building and furniture work. Native caps are made from the fibrous bark in South Nigeria (Dalziel, 1955). The bark is intensely bitter to taste and has a lot of medicinal uses (Burkhill, 1985). The bitterness is attributed to the presence of berberine, known to be haemostatic and febrifuge, which is present in all the species of *Enantia* (Dalziel, 1955). In comparison, *Morinda lucida* (locally called, awopa/oruwo), family Rubiaceae, having a similar texture, and outer bark blackish with deeper inner yellow, is also used as the source of a yellow dye (Adetuyi *et al.*, 2002).

An attempt has been made in this study to examine the dyeability potential of Enantia dye, closely related to Morinda yellow dye, on cellulosic fibres and its fastness properties to light, washing, perspiration and ironing.

Materials and Methods

Sample collection and treatment. The bark of the African yellow wood *E. chlorantha* was purchased from Alade Market in Idanre, Ondo State, Nigeria. The outer part of the wood bark (dark grey) was removed using pen-knife leaving only the inner yellow part which was cut into smaller pieces and oven dried at 110 °C for 6 h to reduce its moisture content considerably before extraction. The sample was finely ground and stored.

Extraction. Pulverized sample (10 g) was extracted with acetone in a Soxhlet extractor for 2 h at a solute-solvent ratio of 1:25. The solvent was removed from the extract by evaporation (atmospheric). The colourant was transferred to an evaporating dish to which 20 ml petroleum ether (60-80 °C) was added and heated to dryness to remove the sticky nature of the extract. It was dried in an oven at 60 °C for 30 min, cooled, weighed and stored.

Determination of physicochemical properties. The following physicochemical properties were determined for the colourant.

Melting point. The melting point of the dye extract was determined using the capillary tube electrothermal method (Furniss *et al.*, 1978).

Solubility test. The solubility of the dye was tested in the following selected solvents: acetone, groundnut oil, hydrochloric acid (5%), methanol, petroleum ether, palm kernel oil (PKO), sodium hydroxide, sulphuric acid (conc), sodium hydrogen carbonate and water. The test was carried out by adding 10 mg of the colourant to each of the above solvents in a test tube, and in case the colourant was not soluble in the cold, gentle heat was applied by placing the test tube inside a heated water bath.
The Effect of Local Materials (Fillers) on the Crosslink Density, Hardness, Resilience and Hysteresis of Natural Rubber

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Abstract. This work reports the influence of local clay, charcoal, silica-sand, limestone and carbon black on the crosslink density, hardness, resilience and hysteresis of the natural rubber compound. The results revealed that all the fillers enhanced the crosslink density and hardness of the gum stock. Charcoal showed higher values of crosslink density, hardness and hysteresis than the other local fillers. At relatively low loading, local fillers showed appreciably higher resilience and slightly lower hysteresis than carbon black charcoal, being the least resilient and most hysteric. The present work suggests that the denser is the crosslink of the composite, the harder, less resilient and the more hysteric the composite becomes.

Keywords: crosslink density, hardness, resilience, hysteresis, carbon black, natural rubber composite

Introduction

Reports show that fillers are used in rubber vulcanization to achieve two purposes, namely: (i) to reinforce the rubber in order to improve the mechanical properties of the resultant composite, and (ii) “beef up” the volume of rubber compounds (Billmeyer, 1984; Maurice, 1981; Studebaker and Beatty, 1978; Garvey, 1970). Reinforcing fillers improve the quality of the final vulcanize, while inert fillers add little or nothing to the reinforcing characteristics of the final composite. However, these inert fillers are added just to reduce cost and sometimes better processing properties are achieved.

Properties of impregnated natural rubber composites have been investigated extensively (Adu, 1991; Bristow, 1986; Elliot, 1986; Bernard et al., 1985). Our earlier work reported the effect of some agricultural wastes on the mechanical and rheological properties of natural rubber (Adeosun, 2000; Adu et al., 2000). Recently, the characterization of natural rubber impregnated with some locally available materials such as clay, limestone, charcoal and silica-sand was investigated and reported (Adeosun and Olaofe, 2003; 2002). The aim was to examine the reinforcing properties of these local materials when incorporated into natural rubber with a view to finding industrial applications for them.

The thermal and electrical conductivities of natural rubber impregnated separately with local clay, limestone, charcoal and silica-sand have been reported (Adeosun and Olaofe, 2002). In the present work, the crosslink density, hardness, resilience and hysteresis of natural rubber, filled with these local materials, have been determined as a function of filler loading.

Materials and Methods

Source of materials. Twenty-two conventional accelerator/sulphur compounds were tested as indicated in Table 1 and 2. The natural rubber used was a Nigerian standard rubber grade 10 (NSR10) produced at Michelin plantation, Araromi-Obu, Ondo State, Nigeria. Clay was collected from Afao-Ekiti, limestone from Arimogija, silica-sand from Igbokoda, and wood charcoal was purchased from Erekesan Market in Akure, all in Nigeria.

Elemental analysis of materials. Elemental analysis was done using atomic absorption spectrophotometer (AAS) and colorimeter following the experimental procedures of Vogel (1961) and AOAC (1981).

Table 1. Formulation of the composites examined

<table>
<thead>
<tr>
<th>Composite</th>
<th>Content in parts per hundred rubber (pphr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>100</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>3</td>
</tr>
<tr>
<td>MBT*</td>
<td>1</td>
</tr>
<tr>
<td>Sulphur</td>
<td>3</td>
</tr>
<tr>
<td>Filler variable*</td>
<td></td>
</tr>
</tbody>
</table>

*mercaptobenzothiazole; *filler loading in parts per hundred rubber (pphr)
Preparation and Characterisation of Alkyd Resins Using Crude and Refined Rubber Seed Oil

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(received February 19, 2002; revised December 7, 2004; accepted December 15, 2004)

Abstract. Six different alkyds were formulated with crude rubber seed oil 45% (I), 50% (II) and 55% (III); refined rubber seed oil 45% (IV), 50% (V) and 55% (VI); phthalic anhydride and glycerol. All the alkyds were formulated to alkyd constant of about 1.0. The alcoholysis method was used. Refining enhanced the quality of rubber seed oil in alkyd resin manufacture. The properties of the finished alkyd resins such as viscosity, number average molecular weights, drying schedule, chemical resistance and film hardness were determined. The intrinsic viscosity (η) was observed to be proportional to the number average molecular weight of the two sets of alkyd resins. However, samples I-III exhibited higher intrinsic viscosity in toluene than samples IV-VI. On the contrary, the films of samples IV-VI were harder, dried faster, and were more chemically resistant than those of samples I-III. The practical implications of these results are discussed.

Keywords: alkyd resins, rubber seed oil, refining, surface coatings, coating binders

Introduction

Generally, surface coatings are composed of binders, solvents and pigments. Binders are film-forming components of the coatings. They are responsible for the performance quality of the coatings such as the rate of drying, gloss, durability of the dry film, and resistance of the dry film to abrasion and chemicals. Alkyds are examples of binders. They constitute over 70% of binders currently used in surface coatings due to their unique qualities like gloss and gloss retention, exterior durability, and compatibility with other film formers for purposes of cost reduction (Bajpai and Seth, 2000). They are essential products of condensation reaction between polyols and polybasic acids modified with fatty acids or triglyceride oils. Glycerol and phthalic anhydride, respectively, are examples of polyols and polybasic acids commonly employed in the preparation of alkyds because of their relative abundance and low cost. They form the main alkyd backbone chain to which fatty acids are attached thereby terminating the growth of the alkyd chain in that direction. Vegetable oils are now most commonly employed in alkyd formation due to their low cost. Drying oils are among the oldest binders used in coating formulations because of their ability to form hard and solid films upon exposure to air (Patel et al., 2000).

The nature of the drying oil used governs the physical and chemical properties such as rate of drying, film hardness, colour and gloss retention, flexibility, and adhesiveness of the alkyd film, thereby making drying oil the most important component of alkyd resins (Wick et al., 1999). Natural forms of the oils seldom fulfil the technical requirements for film properties like resistance to weathering, chemicals, acid, water, alkali and abrasion (OCCAA, 1983). Thus, to enhance their initial quality, several physical and chemical modifications of the oils have been evolved over the years. Examples of such modification techniques include acrylation (Akintayo and Adebawale, 2004a), catalytic and thermocatalytic polymerization (Patel et al., 2000), interesterification (Athawale and Joshi, 2001), phosphorylation, epoxidation (Zhong et al., 2001), copolymerization (Trumbo et al., 2001), dehydration (Thames et al., 1997), and chlorination (Akintayo and Adebawale, 2004b).

Various physical and chemical modifications of rubber seed oil, such as heat treatment (Aigbodion and Pillai, 2001) and monomer-modification (Aigbodion et al., 2003) have been previously reported. In this study, we report on the quality of alkyd resins modified with crude rubber seed oil (RSO) compared with the quality of those modified with refined rubber seed oil. Rubber seed oil has been found to have strong potential for use in the production of alkyd resins with quality comparable to that of commercial alkyd resins (Aigbodion et al., 2001; Aigbodion and Okieimen, 1995). Like other vegetable oils, crude rubber seed oil is composed of a mixture of triglycerides and minor constituents like free fatty acids, which are extraneous to the neutral oil and contaminants. It was then hoped that removal of these minor constituents would enhance the quality of rubber seed oil in the manufacture of alkyd resins.

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