Physical Sciences

Critical Study on Conventional Concept of Entropy
M. K. Afridi and M. Sharif Nizami 373

Simulation of Voltammogram of a Hindered Quinomethylene
Inam-ul-Haque and Asim Khan 379

Cure Characteristics and Physico-Mechanical Properties of Blends of Epoxidised Natural Rubber and Polystyrene
I. O. Asia, A. K. Akinlabi and E. E. Egbon 383

Corrosion of Aluminum Components and Remedial Measures
Shahid T. Sheikh, Abdul Khalique, F. A. Malik and Nusrat Hamid 388

Effect of Base Media on the Stability of Annatto Dye in Industrial Products
A. O. Adetuyi, L. Lajide and A. V. Popoola 391

Solvent Extraction and Separation of Al(III) and Ni(II) from Aqueous Medium by Cyanex-272 [Bis-(2,4,4-Trimethylpentyl) Phosphinic Acid] in Kerosene
M. F. Islam and M. S. Rahman 395

Evaluation of Sorption Capacity of Scrap Tyre in the Removal of Copper (II) Ion from Aqua System
N. A. Oladoja, A. Ofomaja and E. Ebare 400

Short Communication

Investigation of Pine Needles for Pulp/Paper Industry
Asadullah Jan, Amin Ur Rahman, Farid Ullah Khan and Jehangir Shah 407

Biological Sciences

Acute Toxicity Studies of Bombax cieba Flowers In Mice and Rats
Zakir-ur-Rehman, Atiq-ur-Rehman and Shahnaz Ahmad 410

Invertebrates Associated with Ipomea aquatica in Ogbe Creek, Lagos, Nigeria
J. K. Saliu and Y. T. Fashola 414

Investigations on the Use of Poison Baits and Fumigants Against Indian Crested Porcupine (Hystrix indica)
Abdul Aziz Khan, Afsar Mian and Rashad Hussain 418
Eco-physiological Studies on *Gmelina arborea*: I. Pre-germination Treatments and Initial Growth Developments
J. Kayode and J. Agbebi 423

Functional Qualities of Raw and Processed Melon (*Cucumeropsis edulis*) Seeds
F. O. Abulude, L. O. Lawal, M. O. Ogunkoya, Y. S. Akinjagunla and O. E. Obajowolo 427

**Short Communications**

*In-Vitro* Chemical Control of *Aspergillus flavus* Causing Seed Rot of Crops of Family Brassicaceae
Tamoor Khan, Ghulam Mustafa and Zaheer-ud-Din 431

Potentials of *Euphorbia tricucalii* and *Ricinus communis* Products for the Control of *Callosobruchus maculatus*
Joshua Kayode and Sunday Oyeyemi 434

Seasonality in Cyclopoids (Crustacea: Copepoda) and Rainfall Variation of the Forcados River, Nigeria
C. G. Oronsaye 437

Nutrient and Antinutrient Contents of Fermented Roselle Calyx
A. O. Ojokoh, F. C. Adetuyi and F. A. Akinyosoye 440

**Technology**

Sorption of Some Heavy Metal Ions by Chitosan and Chemically Modified Chitosan
A. Jideowno, J. M. Okuo and P. O. Okolo 443

Contents (1-6) i

Author Index ix
Critical Study on Conventional Concept of Entropy

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Abstract. The concept of increase in entropy or disorder as a result of all natural processes has been critically reviewed on the basis of experimental facts and ongoing phenomena on our Globe. Similarly, order-disorder statements have also been judged under new and fresh look. In fact, these are not absolute but depend upon defining specific purpose and considering that whether that purpose is being served or not? The new concept has been elaborated by considering natural biological processes, spontaneous mixing of four different gases, distribution of four points in space and assembling of a packaged electronic gadget. Actually, this order-disorder dilemma is the result of not defining the specific purpose of a process which leads to so-called concept that ‘disorder’ is increasing day by day in our universe. The traditional concept of entropy has been finally tested under heat exchange and probability considerations, which also yield no information to discern it as a measure of disorder. Consequently, increase of entropy translating into increase of disorder could not be applied to all natural processes especially the natural biological systems.

Keywords: critical, entropy, facts

Introduction

According to the Second Law of Thermodynamics, entropy is thought as a measure of disorder of a system and it increases as a result of all natural (spontaneous) processes in universe. Thus, when a system achieves a configuration of maximum entropy, it reaches equilibrium which is disorder or chaos (Moore, 1990). But practically we see life flourishing on our Globe spontaneously in multiple forms. Obviously, the purpose of nature seems to protect, organize and promote life activity in general. However, whole of the material world under the present scientific thought is being governed by the so-called Law of Entropy. It is a serious question that how this contradiction can be resolved. In fact, the concept of entropy is based on the principles of Physics but when we consider Biology, the situation becomes quite different.

A good number of researchers have given due attention to the above referred aspect and offered the views based on their observations. According to Smolin (2003), Physics must explain natural biological processes because living creatures are made of atoms which obey its laws and if it does not make the existence of life comprehensible, must eventually give way to one that does. Kirby (2003) formulated Adaptability Theory by introducing the quantum entropy relationship after reviewing the entropy adaptability concept put forward by Michael Conard who focused the quantum process in life.

Similarly, Schwarz and Inesi (1997) determined the close relationship of entropy with biology and demonstrated the important role of entropic mechanism in some specific enzymes. John (2002) put forward the idea of negative entropy during his study in neurology based on significant variations. Loewenstern and Yianilos (1999) reported entropy estimates for DNA, a highly ordered and purposeful molecule. While mechanism of photosynthesis and respiration under revolutionary Chemiosmotic Hypothesis, giving due consideration to the relationship between accumulated order of bio-organism and entropy was explained later on (Harold, 2001).

Actually, the dilemma under consideration is the result of our lack of understanding that what we really mean by “order” or “disorder”, while referring to various arrangements and forms of matter and having blind faith in the principle of ever increasing entropy. The first thing to do in this regard is to look around afresh and examine down trodden statements deeply, as sometimes a crucial evidence lies right in front of us that has till now lacked any significance when looked at in a new way, it can all of a sudden reveal new meanings (Smolin, 2003).

This becomes more important when we consider the interesting historical fact that the laws of thermodynamics were put in their present form during middle of the nineteenth century (Smolin, 2003). It is also well known that science is based on the belief that definite order is prevailing in this world. The researchers of different disciplines are required to develop co-operation for searching ultimate truths regarding this aspect, as there are still many gaps in science to be filled. The
Simulation of Voltammogram of a Hindered Quinomethylene

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(received December 20, 2005; revised September 24, 2006; accepted November 19, 2006)

Abstract. Electrochemical simulation of the cyclic voltammogram of a sterically hindered quinomethylene in dimethyl formamide (DMF) tetra-n-butylammonium perchlorate at mercury bead electrode was studied using two shareware simulation programs, namely, cyclic voltammetry simulation (CVSIM) and Electrochemical simulation package 2.4 (ESP 2.4). Two cathodic and two anodic peaks were analysed. ESP 2.4 took lesser time for simulations.

Keywords: electrochemical simulation, hindered quinomethylene, cyclic voltammetry

Introduction

The cathodic reactions of a number of relatively stable quinomethides have been examined by cyclic voltammetry, controlled potential coulometry, and rigorous product analysis by following preparative-scale electrolysis. The results of cyclic voltammetric experiments differ in some respects from those of earlier polarographic work. The life times of the electrogenerated radical-anions and dianions, in the absence of an added electrophile, were governed by steric hindrance. Though hindered intermediates are relatively long-lived, yet they hydrogenate in the presence of proton donors and alkylate in the presence of methyl iodide. The less hindered analogs efficiently and rapidly dimerize, at carbon, with concomitant protonation or O-methylation depending on the added electrophile. The ambient cathodically generated nucleophiles alkylate at both carbon and oxygen and the competition is crucially dependent on the cation (tetra-butyrammonium ion or lithium ion). An efficient reaction between oxygen and triarylmethyl radicals has been shown (Goulart and Utley, 1988).

Six extended para-quinones, with sterically hindered keto groups, have been characterized by UV-vis, 1H NMR and 13C NMR spectroscopy. Their electrochemical properties have been investigated in pyridine solution using cyclic voltammetry, differential pulse voltammetry, chronoamperometry and controlled potential electrolysis. All species exhibit two successive one electron reductions leading to the dianions via monoanions. An efficient reaction between oxygen and triarylmethyl radicals has been shown (Goulart and Utley, 1988).

The electrochemical reductions of eight quinones, namely, 9,10-anthraquinone; duroquinone; 2,6-di-tert-butyl-1,4-benzoquinone; 2,6-dimethoxy-1,4-benzoquinone; 9,10-phenanthrenequinone; tetrachloro-1,2-benzoquinone; tetrabromo-1,2-benzoquinone; and 3,5-di-tert-butyl-1,2-benzoquinone, have been studied in acetonitrile. In every case, it was found that cyclic voltammograms differed in significant ways from those expected for simple stepwise reduction of the quinone to its radical anion and dianion. The various types of deviations for the eight quinones have been cataloged and some speculation has been offered concerning their origins (Lehmann and Evans, 2001).

Cyclic voltammetry of QM [=3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylideneacetonitrile] has been investigated at the platinum cathode in dry acetonitrile containing sodium perchlorate. Two peaks, one cathodic and one anodic, were observed. The peak currents in both the cases scaled linearly with square root of the scan rate. The initial heterogeneous electron addition to QM yielded an anion radical that dimerises to bibenzyl dianion. The dianion is a mixture of meso, and (±) isomers. The anodic peak corresponding to the oxidation of these isomers was broad, which resulted from overlap of individual peaks from various bibenzyl isomers (Haque et al., 2005).

The cyclic voltammetry experiments have demonstrated that 2-methoxy-4-[2-(2-methoxyphenoxy)propylidene]-2,5-cyclohexadien-1-one, as the model for lignin, accept electrons...
Cure Characteristics and Physico-Mechanical Properties of Blends of Epoxidised Natural Rubber and Polystyrene

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(received May 4, 2004; revised August 29, 2006; accepted December 5, 2006)

Abstract. Studies in the processing characteristics and physico-mechanical properties of blends of epoxidised natural rubber (ENR) and polystyrene (PS) were carried out using various ratios of their compositions of (100:0, 95:5, 90:10, 85:15, 80:20, 75:25 and 70:30 w/w of epoxidized natural rubber). Epoxidised natural rubber (35% epoxide level) was obtained by reacting natural rubber with peroxyformic generated in situ, using formic acid and hydrogen peroxide. The 35% ENR obtained showed a lower scorch time and cure rates. The blends of ENR with PS (90:10 w/w) showed better physico-mechanical properties in terms of the: tensile strength, elongation at break, hardness, compression set, Plasticity Retention Index (PRI), Mooney viscosity while blends of ENR with PS (95:05 w/w) were very resistance to mineral oil and some organic solvents. However, substitution of ENR with more than 20% of PS showed deleterious effects on the cure characteristics and physico-mechanical behaviour of the vulcanisates.

Keywords: physico-mechanical properties, blends, epoxidised, natural rubber, polystyrene

Introduction

Natural rubber has long been recognized as a major raw material for the production of various consumer-rubber products, such as automobile tyres and tubes, latex-dipped goods like surgical gloves, hoses, and natural rubber foams, etc. (Okieimen et al., 1991; UNIDO, 1989). The attainment of a good quality product from rubber material lie depends in the choice and characteristics of the raw materials used. (UNIDO, 1989). If the raw material is adulterated or inferior, the desirable characteristics are difficult to be attained. There is a need, therefore, to study and improve the procedures to modify natural rubber with other synthetic polymers. Polymers can be broadly grouped into natural or synthetics categories. Natural polymers include proteins, polysaccharides, gums and elastomers, while the synthetic polymers include plastics (thermoplastics and thermosts), non-biological elastomers and fibres (Okieimen et al., 1991). Plastics are the materials which deform under stress and retain the deformation when the stress is removed. An example of plastic is styrene (CH₂ = CPh), which is a petrochemical-based polymer (Daniel et al., 1989).

Technological innovations in rubber processing are increasing rapidly and a great deal of commercial interest is being placed on the blends of rubber that can combine improved processing characteristics with good solubility parameters in solvents (UNIDO, 1989). Modification of natural rubber (NR) by the inclusion of various additives to enhance the processability of the vulcanisate has been well established

Menon et al., 1994; Nguyen et al., 1993; Amin and Scott, 1974). The additives used are mostly from petrochemical sources, which tend to modify the properties of the rubber. (Challioui-Gillet, 1994; Elhamaoud, 1991). Perera et al. 1988 reported that some new generic family of polymers, obtained by modifying natural rubber through epoxidation has lesser solubility problems and good processing characteristics. Epoxidation, which is the formation of oxirane rings (epoxides) by the action of an organic peracid on a carbon= carbon double bond (C=C), can provide materials with added value that can give the desired properties for specific applications (Aigbodion et al., 2000).

This study is aimed at determining the processing and physico-mechanical properties of the vulcanisate made from combining a petrochemical-based polymer (polypropylene) with epoxidised natural rubber (ENR). The paper reports on the processing characteristics and physico-mechanical properties of blends of ENR and various ratios of polypropylene, with the expectation that the results will make NR to have more diverse applications and minimize the use of heavy equipment associated with NR processing.

Materials and Methods

Materials. The natural rubber latex (NRL) used was obtained from the NIG -804 clonal series of Rubber Research Institute of Nigeria. Crumb natural rubber, conforming to Standard African Rubber (SAR) grade 3, was obtained from the Rubber Research Institute of Nigeria (RRIN), Iyanomo, Benin City. Reagents used in the preparation and characterization of natu-
Corrosion of Aluminum Components and Remedial Measures

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(received July 31, 2004; revised October 30, 2006; accepted November 11, 2006)

Abstract. Aluminum has versatile physical properties, mechanical strength, corrosion resistance, and is used in special applications like aerospace, automobiles and other strategic industries. The outdoor exposed structural components of aluminum have very good corrosion resistance due to the thick oxide layer (0.2 - 0.4 μ). This study involves the corrosion of aluminum based components, though aluminum is protected by an oxide layer but due to extreme weather and environmental conditions the oxide layer was damaged. The corroded product was removed, pits or cavities formed due to the material removal were filled with epoxy resins and acrylic-based compounds containing fibreglass as reinforcement. Optimum results were obtained with epoxy resins incorporated with 5% glass fibres. The inner surface of the components was provided further protection with a cellulose nitrate compound.

Keywords: corrosivity, aluminum, components, passivity

Introduction

The properties of aluminum have made this metal and its alloys the most economical and attractive for a wide variety of uses, as related with appearance, light weight, ease of fabrication, physical and mechanical properties, and corrosion resistance. It has good resistance against corrosive elements in most of the environments, such as water, marine atmosphere, oils, and a number of chemicals (Brown and Binger, 1960). Aluminum and its alloys provide high ratio of strength to weight, which can be easily fabricated and joined readily by most of the methods commonly used. Aluminum alloys have high conductance of heat, electricity, high reflectivity of heat radiant energy, visible light and electromagnetic waves. Aluminum and its alloys are also nonmagnetic, therefore, aluminum alloys are widely used in high technology industries, such as air crafts, radars, etc. Aluminum is an active metal having good resistance to corrosion due to the passivity produced by a protective oxide film. The limits of passivity being dependant on the temperature, the form of oxide present, and low dissolution of aluminum (Bohni and Uhlig, 1969). Increased corrosion resistance is secured through the use of alclad alloys and anodic coatings. The corrosion resistance is further improved by the application of special paints (Van Horn, 1967).

Aluminum may corrode because of defects in its protective oxide film. Resistance to corrosion improves considerably as purity is increased, but the oxide film even on the purest aluminum nevertheless contains a few defects where corrosion can develop. The presence of second phase corrosion becomes the more important factor. These phases are present, as the insoluble constituents of intermetallic compounds are produced primarily from iron, silicon and other impurities, and the smaller precipitates of compounds are produced from soluble alloying elements. Most of these phases are cathodic to aluminum, but a few are anodic. In either case, they produce galvanic cells because of the potential difference between them and the aluminum matrix (Hollingsworth and Hunsicker, 1979). Pitting corrosion of aluminum is more prevalent than other forms of damage. Corrosion of this type is produced mostly by halide ions, of which chlorine is the most frequently encountered. Aluminum may develop pitting in aerated solutions of halides simply because the reactions occurring on its cathodic regions are sufficient to polarize it to its pitting potential (Metikos-Hukovics, 2000). The aluminum alloy used in the manufacture of radar parts belongs to the 5XXX series (Al-Mg). Magnesium is the most soluble element in aluminum and remains in solution even at low temperature, though dissolves at elevated temperature exceeding its solubility limit. While studying the pitting in aluminum fuel tanks during the closer inspection, Munikrishnaiah (2003) had found dark spots/patches on the bulkhead forgings. The present work involves the cleaning of aluminum alloy components used in equipments exposed to extremes of atmospheres and were revolving.

The author then flushed the tank with aviation fuel and collected the sediments. The analysis of the sediments revealed that Al₂O₃ particles were the major components of the sediments, besides containing the general corrodents like Cl, Ca and O. This pitting was attributed to the presence of active chloride ion which is the major corrodent of aluminum. The present work involves the cleaning of aluminum alloy components used in equipments exposed to extremes of atmosphere and were revolving.
Effect of Base Media on the Stability of Annatto Dye in Industrial Products

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(received February 4, 2005; revised May 24, 2006; accepted July 6, 2006)

Abstract. Colour stability of the versatile annatto dye was examined to monitor the effects of base media on industrial products. The dye was incorporated in two media, namely, palm kernel oil used in products such as body cream and soap, and paraffin wax used in shoe polish and household candle wax. These products were exposed to various light conditions for a specific period before assessment. The melting point of the dye was determined as 176-178 °C with a molar absorptivity of 13,600 l mol⁻¹ cm⁻¹ at 545 nm. It imparted its brilliant yellow/orange colouration in industrial products as the colour stability depends on the compounding base media of the products. Losses of β-carotene was higher and faster in non-aqueous environment as paraffin wax showed low fastness rating values, than in the palm kernel oil based aqueous medium products.

Keywords: annatto dye, base media, colour stability, industrial product, dye stability, Bixa orellana dye

Introduction

Apart from indigo and logwood, annatto dye is among the oldest colourants known and used by man. It is obtained from the fruit pulp from a tropical tree Bixa orellana, family Bixaceae. The orange-red annatto dye has been used since long by the people of the Caribbean islands and the tropical Americans to colour their bodies red during war time in order to frighten their adversaries (Kochhar, 1981). The plant occurs as a large shrub to a small tree depending on the region and age of the plant. It is now grown in many places outside the tropical America, including most states in Nigeria (Noah, 1995). The fruit pod of the plant houses the seeds coated with a resinous layer of orange/red pod avils from which the commercial pigment is extracted. The annatto dye varies in hues ranging from yellow through orange to orange-red, which is due to a mixture of carotenoids and their degradation products. The structures of the major carotenoids of this dye as, cis- and trans-bixin, and cis- and trans-norbixin, have been studied and reported (Goodwin, 1980; Finar, 1975; Barber et al., 1961; Kuhn and L’Orsa, 1932; Karrer et al., 1929). Bixin, \( (C_{25}H_{30}O_4) \), is a monomethyl ester of a dicarboxylic acid. Under alkaline conditions the methyl group can be saponified yielding the free dicarboxylic acid termed as norbixin \( (C_{24}H_{28}O_4) \). With an excess of alkali, the dicarboxylic acid dissociates to form the alkali metal salt, usually potassium or sodium, in which form the pigment is water-soluble (Finar, 1975). Bixin also exhibits the typical reactivity of carotenoids. A survey of the literature has shown that annatto dye has been in use since antiquity as a colourant for food and textiles as well as cosmetics. A short review of the extraction and chemistry of the annatto dye has also been published (Preston and Richard, 1980).

The present study examines the effect of media on the stability of annatto dye in industrial products. The dye after extraction and purification was incorporated into some industrial products through various base media and their colour stability to light was assessed, or rated, on the 7th day after production using the Gray’s scale, (SDC, 1992).

Materials and Methods

Source and sample preparation. The fruit pods were collected from the Staff Quarters, Federal University of Technology, Akure, Nigeria. They were sun-dried and cracked to obtain seeds. The cracking was done by packing the fruit pods into a jute bag, beaten with a heavy wood to loose the seeds from the pod. The seeds were then sieved to remove the pod pieces and stones and dried in oven at 105 °C for 3 h, cooled, and stored in an airtight desiccator.

Extraction and purification. Dried Bixa orellana seeds (25 g) were shaken with 100 ml chloroform in a separatory funnel for 2-3 min to extract the pigment from the seeds. The pigment was completely extracted by 2-3 repeated extractions, using 50 ml chloroform each time. All the extracted fractions were sieved through mesh (150µm) to remove seed debris from the extract. The extract was allowed to stand overnight and separated with a separatory funnel into two layers. The upper layer contained the pigment and the lower layer was a clear homogeneous deep-red solution. The pigment layer was then purified using column chromatography with silica gel as the adsorbent in the ratio of 1:25. The pigment was washed with a series of mixtures of polar and non-polar solvents at various ratios.

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Solvent Extraction and Separation of Al(III) and Ni(II) from Aqueous Medium by Cyanex-272 [Bis-(2,4,4-Trimethylpentyl) Phosphinic Acid] in Kerosene

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Abstract. The solvent extraction and separation of Al(III) and Ni(II) from aqueous medium using Cyanex-272 [bis-(2,4,4-trimethylpentyl) phosphinic acid] in kerosene has been investigated as functions of contact time, aqueous phase acidity (pH), concentration of extractant in the organic phase, temperature, and loading capacity of the extractant. The equilibrium was reached within 9 min for Al(III) and 2 min for Ni(II). It was observed that the amount of Al(III) extraction was about 65% with 0.1 mol/l Cyanex-272 in kerosene at (26 ± 1) °C and pH 4.2, whereas at the same time the amount of Ni(II) extraction was about 8.5% with the same condition. In both cases, the metal ion [Al(III) and Ni(II)] concentration in the organic phase gradually increased with the time of extraction until the curves levelled off. The extraction of Al(III) increased with increasing concentration of the extractant, aqueous phase acidity (pH), and the temperature. However, the amount of Ni(II) extraction at all temperatures was negligible and decreased with increasing extractant concentration. The temperature dependence data gave ΔH = 15.23 kJ/mol up to 60 °C, suggesting endothermic extraction. The loading capacity of Al(III) and Ni(II) was about 25.75 g and 0.5 g, respectively per mole of Cyanex-272, with 0.2 M Cyanex-272 at pH 4.1. Loading data indicates Al : Cyanex-272 ratio varied from 0.95 : 1 to 1.6 : 1 for Al(III) extraction indicating almost 1 : 1 complex formation in the organic phase.

Keywords: solvent extraction, Al-Ni separation, Cyanex-272, kerosene medium, bis-(2, 4, 4-trimethylpentyl) phosphinic acid

Introduction

One of the most important groups of extraction reagents used in the field of hydrometallurgy is the group of organophosphorus acid derivatives. Among these, the dialkylphosphinic acids were commercialized in 1982 by Cyanamid under the name Cyanex-272, in which the active component was bis-(2,4,4-trimethylpentyl) phosphinic acid. This reagent has been studied extensively for the extraction of cobalt and nickel yielding better separation than dialkylphosphoric and dialkyl phosphinic acids (Rickelton, 1996; Chou and Beckstead, 1990; Sastre et al., 1990; Xun et al., 1990; Rickelton and Boyle, 1988; Xun and Golding, 1987; Preston, 1983). Similar findings have also been reported for zinc-cadmium separation (Sastre et al., 1990). Cyanex-272 has been widely studied for the extraction of several metal ions, mostly from sulfate and chloride medium (Wang and Li, 1994), and is commercially available for more than a decade. Al(III) and Ni(II) separation has been tried by tolyl phosphate by using NH₃ medium in the presence of fluoride ions (Islam and Mostafa, 1995). Most of the commercially available extractants possess poor separating ability for Al(III) and Ni(II) from a mixture of the two cations. The solvent extraction and separation of Al(III) and Ni(II) in aqueous medium have been attempted in the present study by adding Cyanex-272 in kerosene. The study is of commercial importance as the acid leaching of the spent nickel catalyst from fertilizer factories produces aluminum and nickel containing solutions (Islam and Mostafa, 1993), the treatment of which is necessary to separate the two metals.

Materials and Methods

A stock solution of Al(III) was prepared by dissolving exactly 24.66 g of analytical grade aluminum sulfate in 1 litre of distilled water containing 1% of conc HNO₃ by volume. Another 1 litre of Ni(II) was prepared by dissolving exactly 8.96 g of analytical grade nickel sulfate in 1 litre of distilled water containing 0.1 N HCl. After mixing, the phases were quickly separated to guard against mass transfer of metal ions through diffusion from aqueous to the organic phase for the contact time dependance study. Cyanex-272 (85% purity) was used as such without further purification. The diluent, kerosene, was purchased from the local market and distilled to collect the fraction obtained in the range of 200-260 °C. All other chemicals were of reagent grade and used without further purification.

20 ml aliquots containing definite amounts of Al(III) and Ni(II) in the aqueous phase and organic Cyanex-272 in kerosene in the organic phase were collected in 125 ml reagent bottles.

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Evaluation of Sorption Capacity of Scrap Tyre in the Removal of Copper (II) Ion from Aqua System

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Abstract. The use of scrap-tyre (ST), which was both a waste and pollutant was investigated as a low-cost sorbent to sorbed Cu (II) from aqueous solution. The influence of pH, sorbent dosage, contact time, and initial sorbate concentration on the uptake of Cu (II) by ST were studied. Optimum sorption of Cu (II) by ST was achieved at pH 6. The amount of sorbate sorbed per gram of sorbent decreased with increase in sorbent dosage. Maximum uptake of the Cu (II) was achieved within the first thirty minutes of contact between the ST and the Cu (II). The equilibrium relationship between the concentration of the Cu (II) in the fluid phase and the concentration in the ST particles at a given temperature showed that the sorption mechanism was like adsorption rather than distribution into any phase. Analysis of the results using Langmuir and Freundlich models showed that it conformed to Langmuir equation based on the formation of a monomolecular layer. The adsorption capacity due to monolayer coverage was 12.95 mg/g, while the energy of adsorption was 3.95 dm/mg.

Keywords: scrap tyre, Cu²⁺ ion, adsorption

Introduction

Copper is one of the metals whose density is greater than 5 g/cm³ or 5 kg/m³. Its presence, even at low concentration in aqueous medium portends dangers for all forms of the aquatic life or any living organism whose existence is knitted to the aquatic resource. Due to its toxic effects and non-biodegradability, it has emerged as a prominent pollutant. It accumulates in living tissues and may be transferred to human beings through the food chains. The presence of copper and its compounds in the environment could be traced to anthropogenic origin. Copper bearing mining wastes and acid mine drainage discharge significant quantities of dissolved copper in waste water (Ajmal et al., 1998). Other sources of copper bearing wastes include swine waste (Wu et al., 1999), plating baths, fertilizer industry, paints and pigments municipal and storm water run-off (Dean et al., 1972; Tallmange, 1965).

The conventional methods available for the attenuation of Cu and its like from solution include lime precipitation, ion exchange, and sorption on activated carbon (Dean et al., 1972), membrane filtration processes and electrolytic methods (Braukman, 1990). These methods have been found to be limited since they often involve high capital and operational cost. They may be associated with the generation of secondary waste which may present treatment problems e.g. those involving precipitation processes resulting in generation of large quantities of sludge (Williams and Edyvean, 1997).

The diverse problems emanating from the use of existing methods for the removal of copper from solution, active research has been undertaken on ways to improve upon the existing system or to patent new ones. Arrays of low cost sorbents have been studied and the activated carbon and coal have also been extensively used in metal ion adsorption from aqueous solutions (Macias-Garcia et al., 1995; 1993; Petrov et al., 1992; Velenzuela-Calaboro et al., 1990; Ferro-Garcia et al., 1988). The use of biosorbents for metal ion was removed from aqueous effluents (Volesky and Holan, 1995). Some of the biosorbents have been investigated by including agricultural by-products, such as wood, rice-straws, coconut husk and peat-moss (Ho et al., 1994).

An estimated 5 million scrap tyres (ST) existed in Nigeria in 1983 (Ebewele and Dzony, 1990). Out of these, each year about 700 to 850 thousands ST were added into the waste stream. Scrap tires are recalcitrant to biodegradation and they remain in the environment for a long time to come and constitute a waste disposal problem. The applications of ST is used for the removal of Hg (II) ion from aqueous solution (Knocke and Hemphill, 1981), and for immobilization of Hg (II) ion in contaminated soils. The production of active carbons from tyre wastes has been used by Manchon-Vizuete et al. (2005) for the removal of Hg (II) ion from aqueous system.
Short Communication

Investigation of Pine Needles for Pulp/Paper Industry

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Abstract. Pine needles (pine leaves) were analyzed for their chemical constituents, and the dimensions of the extracted fibres were determined to assess their utilization for pulp making. Cellulose content of pine needles (41%) was comparable to softwood (42%), whereas the lignin content (35.1%) was high as compared to both softwood (28%) and hardwood (20%). Ash content of pine needles (3.2%) was less than wheat straw (4-9%) and comparable to bagasse (1.5-5 %). The average length of the pine needle fibre (13 mm) was greater than fibres of sugarcane (1.7 mm), wheat straw (1.4 mm) and esparto (1.2 mm), but less than cotton (30 mm). The average diameter of pine needle fibre (32 μm) was greater than all the common fibres used for papermaking.

Keywords: pine needles, pulp making, paper industry, pine needle fibre

Paper is made from cellulose derived from a limited number of plants. Agro-based or non-wood fibres are the potential sources for pulp and paper making (Ilvessalo-Pfäffli, 1995). The non-wood fibre is usually obtained from the high-cellulose containing materials like cotton, cotton linter, bagasse, flax, abaca and grasses of various types. The use of non-wood fibres in combination with wood fibres is also useful for paper making, as it can reduce the amount of chemicals used and can also shorten the pulping time, thus saving energy. Besides this, the non-wood fibres have some other disadvantages also, because microorganisms can easily attack them and thus deteriorate during storage. Pine needles are among the non-wood materials and are abundantly available in Pakistan.

Pine needles are the long leaves of the evergreen pine trees. Five species of pine trees are available in Pakistan (Nasir and Nasir, 1987). Generally, Pinus longifolia (‘chir pine’) is found in the forests of 1200-1850 m altitudes, while Pinus wallichiana (blue pine) is found in the forests between 1850-2750 m altitudes. These species of the genus Pinus are abundantly available in the Northwestern areas of Pakistan, i.e., Hazara, Murree, Dir, Swat, Chitral, and Azad Jammu and Kashmir. In Pakistan, the total area of these coniferous forests is 1928 thousand hectare spread over the range lands of the North West Frontier, the Punjab and Baluchistan provinces of Pakistan (Siddiqui, 1991).

The length of pine needles of various species varies from 14 to 16 cm. These are bluish to grey-green and turn dark brown when mature. The mature dried needles fall throughout the year and are spread in the entire bed of the forests. The present study deals with the chemical composition of pine needles, their fibre extraction, physical characteristics of the extracted fibre, and suitability for pulp and papermaking.

The mature and dry leaves of the two pine species, namely, Pinus longifolia and P. wallichiana were collected from Hazara forests. The needles were washed, air-dried and milled. The moisture content was determined by heating the sample to a constant weight at 110 °C. The ash content was determined by muffleing the samples at 580-600 °C in a Muffle furnace (ASTM, 2002), and the silica content was determined by heating the sample at 900 °C. The cellulose content was determined by Cross and Bevan chlorination method (Doree, 1950). Oven-dried pine needle sample (5 g) was boiled for 30 min in 200 ml sodium hydroxide (1%) solution. The sample was drained on a cloth filter. After squeezing, the sample was subjected to chlorine gas exposure, until the colour changed to golden-yellow. The chlorine treated sample was thoroughly washed with distilled water, then 100 ml of 2% sodium sulphate solution was added and the temperature was gradually raised to boiling. Sodium hydroxide (0.2 g) was added and boiling was continued for further 5 min. The sample was bleached with 200 ml potassium permanganate (0.15 M) solution. The bleached sample was treated with 200 ml sulphurous acid (10%), washed and digested for 30 min. The percentage of cellulose was then determined. Lignin was determined by the AOAC method (AOAC, 2002). Calcium and magnesium were determined volumetrically (Furman, 1963), while sodium and potassium were determined by using flame photometer (Corning-4000). Atomic absorption spectrophotometer (Hitachi Z-8000) was used for the determination of Fe and Mn.

Chemical procedure was used for the extraction of fibres. NaOH was used for the chemical treatment of pine needles. 10 g of the oven-dried sample of pine needle was boiled with
Acute Toxicity Studies of Bombax cieba Flowers In Mice and Rats

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(received November 24, 2005; revised September 29, 2006; accepted October 10, 2006)

Abstract. Aqueous extract of Bombax cieba (red silk cotton tree) flowers exhibited a marked action on central nervous system. The signs and symptoms observed in non-lethal doses through oral and intravenous routes in rats and mice were found to be solely functional and short-lived, while lethal doses imparted pharmacological and toxicological action by affecting physiological mechanism of the body. Furthermore, the magnitude and intensity of the toxic symptoms exhibited were found to be highly dose dependent. The mortalities that occurred may be due to the direct action on central nervous system. The LD_{50} as calculated for oral route in rats was 6768.730 mg/kg and for intravenous route in rats and mice were 889.496 mg/kg and 467.84 mg/kg, respectively.

Keywords: Bombax cieba flowers, red silk cotton tree, toxicity study, short term toxicity

Introduction

Bombax cieba Linn. (family: Bombaceae), syn. Salmalia malabarica Schout, Bombax malabaricum DC, is one of the trees of infernal regions. It is commonly known as sainbhal, nirma and red silk cotton tree (Anon., 2002; Krishnamurti and Chadha, 1972; Nadkarni, 1954; Dymock et al., 1890). The plant is found abundantly in Pakistan, India (Eastern Himalayas, Assam, West Bengal), Burma and Sri Lanka (Krishnamurti and Chadha, 1972; Nadkarni, 1954; Dymock et al., 1890). The plant is not only valued for its economic importance (Seth, 2004; Chawla and Sharma, 1972; Sharma and Thakur, 1992), but also for its medicinal importance. Almost all parts of the plant are used for different medicinal purposes, locally as well as systemically (Krishnamurti and Chadha, 1972; Nadkarni, 1954). B. cieba is used as a remedy for diarrhoea, dysentery, menorrhagia, leucorrhoea, haemorrhoids, piles, conjunctivitis, skin eruption, boils, sore throat, itch, inflammation, acne, and pimples with great success (Young et al., 2003; Krishnamurti and Chadha, 1972; Yang et al., 1970; Nadkarni, 1954). The plant, specially flowers, also possesses astringent, demulcent, stimulant and aphrodisiac properties. It also acts as a tonic, improves general debility as rejuvenative. Studies have also revealed its antiangiogenic and cytotoxic (Young et al., 2003), musculotrophic (Misra et al., 1968), hypotensive (Rubeena et al., 2003; Rubeena and Mohammed, 1999), and diuretic and antifungal activities (Puckhabar and Stipanovic, 2001).

Ample data regarding the phytochemical analysis of the plant is available, which reveals the presence of alkaloids, glycosides, flavonoids, terpenes, sesquiterpenes and tannins (Sankaram et al., 1981; Rizvi and Saxena, 1974; Yang et al., 1970); phenolic compounds, lupeol and anthocyanins (Seshadri et al., 1973; Niranjan and Gupta, 1973); and polysaccharides, sugars, proteins, essential oils, amino acids, colouring matter and trace metals (Bushe and Mohammed, 1987; Haq and Gomes, 1973; Agarwal et al., 1972; Duong et al., 1969). However, very little has been reported on the toxicity of Bombax cieba. The use and practical implications of the plant, as a source of drug, requires convincing proofs for the absence of toxic and deleterious affects. Therefore, the present work is aimed to quantify the risk of untowards signs and symptoms according to the dose and route of application.

Materials and Methods

Plant material. Fresh flowers of Bombax cieba were collected from the surroundings of the University of Karachi (Karachi, Pakistan) during the month of March 2005. Flowers were authenticated at the Department of Botany, University of Karachi. A voucher specimen was deposited in the same department for further reference.

Preparation of extract. Flowers (without sepal) were washed and dried in air at room temperature. The material was then chopped into small bits and soaked for 72 h in 95% ethyl alcohol (100 g/1 litre), with continuous agitation for 6 h/day. The solvent was decanted and fresh ethyl alcohol was again added to the material. This process was repeated thrice to obtain maximum quantity of the extract. The extracted material was pooled, and the solvent was then removed under reduced pressure at 45 °C ± 5 °C. This afforded a crude ethanolic extract (29.097%). A part (50%) of the alcoholic extract was partitioned with water and petroleum ether.
Invertebrates Associated with *Ipomea aquatica* in Ogbe Creek, Lagos, Nigeria

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(received October 14, 2005; revised August 24, 2006; accepted September 13, 2006)

Abstract. The association of invertebrates in Ogbe creek with *Ipomea aquatica* was investigated within the period from 7th September to 30th November, 2001. 167 invertebrates comprising of 19 species were harvested from 73 weeds. *Corixa punctata* (22.16%) was the most abundant invertebrate on *Ipomea aquatica* while *Gyrinus notator* larvae (0.60%) were the least abundant. The roots sheltered the highest number of invertebrates (113), comprising of 12 species recording a species diversity of 5.36 while the stem sheltered the lowest number of invertebrates (10) comprising of 3 species with a species diversity of 2.00. The ability of *Ipomea aquatica* to harbour invertebrates was influenced by the morphological form of the plant. The root was the preferred site for the invertebrates because it was a suitable substrate for clinging and nutrient supply.

Keywords: *Ipomea aquatica*, niche, invertebrates, ecosystem

Introduction

*Ipomea aquatica* (Convolvulaceae) is an ecologically significant weed widely cultivated as green vegetable in China, India, Malaysia, Africa, Brazil, the West Indies and Central America (Staples, 1996). Though useful as a vegetable crop, *Ipomea* has a great nuisance value, commonly listed as a prohibited plant and noxious weed in many developed countries. Wallace and Webster (1996) considered it as the second greatest problem plant in the Philippines, where it tends to overgrow freshwater marginal areas. It forms dense floating mats of intertwined stems over water surfaces, shading out native submerged plants, competing with native emergent and successfully displacing them (Akobundu and Agyakwa 1998; Staples, 1996). Biological invaders are widespread and can alter population dynamics and community structure of native ecosystems (Jason, 2000). They are known to have a wide variety of impacts on native biota, however such impacts are often poorly understood and difficult to predict (Sax et al., 2005). Some detrimental impacts of invasive species on native biota include, decline in abundance of native biota, contraction of geographic ranges and extinction of native species (Fritts and Rodda 1998; Ebenhard, 1988; Elton, 1958). They have also been known to cause changes in community structure and ecosystem functioning (Mack and D’Antonio 1998; Luken and Thieret, 1997; D’Antonio and Vitousek, 1992). However, most exotic species have not been documented to have any detrimental effect on native biota. Luc et al. (2003) reported that in the Lake Chivero, Zimbabwe, there was no clear support for a considerable difference in overall species diversity at sampling sites covered by plant when compared to non-covered sites.

This study was carried out to ascertain the invertebrates associated with *Ipomea aquatica* in Ogbe creek, Lagos, Nigeria and to establish, if there is a preferred site by these organisms for a particular part of the weed. Understanding the assemblage of invertebrates associated with this aquatic weed is essential for predicting its impact as an invasive species on local ecosystems.

Materials and Methods

Study site. Ogbe creek is located within the University of Lagos campus between latitude 6° 30’N and longitude 3° 29’E. It covers a total area of 77410.84m². It is a sluggish non-tidal, eutrophic body of water that drains into the Lagos Lagoon (Nwankwo and Akinsoji, 1988). The stream is about 80 metres south of works and services department and flows along the commercial road. The stream then widens directly under the bridge along the international school road, crossing the uninhabited lawn of the school, till it gets out of the campus. Then it join another stream that runs eastward into the Lagos lagoon. The creek harbours many aquatic plants. The plants found are *Ipomea aquatica*, *Pistia stratiotes* (Araceae), *Azolla pinnata* (Azollaceae), *Diplazium sammatii* (Athyriaceae), *Eclipa alba* (Asteraceae) and *Cyperus difformis* (Cyperacea). The creek is presently being used as a dump site for refuse by people who live along its course.

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Investigations on the Use of Poison Baits and Fumigants Against Indian Crested Porcupine (*Hystrix indica*)

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**Abstract.** Preventive methods were investigated against the Indian crested porcupine as it seriously damages trees, field crops, and vegetables. Large-scale field trials were conducted to determine the efficacy of two poison baits (0.0375% coumatetralyl and 2% zinc phosphide) and two fumigants (carbon monoxide and calcium cyanide powder) against the Indian crested porcupine, *Hystrix indica*, in forest plantations, ‘barani’ or drylands, and desert rangelands. On the average, carbon monoxide, calcium cyanide and coumatetralyl caused 95.84, 96.52, and 100% mortality, and were equally effective. The zinc phosphide bait yielded 27.78% mortality, indicating that it was less effective and poorly consumed by the porcupines. Use of the two fumigants and the grain bait of coumatetralyl was found to be excellent for the control of Indian crested porcupines in different habitats.

**Keywords:** *Hystrix indica*, poison baits efficacy, fumigants, Indian crested porcupine management

**Introduction**

Porcupines are among the world’s largest rodents and have been recognized as forest pests in many countries of the New and Old Worlds (Walker, 1999; Harrison, 1972; Faulkner and Dodge, 1962; Spencer, 1950). In Pakistan, *Hystrix indica*, an Old World species, is widely distributed in the irrigated and scrub forest plantations, sandy deserts of Punjab and Sindh, Pothwar plateau (Punjab), and is commonly found in the steppe mountains of Balochistan (Roberts, 1998; Mian et al., 1988), upland valleys of Azad Jammu and Kashmir (AJ&K) and in watershed areas of the North-West Frontier Province (Khan et al., 2000).

The Indian crested porcupine is a generalist forager that exploits a wide variety of cultivated and wild plants, and consumes both the aboveground and sub-surface plant tissues. Geddes and Iles (1991) have ranked the Indian porcupine as a pest of crops, vegetables and fruit orchards in Pakistan. Damage and losses of crops, vegetables and fodder have been reported by Khan et al. (2000; 1997), Brooks et al. (1988), and Ahmad et al. (1987). These studies indicated widespread damage to maize in Faisalabad (Punjab) and AJ&K, and in the groundnut growing areas of the Punjab province, while high damage (17.56%) was recorded for potatoes near Taxila (North-West Frontier Province). Safron (*Crocus sativa*) fields near Mustung (Balochistan, Pakistan) were observed to be seriously damaged by 2-3 visiting porcupines (Mian et al., 1988). Alkon (1985) and Alkon and Saltz (1985), reported heavy damage to irrigated potato fields in the Negev desert of southern Israel.

The most important porcupine damage occurs in the forestry and reforestation areas (Greaves and Khan, 1978; Ahmad and Chaudhry, 1977; Chaudhry and Ahmad, 1975; Chaudhry, 1970). The most commonly and heavily damaged tree species include, *Melia azedarach* (neem), *Morus alba*, *Robinia pseudoacacia*, *Dalbergia sisso*, *Pinus roxburghii*, *Bombax ceiba* and *Eucalyptus* spp. Nawaz and Ahmad (1974) calculated a loss of 136,136 ft³ (5,042 m³) of wood in different Changa Manga plantations (5263 ha) in the Punjab, valued at Rs. 0.9 million. Sheikher (1998) reported serious damage to forest trees in the Himachal Pradesh province of India, while Idris and Rana (2001) estimated damage of 30% of neem seedlings and 12% of *Eucalyptus* spp. in the Aravelli Hills near Jodhpur, India. Ahmad et al. (2003) also recorded porcupine damage to neem plantation in the rangelands of lower Sindh, Pakistan. Another study carried out in India revealed that porcupine caused 5.39% damage to young coconut plants in the coastal Karnataka (Charkraborthy and Girish, 2002). The first author of the present study observed serious and wide spread damage to wild *Pistacia* spp. plantations in the mountain valleys of Muslim Bagh, Balochistan.

The measures to prevent porcupine damage have been little studies, except for some preliminary investigations by Arshad et al. (1988), and Chaudhry and Ahmad (1975). They used either aluminium phosphide or baits made from highly toxic...
Eco-physiological Studies on Gmelina arborea: I. Pre-germination Treatments and Initial Growth Developments

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(Received December 9, 2004; revised July 1, 2006; accepted July 22, 2006)

Abstract. This study examined the effects of immersion in cold water, hot water, conc H2SO4, vernalization and mechanical scarification on the germination and initial growth development of Gmelina arborea. In the treated seeds germination was faster than the untreated seeds i.e. the control. While germination was first observed on 9th day after sowing in the treated seeds, in the control it took 16 days after sowing for germination. The results also showed that longer exposure of the seeds to the treatment medium might not necessarily hasten germination. The speed of germination was directly proportional to the germination percent. Manually scarified seeds had the highest germination percent %, followed by cold, hot, vernalization and acid treatments, respectively. Most seedlings from treated seeds grow better than those from the control. The early germination might be responsible for the better growth advantage.

Keywords: Gmelina arborea, cold water, hot water, conc H2SO4, vernalization, mechanical scarification,

Introduction

In the recent years, considerable efforts are being made in Nigeria to encourage tree-planting activities in order to arrest the unprecedented rates of deforestation in the country. These efforts had been met with little or no success. Kayode et al. (1997) attributed a number of factors to this failure. These include the fact that many of the tree planting exercises had advocated the use of exotic species rather than the indigenous. Previous assertion by Osemeobo (1993) had revealed that the rural dwellers have selected, nurtured and used the indigenous species tremendously; Hence they are quite familiar with them.

Although, the exotic species appeared strange, yet the indigenous were quite unsustainable. Also these exotic species are fast growing. Gmelina arborea (locally known as Melina) is one of such fast growing sustainable species introduced in the country. Unfortunately, the biology and silvicultural activities of the species were not clearly understood by those who expressed willingness to invest on the species (Nwoboshi, 1982). Gmelina seeds, which constituted the primary source of its propagation, are thick and hard-coated. Such seeds, according to Dijk (1991) are associated with dormancy, which poses very serious limitations to their germination and probably imposes mechanical resistance to the growth of the embryos (Aghatise and Egahreveba, 1994). The delayed and irregular germination, as previously observed by Borrer et al. (1974), injures nursery management and efficiency. Thus, pre-germination treatments are being considered necessary to break dormancy due to seed coat hardness as such will enable them to germinate uniformly and maintain high germination rates.

Presently a gross dearth of literature exists on the eco-physiological studies of this species in Nigeria. This study is therefore, being considered as a benign approach unders-tanding of the biology of this species and encourages its adaptability in the study area.

Materials and Methods

The study was conducted in the Green House of the Department of Plant Science, University of Ado-Ekiti, Ado-Ekiti, Nigeria (7° 40’N, 5° 15’E). Kayode and Franco (2002) had earlier provided the details for the climatic conditions of the study area. The fruits of Gmelina arborea used in this study were collected from the premises of Teaching and Research Farm, University of Ado-Ekiti. The fruits crushed and seeds obtained, then they were subjected to viability test using the popular floating method, which is widely utilized, in the study area.

The experiment was a complete randomized design with five treatments and twelve replicates. The treatments were immersion in cold water, hot water, conc H2SO4 (trioxosulphate (IV) acid), vernalization, and mechanical scarification while ordinary planting serves as the control.

In each treatment 288 seeds were used at the rate of six seeds per pot, and there were twelve replicates per treatment. For the cold water treatment, each seed (total 72 seeds) was immersed in ordinary water for one, two, three and four days before plantation. The hot water treatment involved the immersion of 72 seeds each for one, two, three and four minutes in hot water at 100 °C. They were later soaked in ordinary water for a night and then the seeds were planted.
Introduction

Melon seed (Cucumeropsis edulis) is a very important component of tropical agriculture. It is easily available and highly nutritious to human and animal food. The parched seeds are chewed or ground into an oily paste, which is called ‘egusi’ in Nigeria. This paste is used in baking and frying or as an addition to soup. The amount of oil present in melon seeds varied from 15 to 45% among different species and cultivars. The dehulled seeds contain a significant amount of protein 25 -35% (FAO, 1989).

The use of plant proteins in food formulations depend largely upon their functional quality, the quality shows the behaviour of plant proteins in a food system (Abulude et al., 2005). In Nigeria, industrial utilization of this seed as a source of oil is in existence. The use of seeds depend largely on knowledge of its functional properties. Little information had been published on the nutritive values of this seed as a source of oil is in existence. The use of seeds depend largely on knowledge of its functional properties. Little information had been published on the nutritive values of this seed (Olaofe et al., 1994; FAO, 1989; Akobundu and Cherry, 1982). There is dearth of information on the possible effect of processing on the functional property of the seed.

The aim of present study is to investigate the effects of processing (germination, boiling and toasting) on the functional quality, with a view of ascertaining its utilization as a food resource and adding to existing data in the literature.

Materials and Methods

The seed samples were obtained in June, 2003, from a market in Akure, Ondo State, Nigeria. The experiments were carried out in the Chemistry Laboratory, Federal College of Agriculture Akure, Ondo State, Nigeria.

Preparation of samples: Raw seed sample (hulled). The samples were hand picked. Stones and unhealthy seeds separated from good ones. 100 g of raw seed sample was washed with distilled water, drained in a sieve and sun dried for 6 h, milled in a Kenwood blender, sieved (40 mm mesh) and stored in an air-tight plastic container at 20 °C prior to analyses.

Boiled seed sample (dehulled). Raw seed sample was dehulled by hand-breaking of the shell. 100 g (dehulled) sample was boiled in 150 ml distilled water for 20 min, cooled at 25 °C, then sun-dried for 6 h. Dried seed sample was milled in a Kenwood blender, sieved through a 40 mm mesh sieve and stored in an air-tight plastic container at 20 °C prior to analyses.

Toasted seed sample. One hundred gram of dehulled seeds were toasted in a saucepan by heating on a gas burner for 35 min, stirring with a wooden spoon at intervals, cooled at 25 °C and subsequently sun dried for 6 h. The seeds after drying were ground to pass 40 mm sieve and stored in air tight container at 20 °C.

Germinated seed sample. One hundred gram of raw seed sample was placed in a 1 liter beaker and moistened with distilled water every day and left for 7 days to germinate. The germinated seeds were sun-dried for 6 h and ground to 40 mm mesh sieve and stored in an air tight plastic container at 20 °C prior to analyses.

Procedure. Oil and water absorption capacities were measured by the procedures of Sosulski (1962), oil emulsion stability...
Short Communication

**In-Vitro Chemical Control of Aspergillus flavus Causing Seed Rot of Crops of Family Brassicaceae**

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(received March 28, 2005; revised November 23, 2006; accepted November 30, 2006)

Abstract. *Aspergillus flavus* was frequently isolated from seeds of four crops of family Brassicaceae at different frequencies: mustard (40%), rape (37%), turnip (18%) and radish (16%). Five fungicides namely, Dithane M-45, Derosal 60 WP, Trimiltox Forte, Baytan 10 DS and Vitavax 200 were tested to evaluate the efficacy of these fungicides for the control of *A. flavus*. Amongst the five fungicides tested, Baytan 10 DS completely controlled the colony growth of the fungus at the dose 100 mg/100 ml potato dextrose agar medium (PDA). This was followed by Vitavax 200 at the dose 25 mg, Derosal 60 WP at the dose of 150 mg, Trimiltox Forte at the dose 100 mg, and Dithane M-45 at the dose 250 mg per 100 ml PDA.

Keywords: *Aspergillus flavus*, family Brassicaceae, seed rot, fungicides

Crops of the family Brassicaceae are economically important, as they are the major source of edible oil. The seeds of these plants are attacked by different fungi (Qasim and Ahmed, 1998). Among these fungi, *Aspergillus flavus*, *A. wentii*, *Fusarium*, spp. and *Penicillium* spp. are very important, causing serious levels of high infection (Nasreen, 2003). Seed rots in these crops are mostly caused by *A. flavus* (Hafiz, 1986). The seed quality parameters, such as oil content, erucic acid and protein content are severely damaged by the fungus (Geeta and Reddy, 1990).

Healthy seeds play an important role in yielding good quality oil, protein and glucosinolate for challengeable markets (Podder and Purohit, 1994). It is, therefore, necessary to produce healthy seeds without serious levels of fungal infestations with the application of fungicides (Ahmed et al., 1993). No specific fungicides are available for the control of seed mycoflora. Different scientists have used various fungicides for the control of seed rots (Siddique et al., 2001; Nan, 1995; Rani and Agarwal, 1995; Kumar and Singh, 1986; Rana and Tripathi, 1983). Keeping in view the importance of crops of the family Brassicaceae and the economic losses due to the attack of *A. flavus*, studies were conducted to evaluate proper doses and specific fungicides for the control of this fungus.

Seeds of mustard, rape, turnip and radish were collected from the local market. One hundred seeds from each variety were randomly separated from seed lots for the isolation and identification of *Aspergillus flavus*.

One hundred seeds of each seed category were thoroughly washed under running tap water for about 20 min, and then surface sterilized with 0.01% HgCl₂ for 1-2 min. Twenty five seeds from each crop were inoculated in each petri plate, already containing sterilized potato dextrose agar (PDA) medium. The petri plates were incubated at 20 ± 2 °C for 7 days (Barnett and Hunter, 1987). *Aspergillus flavus* was identified by observing the growth under microscope using the relevant identification keys (Hosne and Momin, 2000). The infection percentage was calculated as described by Siddique et al., (2001) as below:

\[
\text{Infection} \% = \frac{\text{number of infected seed with fungus}}{\text{total number of plates} \times 25}
\]

**Table 1.** Doses of fungicides used for the control of *Aspergillus flavus*  

<table>
<thead>
<tr>
<th>Fungicide</th>
<th>Dose (mg/100 ml PDA)</th>
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<tr>
<td>Derosal 60 WP</td>
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<td>Dithane M-45</td>
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<td>Vitavax 200</td>
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<td>Baytan 10 DS</td>
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<td>70</td>
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PDA = potato dextrose agar

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*Author for correspondence; E-mail: qumberani1@yahoo.com*
Short Communication

Potentials of *Euphorbia tricucalii* and *Ricinus communis* Products for the Control of *Callosobruchus maculatus*

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(received June 7, 2004; revised November 16, 2006; accepted November 24, 2006)

Abstract. This study examined the pesticidal effects of seed oil, seed kernel and wood ash extracts from *Euphorbia tricucalii* and *Ricinus communis* on cowpea weevil (*Callosobruchus maculatus*). All the extracts brought about significant reductions in the number of this pest, through contact killing, when compared to the control. The proportion of the pest killed was directly proportional to the concentrations of the extracts, though mortality at the varying extract concentrations was not significantly different from one another. Also, percentage mortality at corresponding extract concentrations from the two botanicals were not significantly different from one another in the three extract products. The trend of the effectiveness of the extracts from the two botanicals tends to suggest that extracts from *Ricinus communis* were more effective because of their instantaneous reactions on this pest.

Keywords: *Euphorbia tricucalii*, *Ricinus communis*, *Callosobruchus maculatus*, weevil control

*Callosobruchus maculatus* is the most damaging insect pest of cowpea in Nigeria (Kayode, 2006; Jackai and Adalle 1997). Kayode and Adanlawo (2002) had observed that a lot of factors hindered the control of this pest by chemicals in Nigeria.

The study being reported examined the potentials of the products obtained from *Euphorbia tricucalii* and *Ricinus communis* for the control of *Callosobruchus maculatus*. Both botanicals are members of the family Euphorbiaceae.

Preparation of *Euphorbia* and *Ricinus* oil extracts. Seeds of ripe fruits of *Euphorbia* and *Ricinus* were grounded to fine paste. The pastes of each were poured into clean muslin cloths and the oil was pressed out. 1%, 2%, 3%, 4% and 5% *Euphorbia* oil (EO) and *Ricinus* oil (RO) extracts were prepared by mixing 10, 20, 30, 40 and 50 ml each of the EO and RO with 990, 980, 970, 960 and 950 ml of distilled water respectively with an emulsifier (1% soap solution).

Preparation of *Euphorbia* and *Ricinus* seed kernel extracts. 10, 20, 30, 40 and 50 g each of *Euphorbia* and *Ricinus* seed pastes were soaked in 1 litre of distilled water for 12 h and later filtered through a clean muslin cloth and the filtrates used for the experiments.

Preparation of *Euphorbia* and *Ricinus* wood ash extracts. 10, 20, 30, 40 and 50 g of wood ash from *Euphorbia* and *Ricinus* were soaked in 1 litre of distilled water for 12 h and later filtered through a clean muslin cloth and the filtrates used for the experiments.

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Test of the *Euphorbia* and *Ricinus* oil, seed kernel and wood ash extracts. For each of the botanicals, 75 petri dishes were double-lined with Whatman No.1 filter papers. They were then divided into three equal groups. One group was used to test the effects of the oil extracts, another for the seed kernel extracts and the third for the wood ash extracts.

In each group, the 1%, 2%, 3%, 4% and 5% extracts were used to moisten the filter papers. Each treatment had five replicates assays. The papers were allowed to dry for 10 min after which 5 weevils were introduced to them. Control experiments with filter papers moistened with distilled water were set up and replicated five times. The percentage mortality of the weevils at 24, 48 and 72 hrs were observed and determined as:

\[
\text{% Mortality} = \frac{\text{number of dead weevils}}{\text{total number of weevil treated}} \times 100
\]

The three products from the two botanicals examined in this study brought about significant reductions in the number of *C. maculatus* at all the extract concentrations. The reductions were obtained through contact killing. The seed oil extracts from both botanicals appeared to be highly effective even at lower concentrations, where over 80% of the weevil treated were eliminated within 72 h of the treatments in both 1% and 2% extract concentrations (Table 1). The extracts from *Ricinus communis* appeared to have instantaneous mortality effects on the weevil. Table 1, revealed that the % mortality obtained from the extracts of this botanical varied from 46% in 1% extract concentration to 84% in 5% extract concentration within 24 h of application. In both botanicals, the % mortality...
Abstract. Seasonality of cyclopoids (Crustacea: Copepoda) with regards to rainfall variations was studied in Forcados river. Samples were collected by towing two plankton nets of 55 μm and 100 μm mesh sizes at 5 knots for 5 min behind an engine boat. Site meteorological observations showed low temperature range (27.5-31.5 °C), with high rainfall (25.8-602.6 mm). Eleven cyclopoid species were identified, which exhibited seasonality due to rainfall variations. High numerical abundance was observed in the rainy season months of June to September, with peak during July. From these observations it is concluded that, seasonality in the tropics is due to rainfall variations.

Keywords: cyclopoid seasonality, Cyclopoid: Copepods, rainfall variations, tropical river cyclopoids, Forcados river

Investigations into the occurrence and abundance of cyclopoids (Crustacea: Copepoda) is of universal interest. This is so, as the copepods play an important role in the food chains and food webs in the aquatic environment as they are an integral part of the permanent zooplankton populations in the water bodies. Some cyclopoid species are known to act as vectors of the guinea worm disease, Dracunculus medinensis. In Nigeria such investigations include the work of Oronsaye and Okaka, 2000; Johnson et al., 1990; Khan and Ejike, 1984; Egborge, 1972; Green, 1962; Onabamiro, 1952. A search on the interest shows that no work has been published on the cyclopoid copepods of the Forcados river with regards to rainfall variations. This paper intends to provide such information which would be very useful for further environmental studies in the area. Also since, Forcados town is one of the terminals for the export of crude oil from Nigeria, there is need for such a study which would give a baseline information on the cyclopoid copepods of the area.

The Forcados river (a tropical coastal river) is located within Lat 5° 25′N and long. 5° 50′E (Fig. 1). It is a dendritic river draining a number of mangrove swamps from the Niger delta area. Six sampling stations were chosen, marked (A), (B), (C), (D), (E) (F), covering a distance of 50 km (Fig. 1) from April 2004 to March 2005. The cyclopoid copepods were collected using plankton nets of 55 μm and 100 μm mesh sizes. They were preserved in 4% buffered formalin. Identification was made using works and keys provided by Karanovic (2004), Jeje and Fernando (1986), Wickstead (1965), and Onabamiro (1952). Rainfall data was obtained at the meteorological station in Warri, while surface water temperature was measured with centigrade thermometer by Gallenkamp.

Eleven cyclopoid species were identified, namely; Eucyclops macrurus (Sars) 1863; Eucyclops serrulatus (Fischer), 1851; Halicyclops korodiensis Onabamiro, 1952; Halicyclops troglodytes Kiefer, 1954; Macrocyclops distinctus (Richard), 1897; Mesocyclops ogumnus Onabamiro, 1957; Microcyclops rubellus (Lilljeborg), 1901; Microcyclops varicans (Sars), 1893; Oithona nana (Giesbrecht), 1892; Thermocyclops crassus (Fischer), 1853; Thermocyclops neglectus (Sars), 1909.

The rainfall values were plotted in the form of histograms (Fig. 2). The rainy season months were from April to November, while the dry season months were December, January, February and March. The numerical abundance of the cyclopoids was plotted as a line graph and was superimposed on the rainfall histograms (Fig. 2), showing the seasonality of the cyclopoids with regards to rainfall variations.

Table 1 shows a low temperature range (27.5 °C-31.5 °C) which agrees with the fact that temperature fluctuation is not high in the tropics. Imevbore (1965) reported similar low temperature range when he studied the planktonic organisms of Eleiyele reservoir in Ibadan, Western Nigeria. On the other hand, the histograms on rainfall (Fig. 2) shows a high range (25.8 mm-602.6 mm) and marks two distinct seasons in the year, i.e. rainy and dry seasons. This implies that seasonality in the tropics is mainly due to rainfall variations. This agrees with the findings of Lindberg (1957) when he studied cyclopoid copepods of Ivory Coast in West Africa. Figure 2 also shows that the seasonality of the cyclopoids is due to rainfall variations. They were more abundant in the rainy season months, forming a peak in July. Robinson and Robinson (1977) recorded a similar trend when they studied the seasonal distribution of the zooplankton of Lake Chad basin in Nigeria.
Nutrient and Antinutrient Contents of Fermented Roselle Calyx

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(received August 17, 2005; revised December 8, 2006; accepted December 12, 2006)

Abstract. Pure strains of Aspergillus niger, Aspergillus flavus, Saccharomyces cerevisiae and Bacillus subtilis were isolated, cultured and subsequently used to ferment four portions of 100 g each of roselle calyx for 72 h. A decrease in pH with an increase in total titratable acidity (TTA) was recorded. The results of the proximate analysis revealed a significant increase in the protein content of the fermented calyx samples (10.8 ± 1.1 - 12.6 ± 1.1) compared with the unfermented (4.8 ± 1.3). There was no significant increase in the fat content while there was a significant decrease in the ash content. There was a significant decrease (P < 0.05) in the antinutrient content (phytate from 2143.6 ± 0.8 mg/100 g in the unfermented sample to 488.8 ± 3.7 mg/100 g and tannin from 5.30 ± 1.1% in the unfermented sample to 1.32 ± 0.1%) after 72 h of fermentation.

Keywords: vegetable, nutrients, antinutrients, fermentation, phytochemical, biomass, Hibiscus sabdariffa

The aim of this study is to determine the effect of fermentation on the nutrient and antinutrient content of roselle calyx fermented using cheap and non-pathogenic pure strains isolated from the traditional fermentation.

A 400 g of dry green roselle (Hibiscus sabdariffa) calyx was collected from a farmer at Owena near Akure. The chemicals used were of analytical grade.

Sample preparation. The roselle calyces were soaked in distilled water with 5% sodium metabisulphite added to prevent microbial growth for 6 h after which they were washed and divided into four portions of 100 g each. Each portion was put into separate bowls and 2 litres water added before inoculating with pure strains of Aspergillus niger, A. flavus, Saccharomyces cerevisiae and Bacillus subtilis (isolated, cultured and characterized from the traditional fermentation of roselle calyx by A.O. Ojokoh of the Department of Microbiology, Federal University of Technology, Akure, Nigeria). They were allowed to ferment at room temperature (27 °C) for three days.

Physiochemical changes. The pH of each sample was recorded every 12 h with a Cambridge direct reading pH meter.

Total titratable acidity (TTA) was determined on 5 ml aliquot of the sample against 0.1 M NaOH, using phenolphtalein as indicator.

Samples analysis. The proximate composition (ash, fat, moisture and crude fibre) of the fermented calyx were evaluated using the standard AOAC (1984) method and the protein content was determined using the micro-kjeldhal method (N × 6.25). The phytate content was determined using the method of Young and Greaves (1940). The tannin content was determined by the method of Makkar et al. (1993).

Analysis of data. The data were analyzed by students t-test (Zar, 1984). Fig. 1 and 2 show the physiochemical changes that occurred during the fermentation of the roselle calyx. The pH decrease with increase in fermentation period while the total titratable acidity (TTA) increased during the period. The decrease in pH and increase in TTA could possibly be attributed to the secretion of some organic acids during the course of fermentation by the inoculated organisms (Collard and Levi, 1959).

The result of the proximate composition is shown in Table 1. All the fermented samples had increase in protein content with Aspergillus niger fermented sample having the highest increase (12.6 ± 1.1).

The increase in protein content of the calyx samples could be attributed to the possible secretion of some extracellular enzymes into the calyx, in an attempt to make the use of calyx samples as a source of carbon. Apart from this, the increase in the amount of the microbial biomass in the form of single cell proteins may possibly account for the possible increase in the protein content of the samples (Ojokoh et al., 2002).

The decrease in ash content in the fermented samples may be due to the utilization of minerals by the fermenting microorganisms. Table 2 shows the level of antinutrient (tannin and phytate) which the plants probably use for defense. Tannins
Sorption of Some Heavy Metal Ions by Chitosan and Chemically Modified Chitosan

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Abstract. Chitosan was produced by deacetylation of chitin with sodium hydroxide at a temperature of 117 °C (Randal et al, 1979). In this study, chitosan was prepared from African giant land snail (Archachatina marginata), and acrylamide was grafted onto the chitosan to produce chitosan grafted acrylamide (cga). The two varieties (chitosan and cga) were separately used as adsorbents for the removal of some heavy metal ions (Pb^{2+}, Cd^{2+}, and Ni^{2+}) from aqueous systems. The amount of metal ions (Pb^{2+}, Cd^{2+}, and Ni^{2+}) adsorbed onto chitosan at optimum temperature (45 °C) ranged from 43.88-60.60%, 27.50-58.60%, and 41.30-58.90%, respectively. That adsorbed onto cga ranged from 49.40-65.56%, 56.50-97.90%, and 29.60-64.80%, respectively. Results revealed that cga sorption capacity was approximately twice as high as chitosan.

Keywords: heavy metals, sorption, chitosan, metal ions

Introduction

Industrial revolution has accelerated the release of pollutants into the environment. Among these, heavy metals like Hg, Pb, Cd, Ni, As, and Sn, are important pollutants that are highly toxic to humans and other living organisms. Hence their presence in surface and underground waters above the limit is highly undesirable (Ricordel et al, 2001; Miroslav and Vladimir, 1999; Jackson and Jackson, 1996; Manahan, 1994).

Removal of heavy metals from water is important to protect public health. Natural processes can no longer clean the environment of the enormous quantities of pollutants that are generated daily. Usually, treatment at source is the only practical means of controlling toxic metal pollution (Miroslav and Vladimir, 1999). Waste waters containing toxic metals may be treated by addition of anions that cause the precipitation of the metals as insoluble salts (Jackson and Jackson, 1996), while other methods include membrane filtration, activated carbon adsorption and co-precipitation/adsorption. Ion-exchange resins may also be used to treat industrial effluents.

These processes are efficient but expensive. To develop cheaper methods of industrial effluent treatments, Okolo and Okuo, 2004; Okuo and Ozioko, 2001, had used treated peri-winkle shell, coconut husk/shell, and palm kernel fibre, to remove Pb^{2+}, Hg^{2+}, and Cd^{2+} ions from aqueous systems. Reduction in the cost of industrial effluent treatments by devising cheap and affordable alternatives is highly desirable. This will contribute, to minimize the toxic effects of the heavy metals. This paper is aimed at investigating the readily available and cheap raw materials such as snail shell (which is the source of chitosan) for possible applications in isolating some toxic metals from certain industrial wastes. This would not only solve the problem of littering the environment with these raw materials but also to get a better utilization of them.

Materials and Methods

Chemicals and reagents. Analar grade acetic acid, ether, ethanol, sodium hydroxide, cadmium sulphate, lead nitrate, nickel nitrate, ethylenediaminetetraacetic acid (EDTA), hexamethylenetetramine, sulphuric acid, nitric acid, magnesium sulphate, xylenol orange, eriochrome black T, potassium peroxidisulphate, acetone and quinol, were procurred from BDH.

Preparation of chitosan. Chitin material from African giant snail shell (Archachatina marginata) was used. 25.0 g of powder prepared by grinding dried snail shell (bought from a local market in Benin City, Nigeria) was heated with 1.2 litre of 40% aqueous sodium hydroxide solution at 117 °C for a period of 180 min. The mixture was allowed to cool and then filtered and washed with distilled water. It was air-dried and weighed. This gave an impure chitosan. This was purified by dispersing it in 500 ml of 10% aqueous sodium hydroxide solution at 117 °C for a period of 180 min. The mixture was allowed to cool and then filtered and washed with distilled water. It was air-dried and weighed. This gave an impure chitosan. This was purified by dispersing it in 500 ml of 10% aqueous acetic acid. The mixture was centrifuged after 24 h. A clear supernatant liquid was obtained and treated with dropwise addition of 40% aqueous sodium hydroxide solution until a white flocculant precipitate was formed at pH 6.8. This was recovered by centrifugation. It was washed repeatedly with distilled water, ether, ethanol, respectively and allowed to dry. The product formed was...
# Contents of Pak. J. Sci. Ind. Res. 2006, 49(1-6)

**Vol. 49(1), January - February 2006**

## Physical Sciences

- **Metallogenesis of the Lode Gold Deposit in Ilesha Area of Southwestern Nigeria: Inferences from Lead Isotope Systematics**  
  Akindele O. Oyinloye  
  [1]

- **Search of Clay Deposits in a Dual Geological Environment in the South-Southern Part of Nigeria**  
  O. Ujuanbi and M. B. Asokhia  
  [12]

- **A Comparative Study of the Transient Response Characteristics of Laboratory-Scale Spray Columns and Packed Columns**  
  [19]

- **Effect on Lipid Composition of Groundnuts Roasted in Electromagnetic Waves of Microwave Oven**  
  Hifza Akhter, Shahnaz Hamid and Amran Waheed  
  [23]

- **Studies on the Lipids of Kinnow Orange Seeds**  
  Shahid Mahmud, M. Akhtar Javed, Abdul Qayyum Athar and Sania Mazhar  
  [27]

- **Column Treatment of Brewery Wastewater Using Clay Fortified with Stone-Pebbles**  
  N. A. Oladoja, C. M. A. Ademoroti, J. A. Idiaghe and A. A. Oketola  
  [31]

## Biological Sciences

- **Clinical Studies on the Circulatory Effects of ‘Ramadan’ Fasting in Healthy Volunteers**  
  Naseem M. Qadri and Maryam Mirza  
  [39]

- **Natural Occurrence of Ochratoxin ‘A’ in Raisins in Pakistan**  
  Zuzzer A. Shamsuddin, Mobeen A. Khan and Aftab Ahmed  
  [43]

## Technology

- **Production and Quality Evaluation of Extruded Full-Fat Soy Flour**  
  Hamida Abid, Surruya Wadud and Hussan Ara  
  [48]

- **The Effect of Processing Conditions on the Quality Characteristics of ‘Garri’ Produced from Cassava (Manihot esculenta)**  
  S. I. Ogiehor and M. J. Ikenebomeh  
  [53]

## Review

- **Thermostable Cyclodextrin Glucanotransferases**  
  Naeem Rashid, Azad Hussain Shah, Muhammad Saleem Haider and Javed Iqbal  
  [58]
Vol. 49(2), March - April 2006

Physical Sciences

Dissolution of Chalcopyrite with Hydrogen Peroxide in Sulphuric Acid
A. O. Adebayo, K. O. Ipinmoroti and O. O. Ajayi 65

A Method for the Determination of Relative Crystallinity of Minerals by
X-Ray Diffraction
Abdul Mannan, K. R. Kazmi, Muhammad Shafiq Khan and I. H. Khan 72

Development of Nanoparticles of Alumina by Sol-Gel Method Using Inorganic
Aluminum Salts as Precursors
Fadia Shaheen, Wajid Ali Shah, Pervez Iqbal Qazi and Muhammad Latif Mirza 77

Evaluation of Paint Industry Effluents for Irrigation Purposes
Y. N. Jolly, A. Islam, S. B. Quraishi and A. I. Mustafa 82

Trace Metals in Water and Sediments from Ologe Lagoon, Southwestern Nigeria
K. A. Yusuf and O. Osibanjo 88

Studies on Zinc(II)-Biosorption Capability of a Filamentous Green Algal Species
(Mougeotia viridis) Isolated from Electroplating Wastewater
Asma Saeed, Asia Aslam and Muhammed Iqbal 97

Short Communication

Development and Applications of Animal Amylases for Enzymatic
Desizing of Woven Fabric
A. Farhan Khan and Shoib Arif 103

Biological Sciences

Population Structure of the Juvenile Penaeid Shrimps Occurring in the Sandspit
Backwaters of Karachi Coast, Pakistan
Razia Sultan and Javed Mustaquim 106

Biomass Production of Pleurotus sajor-caju by Submerged Culture Fermentation
Tasnim Kausar, Zahida Nasreen, M. Nadeem and Shahjahan Baig 116

Prevalence of Mycotoxins in Poultry Rations
Nafeesa Qudia Hanif, Muhammad Naseem, Salma Khatoon and Najma Malik 120

Yield and Chemical Composition of Tobacco Leaves of Different Cultivars as
Affected by Four Levels of Potassium Chloride
Hamid Gul, Riaz A. Khattak and Dost Muhammad 125

Genetic Architecture of Yield in Eggplant (Solanum melongena)
A. K. M. Quamrzzaman, M. Nazim Uddin, M. Mashuir Rahman, M. A. Salam and M. K. Jamil 134
Short Communication

Location of Seed-borne Inoculum of *Lasiodiplodia theobromae* and its Transmission in Seedlings of Pumpkin (*Cucurbita pepo*)
Nasreen Sultana

Technology

Control of Chrome Pollution in Tannery Wastewaters with Humic Acids
Surriaya Mir, Zakiuddin Ahmed and Arif Kazmi

**Vol. 49(3), May - June 2006**

Physical Sciences

Thermophysical Properties of Porous Media: Consolidated Sandstones
Asghari Maqsood, I. H. Gul and Kashif Kamran

Electrical Conductances of Some Ammonium and Tetraalkylammonium Halides in Aqueous Binary Mixtures of 1, 4-Dioxane at 298.15 K
Mahendra Nath Roy, Biswajit Sinha, Vikas Kumar Dakua and Anuradha Sinha

Determination of Densities of Amino Compounds for Molar Volumes in Aqueous Solutions with Magnetic Float Densimeter at Various Temperatures
Man Singh

Crystallization Studies of Lithium Borosilicate Glasses
Pervez Iqbal Qazi, Wajid Ali Shah and Fadia Shaheen

Some Copper(II) Complexes of Tetradentate β-Ketoimines and their Adducts
Aderoju A. Osowole

Evaluation of the Three-Stage BCR (European Community Bureau of Reference) Sequential Extraction Procedure to Assess the Potential Mobility and Toxicity of Heavy Metals in Roadside Soils
K. A. Yusuf

Mumtaz Khan, A. R. Khan, Tabraiz Anwer, Tahseen Aslam and Shahab Ahmad

Biological Sciences

Culture of the Microalga *Chlorella vulgaris* on Different Proportions of Sugar Mill Effluents
A. N. M. A. I. Khan, M. A. B. Habib, M. R. Islam, M. S. Hossain and M. I. Miah
Regeneration and Acclimatization of Salt-Tolerant *Arachis hypogaea* Plants Through Tissue Culture

Ejaz Gul Ghauri 203

Yield and Quality of Two Cultivars of Sugar Beet as Influenced by Fertilizer Applications

Zahoor ul Haq, Aurang Zeb and F. Mahmood 211

**Technology**

Solvent Extraction and Electrowinning of Copper from Hot Rolling Mill Scale Liquor

Rehmat Ali Gohar, Sameer Ahmad and Asma Haleem Khan 215

**Short Communication**

Cathodic Efficiency of Industrial Chromium Plating

Inam-ul-Haq, Asim Khan and Abdul Rasheed 222

**Physical Sciences**

Studies on Dielectric Behaviour of Some Long Chain Alcohols and Their Mixtures With a Non-Polar Solvent at Various Concentrations

Muhammad Yaqub, S. Shakeel Ahmed and Altaf Hussain 225

Role of Nucleosides on Nickel Electroplating from a Formamide Bath

Ashutosh K. Gupta, H. K. Srivastava, Jyotsna Singh and Rahul Kashyap 231

Absorption Mechanism of Sulfur Dioxide into Alcoholic Sodium Hydroxide Solutions

Abdul Khalique, Adnan Akram, Nusrat Hamid and Izhar H. Khan 237

Investigations on Indigenous Fuller's Earth and its Evaluation After Acid Activation

M. Sharif Nizami and M. Iqbal Chaudhry 242

Synthesis and Spectral Studies of Some Magnesium Complexes of Aromatic Hydrazones

A. A. Adeniyi, O. O. Oyedoji, J. A. Aremu, J. O. Okeledy and S. A. Bourne 246

Physical Characteristics, Inorganic Constituents and Trace Metals Determination in the Street-Vended Samples of Heroin

Imdad Ullah Mohammadzai, Mumtaz Khan, Muhammad Irfan, Nadir Khan and Saadya Usman 251

Traffic Noise in Lahore City, Pakistan. Part II. Vehicular Contribution to Traffic Noise

G. H. Shaikh, Tanveer Ahmad and Khalid Islam 256

Environmental Study of a Pulp and Paper Mill in NWFP, Pakistan

Jehangir Shah, Asadullah Jan and Amin ur Rahman 261
Short Communication

Removal of Phenolic Compounds from Industrial Wastewater by Activated Carbon
Tayyaba Aftab, Naz Imtiaz and Tahira Shafiq 266

Biological Sciences

Anticonvulsant Activity of *Emilia sonchifolia* Leaf Extracts
O. Asije, S. A. Adelusi and C. O. Usifoh 269

The Nutritional Value of *Sorghum bicolor* Stem Flour Used for Infusion Drinks in Nigeria
A. O. Adetuyi and V. O. E. Akpambang 276

Some Factors Affecting the *In Vitro* Culture of Banana
Tauqeer Ahmad, Nasreen Zaidi, Nuzhat Habib Khan and Zia-ur-Rehman 281

Quality Evaluation of Some Sindh (Pakistan) Wheat Varieties. II. Correlation Among Various Quality Traits
Saqib Arif, Mubarik Ahmed and Kamran Kadir Khanzada 285

Contribution of Cereal-Legume Association to the Yield and Grain Quality of Cereals
Abdur Rashid, Himayatullah and Rahmatullah Khan 290

Short Communication

The Effect of Aqueous Extracts from Leaf Leachates and the Soil Beneath *Chromoleana odorata* and *Euphorbia heterophylla* on the Germination of Cowpea Seeds
J. Kayode 296

Vol. 49(5), September - October 2006

Physical Sciences

Geology, Geochemistry and Geotectonic Setting of the Pan-African Granites and Charnockites Around Ado-Ekiti, Southwestern Nigeria
Akindele O. Oyinloye and Romanus Obasi 299

Effect of Excess Metal Concentration on the Extraction Potential of Di-(2-Ethylhexyl) Phosphoric Acid

Evaluation of Locally Available Fuller's Earth for the Bleaching of Soybean Oil
M. Sharif Nizami and M. Iqbal Chaudhry 314

Studies on the Laboratory Scale Synthesis of 4, 4'-Diaminodiphenylurea and Preparation of Direct Dyes from the Compound
S. Rehman Khan, A. M. Gilani, Asma Inayat and Shaheena Waheed 319
Synthesis and Fungicidal Activity of Some Sulphide Derivatives of O-Ethyl-N-Substituted Phenylcarbamates
F. Adelowo-Imeokparia and I. A. O. Ojo 324

Isolation and Characterization of Kappa-Carrageenan from Hypnea musciformis (Red Alga) Collected from Karachi Coast, Pakistan
Fatima Bi, Muhammad Arman, Mahmood-ul-Hassan and Seema Iqbal 330

Comparative Studies on the Adsorption Properties of Powdered Activated Carbon and Propenoic Acid Modified Sawdust in the Treatment of Secondary Palm Oil Mill Effluent
M. O. Osuide, C. M. A. Ademoroti, V. U. Okojie and F. E. Igbinavbiere 335

Short Communication

Some Studies on the Changes in the Composition of Coal Ash and Bottom/Fly Ash Produced in Atmospheric Fluidized Bed Combustor
Ismat Ali and M. Mohsin Ali 341

Biological Sciences

High Frequency In vitro Propagation of Polianthes tuberosa
Muhammad Saeed Ahmad, Tauqeer Ahmad, Nasreen Zaidi and Idress Ahmad Nasir 344

Morphological Changes in Cotton Roots in Relation to Soil Mechanical Impedance and Matric Potential
Ghulam Nabi and C. E. Mullins 349

Multiple Parameters for Ascertaining Yield Stability of Upland Cotton Varieties Tested Over Number of Environments
Muhammed Jurial Baloch and Nasreen Fatima Veesar 355

Technology

Isolation and Stabilization of Dark Red Food Dye from Beta vulgaris
Alim-un-Nisa, Shamma Firdous and Nusrat Ijaz 360

The Effect of Substitution on the Dyeing and Spectroscopic Properties of Some Monoazo Disperse Dyes
Ausaf Aleem, Mohammad Naeem, M. Aleem Ahmed, Kamran Ahmed and Mansoor Iqbal 364

Physicochemical Characteristics of Rayon Grade Dissolving Pulp and the Effects of Metallic-Ions on the Viscose Rayon Process
Atif Latif, Asad Ullah Jan, Farid Ullah Khan and Amin Ur Rahman 368

Short Communication

The Study of Electrolytes on the Dye Uptake of Bifunctional Reactive Red Dyes on a Cellulosic Substrate (Cotton K-68)
Javaid Mughal, Ausaf Aleem, Qasim Siddiqui and Mansoor Iqbal 371
Vol. 49(6), November - December 2006

Physical Sciences

Critical Study on Conventional Concept of Entropy
M. K. Afridi and M. Sharif Nizami 373

Simulation of Voltammogram of a Hindered Quinomethylene
Inam-ul-Haque and Asim Khan 379

Cure Characteristics and Physico-Mechanical Properties of Blends of Epoxidised Natural Rubber and Polystyrene
I. O. Asia, A. K. Akinlabi and E. E. Egbon 383

Corrosion of Aluminum Components and Remedial Measures
Shahid T. Sheikh, Abdul Khalique, F. A. Malik and Nusrat Hamid 388

Effect of Base Media on the Stability of Annatto Dye in Industrial Products
A. O. Adetuyi, L. Lajide and A. V. Popoola 391

Solvent Extraction and Separation of Al(III) and Ni(II) from Aqueous Medium by Cyanex-272 [Bis-(2,4,4-Trimethylpentyl) Phosphinic Acid] in Kerosene
M. F. Islam and M. S. Rahman 395

Evaluation of Sorption Capacity of Scrap Tyre in the Removal of Copper (II) Ion from Aqua System
N. A. Oladoja, A. Ofomaja and E. Ebare 400

Short Communication

Investigation of Pine Needles for Pulp/Paper Industry
Asadullah Jan, Amin Ur Rahman, Farid Ullah Khan and Jehangir Shah 407

Biological Sciences

Acute Toxicity Studies of Bombax cieba Flowers In Mice and Rats
Zakir-ur-Rehman, Atiq-ur-Rehman and Shahnaz Ahmad 410

Invertebrates Associated with Ipomea aquatica in Ogbe Creek, Lagos, Nigeria
J. K. Saliu and Y. T. Fashola 414

Investigations on the Use of Poison Baits and Fumigants Against Indian Crested Porcupine (Hystrix indica)
Abdul Aziz Khan, Afsar Mian and Rashad Hussain 418

Eco-physiological Studies on Gmelina arborea: I. Pre-germination Treatments and Initial Growth Developments
J. Kayode and J. Agbebi 423
Functional Qualities of Raw and Processed Melon (*Cucumeropsis edulis*) Seeds
F. O. Abulude, L. O. Lawal, M. O. Ogunkoya, Y. S. Akinjagunla and O. E. Obajowolo

Short Communications

*In-Vitro* Chemical Control of *Aspergillus flavus* Causing Seed Rot of Crops of Family Brassicaceae
Tamoor Khan, Ghulam Mustafa and Zaheer-ud-Din

Potentials of *Euphorbia tricacali* and *Ricinus communis* Products for the Control of *Callosobruchus maculatus*
Joshua Kayode and Sunday Oyeyemi

Seasonality in Cyclopoids (Crustacea: Copepoda) and Rainfall Variation of the Forcados River, Nigeria
C. G. Oronsaye

Nutrient and Antinutrient Contents of Fermented Roselle Calyx
A. O. Ojokoh, F. C. Adetuyi and F. A. Akinyosoye

Technology

Sorption of Some Heavy Metal Ions by Chitosan and Chemically Modified Chitosan
A. Jideowno, J. M. Okuo and P. O. Okolo

Contents (1-6)

Author Index
AUTHOR INDEX TO VOLUME 49

Abdul Aziz Khan, ................................................................. 418
Abdul Khalique, .................................................................... 237, 388
Abdul Mannan, .................................................................... 72
Abdul Qayyum Athar, ........................................................... 27
Abdul Rasheed, .................................................................... 222
Abdur Rashid, ........................................................................ 290
Abulude, F. O. ..................................................................... 427
Adebayo, A. O. .................................................................... 65
Adelowo-Imeokparia, F. ......................................................... 324
Adelusi, S. A. ........................................................................ 269
Ademoroti, C. M. A. ............................................................... 31, 335
Adeniyi, A. A. ....................................................................... 246
Aderoju A. Osowole ............................................................. 174
Adetuyi, A. O. ...................................................................... 276, 391
Adetuyi, F. C. ....................................................................... 440
Adnan Akram, ...................................................................... 237
Afridi, M. K. ......................................................................... 373
Afridi, S. K. ........................................................................... 309
Afzar Mian, ............................................................... 418
Aftab Ahmed, ....................................................................... 43
Agbebi, J. .............................................................................. 423
Ahmed, A. S. ....................................................................... 309
Ajayi, O. O. .......................................................................... 65
Akhtar Javed, M. ................................................................. 27
Akindele O. Oyinloye, ........................................................... 1, 299
Akinjagunla, Y. S. ................................................................. 427
Akinlabi, A. K. ..................................................................... 383
Akinyosoye, F. A. ................................................................ 440
Akpambang, V. O. E. ............................................................ 276
Aleem Ahmed, M. ................................................................. 364
Alim-un-Nisa, ........................................................................ 360
Altaf Hussain, ...................................................................... 225
Amin ur Rahman, ................................................................. 407
Amran Waheed, ................................................................... 23
Anuradha Sinha, ................................................................... 153
Aremu, J. A. ......................................................................... 246
Arif Kazmi, ........................................................................... 143
Asadullah Jan, ...................................................................... 418
Asadullah, M. ....................................................................... 19
Asghari Maqsood, ................................................................. 147
Ashutosh K. Gupta, ............................................................... 231
Asia Aslam, .......................................................................... 97
Asia, I. O. ............................................................................. 383
Asije, O. .................................................................................. 269
Asim Khan, .......................................................................... 222, 379
Asma Haleem Khan, ............................................................... 215
Asma Inayat, ......................................................................... 319
Asma Saeed, ......................................................................... 97
Asokhia, M. B. ..................................................................... 12
Atif Latif, ............................................................................... 368
Atiq-ur-Rehman, ................................................................... 410
Aurang Zeb, ........................................................................... 211
Ausaf Aleem, ........................................................................ 364, 371
Azad Hussain Shah, ............................................................... 58
Azad, M. A. K. ...................................................................... 19
Bhatti, M. B. ........................................................................... 309
Biswajit Sinha, ....................................................................... 153
Bourne, S. A. ......................................................................... 246
Dost Muhammad, ................................................................. 125
Ebene, E. .............................................................................. 400
Egbon, E. E. .......................................................................... 383
Ejaz Gul Ghauri, ................................................................. 203
Fadia Shaheen, ...................................................................... 170
Fadia Shaheen, ...................................................................... 77
Farhan Khan, A. ................................................................... 103
Farid Ullah Khan, ................................................................. 368, 407
Fashola, Y. T. ........................................................................ 414
Fatima Bi, .............................................................................. 330
Ghulam Mustafa, ................................................................. 431
Ghulam Nabi, ....................................................................... 349
Gilani, A. M. .......................................................................... 319
Gul, I. H. ............................................................................... 147
Habib, M. A. B. ..................................................................... 196
Hamid Gul, ............................................................................ 125
Hamida Abid, ......................................................................... 48
Hifza Akhter, .......................................................................... 23
Himayatullah, ....................................................................... 290
Hossain, M. S. ...................................................................... 196
Hussain Ara, .......................................................................... 48
Idiaghe, J. A. ......................................................................... 31
Idress Ahmad Nasir, ............................................................. 344
Igbinavbiere, F. E. ................................................................ 335
Ikekube, M. J. ........................................................................ 53
Imdad Ullah Mohammadzai, ................................................. 251
Inam-ul-Haq, ......................................................................... 222, 379
Ipinniroti, K. O. .................................................................... 65
Iqbal Chaudhry, M. ............................................................... 242, 314
Islam, A. ................................................................................ 82
Islam, M. F. .......................................................................... 395
Islam, M. R. .......................................................................... 196
Ismat Ali ................................................................................ 341
Izhar H. Khan, ................................................................. 237, 379
Jamil, M. K. ........................................................................... 134
Javaid Mughal, ................................................................. 371
Javed Iqbal, ............................................................................. 58
Author index

Nafeesa Qudsia Hanif, ........................................ 120
Najma Malik, ..................................................... 120
Naseem M. Qadri, .............................................. 39
Nasreen Fatima Veesar, ....................................... 355
Nasreen Sultana, .................................................. 140
Nasreen Zaidi, ....................................................... 281, 344
Naz Intiaz, .............................................................. 266
Nazim Uddin, M. .................................................. 134
Nusrat Hamid, ...................................................... 237, 388
Nusrat Ijaz, ............................................................ 360
Nuzhat Habib Khan, .............................................. 281
Obajowolo, O. E. ................................................... 427
Ofomaja, A. .......................................................... 400
Ogiehor, S. I. .......................................................... 53
Ogunkoya, M. O. ..................................................... 427
Ojo, I. A. O. ............................................................ 324
Ojokoh, A. O. ......................................................... 440
Okebedey, J. O. ....................................................... 246
Oketola, A. A. ......................................................... 31
Okojie, V. U. ........................................................... 335
Okolo, P. O. ............................................................ 443
Okuo, J. M. ............................................................ 443
Oladoja, N. A. ......................................................... 31, 400
Oronsaye, C. G. ..................................................... 437
Osibanjo, O. ............................................................ 88
Osuide, M. O. .......................................................... 335
Oyedeji, O. O. .......................................................... 246
Pervaz Iqbal Qazi, .................................................. 77, 170
Popoola, A. V. ........................................................ 391
Qasim Siddiqui, ....................................................... 371
Quamruzzaman, A. K. M. ....................................... 134
Quraishi, S. B. .......................................................... 82
Rahman, M. A. ....................................................... 19
Rahman, M. S. ....................................................... 19, 395
Rahmatullah Khan, ............................................ 290
Rahul Kashyap, ..................................................... 231
Rani, M. ................................................................. 19
Rashad Hussain, .................................................... 418
Razia Sultana, ....................................................... 106
Rehman Khan, S. .................................................. 319
Rehmat Ali Gohar, ............................................... 215
Riaz A. Khattak, ..................................................... 125
Romanus Obasi, ..................................................... 299
Saadya Usman, ..................................................... 251
Saeed, M. T. ............................................................ 134, 309
Saliu, J. K. .............................................................. 414
<table>
<thead>
<tr>
<th>Author</th>
<th>Page(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salma Khatoon</td>
<td>120</td>
</tr>
<tr>
<td>Sameer Ahmad</td>
<td>215</td>
</tr>
<tr>
<td>Sania Mazhar</td>
<td>27</td>
</tr>
<tr>
<td>Saqib Arif</td>
<td>285</td>
</tr>
<tr>
<td>Seema Iqbal</td>
<td>330</td>
</tr>
<tr>
<td>Shahab Ahmad</td>
<td>189</td>
</tr>
<tr>
<td>Shaheena Waheed</td>
<td>319</td>
</tr>
<tr>
<td>Shahid Mahmud</td>
<td>27</td>
</tr>
<tr>
<td>Shahid T. Sheikh</td>
<td>388</td>
</tr>
<tr>
<td>Shahjahan Baig</td>
<td>116</td>
</tr>
<tr>
<td>Shahnaz Ahmad</td>
<td>410</td>
</tr>
<tr>
<td>Shahnaz Hamid</td>
<td>23</td>
</tr>
<tr>
<td>Shaikh, G. H.</td>
<td>256</td>
</tr>
<tr>
<td>Shakeel Ahmed, S.</td>
<td>225</td>
</tr>
<tr>
<td>Shamma Firdous</td>
<td>360</td>
</tr>
<tr>
<td>Sharif Nizami, M.</td>
<td>242, 314, 373</td>
</tr>
<tr>
<td>Shoib Arif</td>
<td>103</td>
</tr>
<tr>
<td>Srivastava, H. K.</td>
<td>231</td>
</tr>
<tr>
<td>Sunday Oyeyemi</td>
<td>434</td>
</tr>
<tr>
<td>Surriaya Mir</td>
<td>143</td>
</tr>
<tr>
<td>Surruya Wadud</td>
<td>48</td>
</tr>
<tr>
<td>Tabraiz Anwer</td>
<td>189</td>
</tr>
<tr>
<td>Tahira Shafiq</td>
<td>266</td>
</tr>
<tr>
<td>Tahseen Aslam</td>
<td>189</td>
</tr>
<tr>
<td>Tamoor Khan</td>
<td>431</td>
</tr>
<tr>
<td>Tanveer Ahmad</td>
<td>256</td>
</tr>
<tr>
<td>Tasnim Kausar</td>
<td>116</td>
</tr>
<tr>
<td>Tauqueer Ahmad</td>
<td>281, 344</td>
</tr>
<tr>
<td>Tayyaba Aftab</td>
<td>266</td>
</tr>
<tr>
<td>Ujuanbi, O.</td>
<td>12</td>
</tr>
<tr>
<td>Usifoh, C. O.</td>
<td>269</td>
</tr>
<tr>
<td>Vikas Kumar Dukua</td>
<td>153</td>
</tr>
<tr>
<td>Wajid Ali Shah</td>
<td>77, 170</td>
</tr>
<tr>
<td>Yusuf, K. A.</td>
<td>88, 181</td>
</tr>
<tr>
<td>Zaheer-ud-Din</td>
<td>431</td>
</tr>
<tr>
<td>Zahida Nasreen</td>
<td>116</td>
</tr>
<tr>
<td>Zahoor ul Haq</td>
<td>211</td>
</tr>
<tr>
<td>Zakir-ur-Rehman</td>
<td>410</td>
</tr>
<tr>
<td>Zakriuddin Ahmed</td>
<td>143</td>
</tr>
<tr>
<td>Zia-ur-Rehman</td>
<td>281</td>
</tr>
<tr>
<td>Zuzzer A. Shamsuddin</td>
<td>43</td>
</tr>
</tbody>
</table>