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Geology, Geochemistry and Geotectonic Setting of the Pan-African Granites and Charnockites Around Ado-Ekiti, Southwestern Nigeria

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Abstract. The geology, petrology and geochemistry of the coarse-grained and fine-medium-grained gneissic charnockites and the porphyritic biotite-hornblende and medium-grained older granites in the Ado-Ekiti area were studied. Xenoliths of schistose quartzite occur within these charnockitic and granitic rocks. The porphyritic older granite and the coarse-grained charnockite occur in very close association in the field. All these rocks contain monazite, in their mineralogical composition, which indicate crustal input into their original magma. Aluminium-total iron-magnesium (AFM) plot for these rocks indicated that they were calc-alkaline in nature and were formed in a subduction related tectonic setting. Percentage normative corundum versus mol. \( \text{Al}_2 \text{O}_3/(\text{Na}_2+\text{K}_2+\text{Ca}_2+\text{Fe}_2+\text{Si}_2) \) plots for the older granites and the charnockites from the Ado-Ekiti area revealed that their original magma was derived from a mixed source (igneous and crustal). \( \text{Y}^+/\text{Nb} \) versus \( \text{Rb} \) plots for the older rare earth elements and the charnockites indicated that they originated from a volcanic arc and within-plate environments. The normalised rare earth elements (REE) patterns showed that these rocks were genetically related, and the feldspar fractionation took place during their formation as revealed by Eu depletion patterns in the REE diagrams. The negative Eu/Eu* (ratio of absolute europium to normalized europium) anomaly and (La/Yb) ratios higher than 5 obtained in these rocks indicated that they were emplaced through magmatic fractionation. The mixed magma from which these rocks were derived was formed in a back arc tectonic setting where an ocean slab was subducted into the mantle leading to the generation of magma, which intruded into the earlier formed rocks in a back arc basin. The charnockites and the older granites were the end products of the differentiation of such magma.

Keywords: monazite, xenolith, calc-alkaline, subduction, southwestern Nigeria, geotectonic setting, Pan-African granites, charnockites

Introduction

Nigeria lies within the Pan-African mobile belt in between the West African and Congo cartons (Akande, 1991; Woakes et al., 1987; Odeyemi, 1981). The geology of Nigeria is dominated by the pre-cambrian basement (crystalline and schistose metasediments) and recent-cretaceous sedimentary rocks, almost in equal proportions (Rahaman et al., 1988). There is a high level intrusion of jurassic younger granites into the basement complex in Jos area of central-northern Nigeria. The pre-cambrian basement in Nigeria consists of migmatite-gneissic complex within the muscovite-quartzite schists. In the Ado-Ekiti area, the basement complex, apart from the migmatite-gneissic-quartzite complex, includes granitoid plutons which are mostly older granites and charnockites with other minor granite associations (Fig. 1). These rocks have intruded into both migmatite-gneissic complex and the schists. Older granites and charnockites occur prominently in southwestern Nigeria at Iwo, Akure, Idanre, Ikare, Ikere and Ado-Ekiti (Olarawaju, 1987). According to Dada et al. (1989), charnockites also occur at Bena, Makichi, Toro and Zurami in northern Nigeria. The Toro charnockite complex in the north-central Nigeria is Pan-African in age based on a U-Pb-zircon dating, which places the Toro complex in the context of Pan-African granitoid (Dada et al., 1989), making Toro charnockite to be similar in occurrence to those described in the southwestern Nigeria. Recently, Ekwueme (2003) also reported the occurrence of similar Pan-African charnockites in the Oban massives and Obudu plateau in the southeastern Nigeria. On the basis of geochronological and structural evidence, Tubosun et al. (1984) and Annor (1995) believe that the emplacement of granitic and charnockitic complex in southwestern Nigeria took place during the Pan-African tectonic episodes. Olarewaju (1988) suggested on the basis of chemical studies that the Pan-African granites and charnockites in the Ado-Ekiti area are ‘magmatic’ in origin.

The present study focuses attention on the geology and geochemistry of the older granites and the charnockites in the Ado-Ekiti area with a view to explaining their possible geotectonic origin by comparing the concentration of some index elements in the rocks with those of a pure mantle. Discrimination diagrams, based on the chemical contents of the rocks, have been also used to infer the possible tectonic environment(s) in which their magma originated.
Effect of Excess Metal Concentration on the Extraction Potential of Di-(2-Ethylhexyl) Phosphoric Acid

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Abstract. The extraction potential of di-(2-ethylhexyl) phosphoric acid (DEHPA) in kerosene increases manyfold on loading calcium into the organic phase before equilibration with aqueous copper feed. The control of pH was unnecessary in the range from pH 5.0 to pH 3.0. It was found that copper can easily replace nickel, sodium and calcium in the organic phase because of the difference in the dissociation constants of copper and other metals studied. The hydrolysis of calcium maintains the pH of the aqueous phase in favour of higher extraction of copper by DEHPA.

Keywords: dissociation constant, di-(2-ethylhexyl) phosphoric acid, copper extraction

Nomenclature
A− = anions in the aqueous phase
CaR2 = calcium-DEHPA complex
H+ = free hydrogen ions
HR = concentration of organic acidic extractant
OH− = hydroxyl ions
M2+, X2+ = free metal ions (M2+ refers to free metal ions of low dissociate constants, while X2+ refers to free metal ions of high dissociate constants)
MR2, XR2 = concentration of metals in the organic phase
R− = dissociated ions of extractant
XA = concentration of metal salt in the aqueous phase

Introduction
Hydrometallurgical operations using di-(2-ethylhexyl) phosphoric acid (DEHPA) for the extraction of copper have been reported to give lower loadings, as compared with the more expensive second generation extractants (Borowiak-Resterna and Lenarcik, 2004; Cox, 1992; Yoshizuka et al., 1990), such as LIX 864, 865, 984, 622, P5100, 5300, PT5050, SME529, ABF2, and OMG. A number of authors have tried to improve extraction with DEHPA by studying various factors, such as concentration of solvent and solute, effect of pH, influence of sulphate and chloride ions, and the nature of diluents (Cerpa and Alguacil, 2004; Saeed and Jamil, 1998; Ahmed et al., 1994). The principal objective in the application of solvent extraction process is to minimize the control of influencing factors on the separation of competing metals and hence to attain maximum loading of the desired metal in the organic phase.

In order to improve the extraction potential of DEHPA, some researchers (Ajawin et al., 1983; Joe et al., 1966) have used sodium or ammonium salts of DEHPA. The presence of sodium or ammonium ions suppresses the ionization of the metal hydroxide and increases the metal loadings of the organic phase. However, in most cases, a third phase is formed (Ajawin et al., 1983), which reduces the concentration of the metal in the extract phase.

In the present study, a series of experiments were conducted to find out the most suitable metal to form a metal salt of DEHPA that can be employed to achieve maximum extraction. Apropose to this, a number of metal hydroxides, such as sodium hydroxide, calcium hydroxide and nickel sulphate, were initially contacted with DEHPA to make a metal-DEHPA complex before equilibrating it with the aqueous phase. The presence of metal iron in the form of metal-DEHPA complex in the organic phase increased the total metal ions concentration in the equilibrated phases, as compared to the anion concentration in the system. At equilibrium, the exchange of competing metal ions in the aqueous phase was elucidated in the light of much less considered dissociation constants of these metals involved in the process. Other factors, such as concentrations of the solvent and solute and pH of the aqueous phase, were also considered to describe the present process.

Theoretical background. The extraction of metal ions from the aqueous phase by DEHPA in the organic solute has been shown to conform to the following general equation (Ahmed et al., 1994; Rydberg and Serine, 1992):

\[ [\text{Cu}^{2+}]_a + 2[\text{HR}]_o \rightleftharpoons [\text{CuR}_2]_o + 2[\text{H}^+]_a \]  

This is an ion exchange reaction and the final equilibrium depends on dissociation and distribution constants of the various species in the system. The release of hydrogen ions decreases pH of the aqueous solution causing the formation
Evaluation of Locally Available Fuller’s Earth for the Bleaching of Soybean Oil

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Abstract. Locally available Fuller’s earth was investigated for bleaching soybean oil. Investigations showed that raw earth samples possessed desirable physical properties and consisted of the clay minerals suitable for bleaching edible oils. The Fuller’s earth sample was also activated by refluxing with 4 N hydrochloric acid for 3 h at 100 °C. Fresh volumes of soybean oil were bleached with 3% of the activated earth and its bleachibility was determined by Lovibond tintometer. The efficiency of bleachability was compared with that of Tarana Optimum, the standard bleaching earth of German origin for comparison. It was found that bleachibility of the activated earth samples and that of Tarana Optimum was quite comparable.

Keywords: oil bleachibility, Fuller’s earth, soybean oil, Fuller’s earth activation

Introduction

Impurities resulting from the raw material breakdown, or oxidation, impart undesirable colouration to edible oils, which is therefore required to be bleached during the refining process. Oxi-
dation, impart undesirable colouration to edible oils, which is therefore required to be bleached during the refining process, (Hamilton and Bhatti, 1980). Activated charcoal and earths of specific nature are commonly utilized for this purpose. However, the latter being low cost materials are economically very attractive and popular (Brady et al., 1997; Mahatta, 1985). Fuller’s earth, the most important among these, is widely used on account of its low cost. In addition to the cost factor, it has large surface area and possesses the desirable adsorptive properties (Worrall, 1986). Several researchers, due to this reason, have studied and attempted to activate such type of earths/clays for their optimum utilization as edible oil bleaching agents.

Theng and Wells (1995) investigated naturally occurring acid clays of hydrothermal geological formation from New Zealand and found that these were rich in Allophane, Halloysite, Kaolinite and Montmorillonite. They reported, as a result of their studies, that decolourizing capacity decreased in the order Halloysite > Kaolinite > Montmorillonite > Allophane. They also found that the naturally acid leached clays were more effective and required only minor treatment with HCl for optimizing their performance regarding decolourizing properties. Two activated clays, one imported and the other of Brazilian origin, were studied by Cardello et al. (1995), who reported that these were equally effective for bleaching the vegetable oil of Gossypium hirsutum (cotton). Similarly, a patent was registered in Germany (Haehn and Eisgruber, 1995) showing the importance of Fuller’s earth in view of bleachibility of edible oils. It involved the regeneration of the used oil-containing bleaching clays through different steps, such as, decolourization by extraction with a suitable solvent, thermal treatment at 500-650 °C upto 5 h in oxidizing atmosphere, without disturbing the Montmorillonite contents, and treatment with an aqueous acid solution (15-50%) at acid : clay ratio of 0.2-2 : 100.

As Pakistan imports large quantities of bleaching earths for the vegetable oil refining industry, efforts have been made to explore, investigate and activate the locally available earths that have oil bleachability potential. A preliminary attempt was made to achieve the objective by Bogue under the Soil Survey of Pakistan (GSP-GSU, 1962). He investigated a small deposit at Thano Bulla Khan in the Sindh province of Pakistan and determined its chemical composition. Later on, a huge deposit of Fuller’s earth was explored in Dera Ghazi Khan district of the Punjab province of Pakistan. Yousaf et al. (1989) investigated the deposit physicochemically upto some extent, and reported it to be promising if studied further and activated properly. This source has been, therefore, further investigated for its utilization for bleaching edible oils, which is reported here.

Materials and Methods

Fuller’s earth samples. Sixteen samples, belonging to the Dera Ghazi Khan deposit, obtained from four different sites (four replicate samples from each) were selected for the present investigations.

Cation exchange capacity. Since the cation exchange capacity (CEC) of minerals may vary with several factors, it can be exactly comparable only if the values are obtained by the same
Studies on the Laboratory Scale Synthesis of 4,4'-Diaminodiphenylurea and Preparation of Direct Dyes from the Compound

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Abstract. 4,4'-Diaminodiphenylurea has been synthesized as a potential replacement for benzidine by reaction between p-phenylenediamine and urea under different catalytic and reaction conditions. Reaction conditions have been optimized to obtain maximum yield of intermediates. Direct dyes have been prepared from the title compound. The synthesized dyes were used to dye cotton and leather and the colour fastness properties of the dyed cotton and leather were assessed. Results showed that the synthesized dyes have fair to good fastness properties for cotton.

Keywords: 4,4'-diaminodiphenylurea, benzidine substitute, direct dyes

Introduction

The second amendment to German regulations on consumer goods states that the azo dyestuffs, which can release one or more of the listed 23 carcinogenic amines should no longer be used in dyeing of consumer goods (IARC, 1975). Several acid and direct dyes liberate harmful amines, such as benzidine, o-tolidine and dianisidine (benzidine derivatives) after reduction. Benzidine is both a genotoxic and harmful carcinogen (IARC, 1975; Case et al., 1954; Scott, 1952). Human exposure to benzidine leading to bladder cancer has been related to the handling of the intermediate itself during the course of tetrazotization (Calogero et al., 1987). Similarly, genotoxic metabolites have been isolated from the urine of animals, which had been fed with some azo dyes containing benzidine as the intermediate (Joecclion et al., 1985). Due to the above stated risks, efforts were made to replace the carcinogenic benzidine and its derivatives by non-benzidine (benzidine-free) based direct dyes. Amide derivatives of the iso- and terephthalic acid (Wajciechowski and Gumulak, 2003), and iso- and terephthalic acid as such, have been used in the synthesis of direct dyes (Wajciechowski et al., 2003). Also, benzidine substituted intermediates, and dyes based on them, have been synthesized in order to overcome the mutagenicity of benzidine (Gong et al., 2002).

In this regard, 4,4'-diaminodiphenylurea (DADPU) has been proposed as a replacement for benzidine (Zhang, 1995), and it has been used to prepare direct dyes. DADPU contains ureylene group (-NHCONH-). 4,4'-Diaminodiphenylurea is normally synthesized using phosgene. Triphosgene has also been used as a substitute for phosgene to prepare urea containing intermediates having ureylene group (Shi et al., 1998; Peng et al., 1996). Keeping in view the toxicity of phosgene and triphosgene, DADPU has been prepared in the present work using p-phenylenediamine and urea. The method is economical and reliable, but requires very long reaction time. Also, in the present work, the optimization of the process has been carried out under variable reaction conditions, such as reflux time, and by using different catalysts, which have resulted in better yield of the final DADPU product. DADPU has been further used to prepare direct dyes. Structure of DADPU is shown in Fig. 1(a).

Materials and Methods

p-Phenylenediamine (5.4 g), urea (3.6 g) and water (50.0 ml) were transferred to a flat bottom flask, and stirred on a hot plate. NaHSO₃ (39%; 3.0 ml) was added to the flask and stirring continued. Glacial acetic acid (2.5 ml) was then added, and the contents of the flask were refluxed with continuous stirring at a constant temperature of 102 °C. After refluxing for 24 h, the product was filtered with the help of vacuum filtration apparatus, using Whatman 40 filter paper. The filtered cake was washed thoroughly, first with normal and then with hot distilled water to remove residual urea. The reaction was carried out under the same reaction conditions, but changing the reflux time to 30, 36 and then 40 h. The yields of the DADPU obtained under different refluxing periods are shown in Table 1. The reaction was similarly carried out using ZnCl₂ + CH₃COOH, and Zn + CH₃COOH as catalysts, keeping the reaction time of 30 h constant. Physical appearance and the yield of the final products varied under different catalytic conditions as shown in Table 2.

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Synthesis and Fungicidal Activity of Some Sulphide Derivatives of O-Ethyl-N-Substituted Phenylcarbamates

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Abstract. Monosulphides of O-ethyl-N-substituted phenylcarbamates were prepared by the reaction between O-ethyl-N-substituted phenylcarbamates and sulphur dichloride, while the corresponding disulphides were prepared by the reaction between O-ethyl-N-substituted phenylcarbamates and sulphur monochloride. The synthesized compounds were characterized by elemental analysis, thin layer chromatography (TLC), Fourier-transform infrared, and 1H and 13C nuclear magnetic resonance spectroscopic techniques.

In vitro fungicidal assay of these sulphides against Fusarium oxysporum, Aspergillus niger, Aspergillus flavus and Rhizopus stolonifer showed that they had greater fungicidal activity than their parent carbamates. The synthesized sulphides were more active towards A. niger and A. flavus. Unlike the parent carbamates, the type of substituents attached to the aromatic nucleus of these sulphides had little or no effect on their fungicidal activity as there was insignificant variation in the fungicidal activity of the monosulphide and the disulphide derivatives of O-ethyl-N-substituted phenylcarbamates.

Keywords: fungicidal activity, sulphide derivatives, O-ethyl-N-substituted phenylcarbamate, fungicides, organosulphur compounds

Introduction

Countless sulphur compounds have been tested as fungicides, but only few of these have found worldwide applications (Ayodele, 2005; Lamberth, 2004; Tanaka et al., 1978). Organosulphur compounds are economically important fungicides that play a significant role in the production of agricultural crops and in the preservation of industrial products (Lukens, 1971).

Stability of the metal-chelate formed between heavy metals present in fungal cells and the fungicide sulphur determines the fungicidal activity of these organosulphur compounds (Rich, 1960). Formation of such metal-chelates increases the hydrophobic property of metal ions, which enables them to pass through lipid layers of cellular membranes to inside the fungus cells, thereby leading to their poisoning (Eyring, 1966).

The toxicity of carbamates lies in their ability to inhibit the nervous system enzyme, acetylcholinesterase. Blockage of this enzyme results in a failure of the nervous system due to accumulation of acetylcholine in the nerve synapse. The inhibition of acetylcholinesterase in mammals (including man) leads to muscular spasm, headaches, diarrhoea, convulsion, respiratory failure and finally cardiac arrest (Kuhr and Dorough, 1976). The substitution of proton on the nitrogen atom of carbamates by a variety of functional groups results in derivatives that have lower anticholinesterase activity and reduced mammalian toxicity when compared to their parent compounds (Fahmy and Fukuto, 1982). The possible attack of carbamates on the nervous system of humans involved in the fungicidal applications is reduced when derivatized carbamates are used in place of N-methylcarbamates (Fahmy et al., 1970).

In continuation of the earlier research efforts (Ayodele et al., 2000; Fahmy et al., 1970) on the synthesis and structure-activity relationships of oligosulphides of the type $PhCH_2S_xCH_2CH_2OH$ (where $x = 1-4$), a consideration was given to the study of the following types of molecules.

$$\text{EtO-}$$
$$\text{N-S}^\cdot_2\text{N-C-OEt}$$

$x = 1$ and $2$ in the presently investigated molecules

Carbamates of this design were likely to cause less health hazards to the operators in particular as reported earlier (Fahmy et al., 1982).

A wide variety of functional groups have been introduced into carbamates, which include sulfenyln, thiono, thiocarbonyl, acyl, sulfinyl, sulfonyl and phosphinothioyl (Szczepanski et al., 1977; Field et al., 1961; Grogan et al., 1955). However, the most widely used functional group for derivatization of carbamates is the sulfenyl group (Black et al., 1973; Kuhle, 1970; Kharasch, 1961; Reid, 1960). Several types of N-sulfenylated...
Isolation and Characterization of Kappa-Carrageenan from Hypnea musciformis (Red Alga) Collected from Karachi Coast, Pakistan

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Abstract. Hypnea musciformis, collected from Karachi coast of Pakistan, was used for the isolation of a thickening and emulsifying agent, carrageenan. Various extraction procedures were employed and the yield of carrageenan obtained was in the range of 34-44%. Total sugar contents were found to be 31.8-55.4%. 3,6-Anhydrogalactose, a component of the total sugar, was present in the range of 19.9-27.6%. Sulphate and ash contents were high, 14.8-41% and 15.4-53%, respectively. The positive rotation of these polysaccharides indicated a predominance of α-D-glycosidic linkages in their structure. IR spectral studies showed kappa-carrageenan as the major phycolloid, with a very small contamination of iota-type carrageenan, whereas lambda-type was not detected. Polysaccharides obtained showed a positive elicitor activity in garden peas (Pisum sativum). HPLC analysis indicated the presence of a single major component.

Keywords: carrageenan, Rhodophyta, polysaccharides, elicitor activity, Hypnea musciformis, phycolloid

Introduction
Commercially important polysaccharides from red seaweeds (Rhodophyta) belong to the group of polydisperse, long chain, water-soluble galactans. Their building block is made up of alternating 3-linked β-galactopyranose and 4-linked β-galactopyranose, which can be variably modified and/or substituted. In carrageenans, the 4-linked units are in the D-configuration, whereas in agars they are in the L-configuration (Usov, 1992). The gelling and thickening properties, and the protein reactivity of these phycolloids have led to their widespread commercial uses in the industry, including food and beverages, pharmaceuticals and cosmetics (Nishizawa, 2002). These are also used as biofertilizers in the agriculture sector. Because of the wide commercial applications of carrageenans, various extraction procedures to obtain this product from red algal plants have been reported in literature, while their structural determinations are done using spectroscopic techniques (Greer et al., 1984). Karachi, Pakistan has a large coastal area yielding large quantities of marine algae. Unfortunately, these seaweeds are not utilized in Pakistan, either as marine vegetables or for extracting commercial compounds (Husain et al., 2001), whereas huge amounts are spent on the import of seaweed products. The aim of the present study was to develop an effective procedure for the exploitation of these seaweeds so that carrageenans may be extracted in good quality and quantity from Hypnea musciformis. Another objective was to explore the nature of these polysaccharides as the inducers of hypersensitive response, characteristic of resistance mechanism in plants against diseases, especially in terms of induced browning and production of phytoalexins (Nicholson and Wood, 2001). Garden peas (Pisum sativum) were used as the test plant for the elicitor activity experiments.

Materials and Methods
General method of extraction. Hypnea musciformis (red alga) was collected from Karachi coast, Pakistan in February and November 2003. The plant was cleaned of epiphytes, washed, dried, and ground to a fine powder. Representative material of the plant sample (25 g) was pretreated with HCl (0.1 N)/formaldehyde (20%), and extracted with water (tap/distilled) at 70-80 °C, with constant stirring for 6 h. Supernatant was collected and the residue was re-extracted twice under similar conditions. Experimental conditions were varied for optimizing the extraction procedures and carrageenans were obtained, as detailed below in different extraction protocols, by ethanol precipitation or by direct drying on a waterbath.

Extraction-1. Dry plant powder, pretreated with HCl (0.1 N), was stirred for 30 min in an icebath, washed extensively with tap water to remove traces of acid, followed by washing with distilled water. The supernatant was dried in a waterbath.

Extraction-2. Dry plant powder, pretreated with HCl (0.1 N), was washed, followed by extraction with distilled water. Supernatant was precipitated with 95% ethanol (three volumes of the extract), and the precipitate was dried.

Extraction-3. Dry plant material, pretreated with HCl (0.1 N), was washed and extracted with tapwater and dried in a waterbath.
Comparative Studies on the Adsorption Properties of Powdered Activated Carbon and Propenoic Acid Modified Sawdust in the Treatment of Secondary Palm Oil Mill Effluent

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Abstract. Propenoic acid monomer was used to modify pulped cellulosic materials (sawdust). The sorption properties of the propenoic acid modified sawdust (PAMS) were compared with those of powdered activated carbon (PAC) in the tertiary treatment of palm oil mill effluent, previously clarified with iron(III) chloride plus lime (secondary effluent). The adsorption processes were effected in a fluidized bed reactor (FBR) at a pressure of 80 kiloNewton per meter square (kNm⁻²). Optimum amount of PAC and PAMS used for the fluidized adsorption of contaminants from the secondary palm oil mill effluent (POME) were 2.5 g/l and 4.0 g/l, respectively. These sorption processes were found to be optimum at 10 min and 50 min for PAC and PAMS, respectively. At optimum sorption conditions, removal differentials of 28.6%/g chemical oxygen demand, 19.1%/g suspended solids, and 19.3%/g colour in favour of PAC were established. The application of optimum conditions for adsorption, for both adsorbents, to the bulk treatment of the palm oil mill effluent yielded a clear effluent with wider reuse applicability.

Keywords: metal adsorption, palm oil mill effluent, propenoic acid treated sawdust, fluidized bed reactor, activated carbon, wastewater treatment

Introduction

Adsorption processes are becoming viable options for the removal of non-biodegradable substances from conventionally treated wastewaters (Osuide et al., 2003; Lopez-Delgado et al., 1998; Allen and Brown, 1995; Lo and Lin, 1989; AWTR-19, 1967). These substances exist as fine colloids or true solutes in these wastewaters, even after the wastewaters have been subjected to primary and secondary treatment processes.

Large-scale palm oil processing industries use waste stabilization ponds (WSPs) for the secondary treatment of their effluents. These ponds stabilize wastewaters through biodegradation processes. It has been observed that these pond systems, in typical cases, are quite elaborate in design and construction. The effluents so produced, do not fully meet the effluent discharge guidelines as stipulated by the Ministry of Environment, Nigeria (FEPA, 1988). With an average chemical oxygen demand (COD) value of 1096 mg/l, dissolved oxygen (DO) of 2.0 mg/l, and an oil and grease (O-G) value of 19,446 mg/l, in a typical study case, the usual treatment methods still leave a lot to be desired (Osuide, 2004).

Dependence on the natural purification schemes to continue the stabilization processes does not guarantee the protection of the environment owing to the large volume of wastewater involved. It also does not provide for the extension of available water resources via the possibility of recycling.

Studies have generally shown the removal differentials of between 45% and 75% for most water quality parameters in favour of chemical treatment of industrial wastewaters as against treatment by waste stabilization pond systems (AWTR-19, 1967). Besides, chemical treatment provides for the possibility of recycling of industrial effluents.

Powdered activated carbon (PAC) is the most popular adsorbent for removing such recalcitrant pollutants from solutions in tertiary treatment steps (Lo and Lin, 1989; AWTR-19, 1967). However, the cost of preparing PAC is becoming quite prohibitive. In recent times, alternative materials are being sought to replace PAC in adsorption processes. Cellulosic materials available in the form of agricultural byproducts are now the choice. The capacity of these cellulosic materials to take up contaminants, particularly heavy metal ions from synthetic and natural standard solution have been examined variously by people working in this area (Saeed et al., 2005; Saeed and Iqbal, 2003; Saeed et al., 2002; Pelekani and Snoeyink, 1999; Lopez-Delgado et al., 1998; Allen and Brown, 1995). The results show not much of a success story, though indicate the inherent potential. More recently, however, some workers have used active monomers and other reactive groups to modify cellulosic materials before application to sorption processes.
Short Communication

Some Studies on the Changes in the Composition of Coal Ash and Bottom/Fly Ash Produced in Atmospheric Fluidized Bed Combustor

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(issued October 26, 2004; revised November 16, 2005; accepted November 19, 2005)

Abstract. A study on the ash of Lakhra lignite coal and the bottom/fly ash, obtained from combustion of Lakhra lignites in atmospheric fluidized bed combustor (AFBC) was carried out. It has been observed that the absence of alkali metals was of significant importance, as alkali metals were responsible for agglomeration in the AFBC.

Keywords: atmospheric fluidized bed combustion, coal energy, environmental pollution, coal, Lakhra lignites

The role of mineral coal in the energy consumption of Pakistan is insignificant (Table 1). This needs to be given urgent attention. Annual mining of coal in Pakistan is less than three million ton (Ali, 1995), whereas coal deposits in the country have been estimated to be 185 billion ton (ESP, 1999). The Thar coal-fields are the largest coal deposits in the country, but these have yet to be developed. The Lakhra coal-fields are considered to be the largest fields from the point of view of coal mining. According to a survey report, about 91% of the mined coal is used for burning in brick kilns, while the remainder is used for power generation (ESP, 2000). Based on the indigenous source of coal, only one coal-fired power plant is operating in the country. The analyses of Lakhra coal used in the plant are given in Tables 2 and 3. The three coal-fired power plant units of 50 MW each, situated at Khanot, Sindh, Pakistan, which were based on the Lakhra lignite atmospheric fluidized bed combustion (AFBC), and the 15 MW Sor-Range coal-based power plant at Quetta have since been scrapped.

This paper reports a study carried out on the ash of Lakhra lignites and bottom/fly ash, obtained from atmospheric fluidized bed combustion (AFBC), which are burnt along with limestone to trap sulphur. These studies were aimed at determining the alkali metals present, the extent of sulphur fixed, and the utilization of ash for some useful purposes such as insulation bricks, road construction and as a soil conditioner.

The commercial power plants, based on atmospheric fluidized bed combustion of coal, have the necessary quality control facilities to routinely analyse coal and limestone, as supplies of these materials vary considerably in their compositions from lot to lot. The analyses of coal ash and bottom/fly ash, therefore, also show wide variations. The results reported in the present studies represent only one batch of the supplies obtained from a testing atmospheric fluidized bed combustor. Analyses of these supplies were carried out on standard analytical computerized equipment.

Table 1. The percentage contribution of various fuels in Pakistan*

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>48.0</td>
<td>46.8</td>
<td>47.7</td>
</tr>
<tr>
<td>Natural gas</td>
<td>29.4</td>
<td>31.3</td>
<td>31.0</td>
</tr>
<tr>
<td>Electric</td>
<td>15.4</td>
<td>15.5</td>
<td>14.6</td>
</tr>
<tr>
<td>Coal</td>
<td>6.3</td>
<td>5.4</td>
<td>5.7</td>
</tr>
<tr>
<td>LPG</td>
<td>0.9</td>
<td>1.0</td>
<td>1.1</td>
</tr>
</tbody>
</table>

* = ESP (2000; 1999); LPG = liquified petroleum gas

Table 2. Ultimate analysis of Lakhra lignites (dry; ash-free basis)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>58.5 - 72.4</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.5 - 5.8</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.9 - 1.4</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.4 - 16.7</td>
</tr>
<tr>
<td>Oxygen</td>
<td>14.4 - 22.3</td>
</tr>
</tbody>
</table>

Table 3. Proximate analysis of Lakhra lignites

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (%)</td>
<td>13.01 - 20.12</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>17.49 - 42.8</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>28.82 - 37.37</td>
</tr>
<tr>
<td>Fixed carbon (%)</td>
<td>12.68 - 31.07</td>
</tr>
<tr>
<td>Heating value (MJ/kg)</td>
<td>14.31 - 21.05</td>
</tr>
</tbody>
</table>

*Author for correspondence
High Frequency *In vitro* Propagation of *Polianthes tuberosa*

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(received February 7, 2006; revised September 9, 2006; accepted September 19, 2006)

**Abstract.** Calli induced on MS medium supplemented with 10 μM α-naphthaleneacetic acid (NAA) grew extensively when cultured on MS medium modified with 4 μM 2,4-dichlorophenoxyacetic acid (2,4-D), producing on an average four shoots per callus culture. The addition of 1 mM L-arginine in the culture media enhanced the induction rate upto 10 shoots per callus culture in 12 weeks. When 2-3 cm long regenerated shoots were replanted on MS medium with 20 μM 6-benzyladenine (BA) and 4 μM 2,4-D, shoots the proliferated at the cut ends. Floral axis buds produced 3-4 cm long multiple shoots on NAA and BA. New shoots regenerated from the calli produced at the base of shoots subcultured on 10 μM NAA. Repetition of shoot development, callus formation, and again shoot formation on 10 μM NAA and 2 μM BA greatly increased the number of plants from single shoots. Eighty five percent bulb explants produced 290 shoots in 12 weeks directly on 15 μM BA and 5 μM NAA. The somatic pseudoembryos formed in the calli were dormant.

**Keywords:** L-arginine, clonal propagation, *Polianthes tuberosa*, tuberose plant

**Abbreviations:** IAA = indol-3-acetic acid; IBA = indole-3-butyric acid; BA = N⁶-benzyladenine; CH = casein hydrolysate; CW = coconut water; 2,4-D = 2,4-dichlorophenoxyacetic acids; Kin = kinetin; NAA = naphthalene acetic acid; MS = Murashige and Skoog medium

**Introduction**

*Polianthes tuberosa* (family: Amaryllidaceae) is one of the important cut flower. Its fragrance particularly makes it second to none. It is widely used for the extraction of essential oils and aromatic compounds, used as raw material in the fast growing perfume industry. Attention has been, therefore, focused on developing new techniques for the genetic manipulation of this species, requiring the *in vitro* culture of tuberose tissues from which whole plant can be propagated.

Very few studies have been reported on the *in vitro* culture of this species. Amongst these the work of Narayanaswami and Prabhudesai (1979) was the foremost on the culture of the tuberose *in vitro*, which reported direct and indirect regenerations from its meristematic tissue explants. Gi and Tsay (1989) reported studies on anther culture, and induced somaclonal variations in *P. tuberosa*. Later on, Nisar *et al.* (1989) reported regeneration multiple shoots from callus cultures, which was followed by studies on multiple shoots from quiescent nodal buds of floral stalk, plantlets from nodal segments, and the evidence of formation of protocorm-like bodies from anther stalk calli (Zaidi *et al*., 1994). Regenera-

tive potential of bulb, leaf and scale of the tuberose were also investigated by Khan *et al.* (2000). Krishnamurthy *et al.* (2001) reported micropropagation of the ‘single’ and ‘double’ types of tuberose.

In an effort to explore further, *in vitro* cultural features about the enhancement in shoot multiplication rate, were investigated. The present study reports findings on shoot differentiation from bud explants and the calli, and somatically regenerated pseudoembryos.

**Materials and Methods**

**Stock plant.** *Polianthes tuberosa* plants, commonly called as tuberose, were obtained from local nurseries. Bulbs, inflorescence axis and floral buds of the plant were used as the source material. The floral stalks were separated from the bulbs at their bases. Leafless floral stalks and bulbs were scrubbed clean with detergent and treated individually for sterilization. Hot water and fungicide treatment of the bulbs preceded the surface sterilization process for bulb explants. The bulbs were treated with hot water at 58 °C for 30 min, and dried on filter paper at room temperature for one day. Roots were then removed, the tunica dried, and the bulbs submerged in 3 g/l solution of Diathane M-45 (AgrEvo Chemical Company, Berlin, Germany) for 30 min prior to explant preparation. Bulb explants (3-5 mm³) were removed from the inner core of the peeled off bulbs. For axillary bud explants, 1 cm³ lump of the bulb, with at least one bud near the basal plate, were obtained. Axillary bud and storage tissue explants of the bulb were surface sterilized in 0.1% (w/v) mercuric chloride solution with

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Morphological Changes in Cotton Roots in Relation to Soil Mechanical Impedance and Matric Potential

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Abstract. Soil mechanical impedance (MI) and matric potential can both cause reduction in the root growth rate, modify rooting pattern and root diameter. Cotton seedlings are sensitive to the soil physical environment, particularly during early stages of growth. Soil matric potential and MI effect on root biomass, axial root length and diameter, and the number and length of lateral roots in soil packed to penetration resistances (PR) of 0.1, 1.0, 1.1 and 1.2 MPa (megaPascal = 10^6 Pascal), each at three matric potentials of −10, −100 and −500 kPa (kiloPascal = 10^3 Pascal), were determined. Total root lengths were reduced by 29, 50 and 53% at impedance of 1.0, 1.1 and 1.2 MPa, respectively, as compared to the control, whereas MI of 1.2 MPa resulted in 60% reduction in axial root length. A similar increase in diameter was caused by increasing mechanical impedance, while decreasing matric potential had little effect. Roots that were water stressed did not change their diameter but had a shorter axis and longer lateral length. In contrast, the impeded roots (PR = 1.0, 1.1 and 1.2 MPa) had both a shorter axis and a smaller total length, but had increased diameter. These results not only illustrate the plasticity of root response to stress but also demonstrate how the response differs between different types of stresses.

Keywords: soil mechanical impedance, soil matric potential, root plasticity, root length, penetration resistance, soil physical environment

Introduction

Plants require networks of roots to absorb water and nutrients from the soil. Soil factors, which influence the distribution of plant root system, often limit plant productivity by modifying the extent of plant root exploration and by reducing the efficiency of water absorption. Soil physical factors, such as soil matric potential and mechanical impedance, affect the root growth. Mechanical impedance is the resisting pressure encountered by growing roots. It is ubiquitous within the root environment. Penetration resistance of 0.5-1.0 MPa (megaPascal = 10^6 Pascal), and greater, are commonly experienced in soils that can reduce root elongation rates considerably (Martino and Shaykewich, 1994). It increases with increase in soil bulk density. It also usually increases as the soil matric potential decreases during soil drying. Unless roots are able to exploit soil structural features to bypass the bulk of soil, their growth rate reduces as mechanical impedance is increased (Bengough and Mullins, 1990). Indeed, drying soils can become strong enough to affect root growth at matric potential as high as −0.1 MPa (Mullins et al., 1992). Water potential of −0.1 MPa appears to have little direct effect on root elongation, or root growth pressure (Whalley et al., 1998). Under controlled conditions, root growth rate varies in approximately inverse proportion to mechanical impedance.

This is in consequence of both a reduction in the rate of cell division in the meristem and a decrease in the length of fully expanded cells (Smucker and Atwell, 1988; Eavis, 1967). Wilson et al. (1977) reported that under impeding conditions, cell length and the volume of inner cortical cells decreased but the diameter and volume of the outer cortical and epidermal cells was considerably increased. The epical meristem and zone of cell expansion of impeded roots is short and the cells on the surface of the tips may slough off (Bengough and McKenzie, 1997). In barley, initiation of lateral roots and growth of root hair took place nearer the tip under impeded conditions (Goss and Russell, 1980). In roots that bent after an encounter with an obstacle, lateral roots predominated on the concave side of the bent while root hairs dominated on the convex side.

Under field conditions, plant root systems encounter considerable spatial variations in mechanical impedance. Even in compact soils, areas of lower mechanical impedance will occur due to shrinkage cracks and channels formed by earthworms or roots of previous crops (Tardieu, 1988). Furthermore, dense compact layers frequently underline the loosened top soil in cultivated soils. Under these conditions, a root system encountering hard compact zones of soils has
Multiple Parameters for Ascertaining Yield Stability of Upland Cotton Varieties Tested Over Number of Environments

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(received October 5, 2005; revised August 16, 2006; accepted August 29, 2006)

Abstract. Thirteen upland cotton varieties were evaluated in 12 different environments of the Sindh province, Pakistan, so as to arbitrate their stability in yield performance. The regression coefficient (b) parameter was used as a measure of varietal adaptability, whereas the sum of squared deviations from regression (s²d) and coefficient of determination (r²) were implied as the measure of stability. The regression coefficients (b) of all the varieties, though did not deviate significantly from a unit slope (b = 1.0), yet varieties FH-1000, VH-142, BH-147 and FH-945 exhibited (b) values very close to a unit slope suggesting their better adaptation to the test environments. Varieties CRIS-467, DNH-57 and FH-945 displayed lower s²d and higher r² values implying that these varieties were relatively more stable in yield performance than others in the test environments. Generally, not all the stability and adaptability parameters simultaneously favoured the same variety except FH-945, which was thus considered more stable, based on majority of the parameters. Principal component analysis (PCA) revealed that latent vectors of first two components, i.e., PCA-1 and PCA-2 accounted for about 91.24 % of the total variation. The eigen vectors of first PCA-1 were smaller and all were positive, which further suggested that the test varieties were quite adaptive to all the test sites. However, in PCA-2, some varieties gave positive and some negative eigen values, yet varieties FH-1000, CIM-499, CRIS-467 and FH-945 expressed smaller and positive PCA-2 scores suggesting less genotype-environment interactions for these particular varieties.

Keywords: stability and AMMI analysis, genotype-environment interaction, upland cotton varieties, environmental index, multivariate analysis

Introduction

Cotton breeders are always tempted to assess the magnitude of genotype-environment interactions and their pattern. These attributes, of course, help plant breeders to decide whether the newly evolved varieties are suitable for multiple environments or for specific environments. To answer this complicated question, a broad range of multivariate statistical procedures has long been used. The most common and earlier approach was the regression analysis (Eberhart and Russell, 1966; Finlay and Wilkson, 1963). However, several researchers have pointed out some limitations of the regression method (Crossa, 1988). Lin and Binns (1988) concluded that the ten most commonly used parameters, representing stability and adaptability of genotypes are actually different approaches of statistics that measure the same attribute. Thus, among the ten parameters of stability analysis, the similar ones were grouped together. As a consequence, only three major groups, namely, deviation of average performance of genotypes, the genotype-environment interaction (G x E), and regression of environmental index were arbitrated. Lin et al. (1986) used multivariate analysis (MA), so as to ensure thorough elucidation of the response of cultivars within the scope of three new classifications representing the stability of genotypes. By regressing each variety over environmental index, Bilbro and Ray (1976) demonstrated regression coefficient (b) as a measure of adaptability, whereas coefficient of determination (r²) and the sum of squared deviation (s²d) were shown as a measure of stability. It is still, however, questionable whether these parameters are completely reliable in describing the stability and adaptability response of genotypes tested in both favourable and unfavourable environments. By using multivariate analysis, nevertheless, Lin et al. (1986) succeeded to a large extent, in explaining the most complicated situation of genotype-environment interaction pattern. To further overcome the limitations of the previously used statistics, the additive main effects and multiplicative interaction (AMMI) as proposed by Gauch (1992) has been incorporated in the present studies. The important feature of the AMMI model is that it integrates the analysis of variance and principal component analysis (PCA) into a unified approach (Gauch, 1992; Crossa et al., 1990), which better explains the genotype-environment interaction pattern. However, Dos Santos Dias and Krzanowski (2006) compared AMMI models as proposed by Gabriel (2002), Cornelius and Crossa (1999), Eastment and Krzanowski (1982), and Gollob (1968) for the detection of interaction patterns between genotypes and environments. The authors observed that all the four statistical methods adopted by these researchers produced different results for the same set of data and yielded a rather mixed picture. They
Isolation and Stabilization of Dark Red Food Dye from Beta vulgaris

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Abstract. Natural highly coloured dark red pigment was isolated from Beta vulgaris, in paste and powdered form. Total colouring matter of the concentrated colour was 1.86% and 4.5%, respectively, for the paste and powdered forms, calculated as betanine. Sodium benzoate (0.01%) was used as the stabilizer for paste, while silicon dioxide (2%) was added in addition to sodium benzoate (0.01%) for storage of the red colour in powdered form. Other parameters that may influence the stability of the colour, such as pH, temperature and relative humidity, were studied. Toxicity evaluation, and lead and arsenic levels were determined. The addition of stabilizers, like citric acid, ascorbic acid, EDTA and sodium chloride, were also investigated, none of which showed useful effect.

Keywords: food colour, betanine, beetroot colour, Beta vulgaris red colour, food colour isolation, food colour stabilization

Introduction

Beetroot contains betenine (C24H26N2O13) as the principal pigment, which is the D-glucopyronoside of betanidine (FAO, 1984). It is obtained from the roots of red beet (Beta vulgaris). The red colour of beetroot is suitable for products having relatively short shelf-lives and where the food stuff has not to undergo high or prolonged heat treatment (Coulson, 1980). Stability is higher in the pH range of 4-5, though the stability is reasonable in the pH range of 3-7. Adding colour, after the heating process has ceased, can be successfully done for the colouration of foods that have to undergo heat treatment. Adding small amount of benzoate, sorbate or EDTA can enhance stability of the colour. Beetroot red colour may be used, with the addition of a suitable stabilizer, in soft drinks, ice cream, meat and soyabeen protein products, and in dry mixes such as gelatin desserts (Coulson, 1980).

Various laboratory techniques have been reported for the isolation of colour from beetroot (Krasnikova et al., 1996). The rich red dye in powdered form has been obtained by heating beetroots at 100 °C for 5 min. The peroxide present can be inactivated, and the colour extracted with aqueous citric acid (Lozano et al., 1993). The red dye has been also obtained by the aqueous extraction of colour from beetroots (Kutsakova et al., 1997). Red dye from beet was earlier obtained by pre-heating beet slices with 0.125% citric acid at 100 °C for 20 min and the average recovery was reported as 63.3% (Liu, 1981).

The presently developed procedure involves the extraction of red food dye from beetroots with salicylic acid (0.125%), which was then concentrated by freeze drying. The purpose of the present study was to produce natural red dye in powdered as well as in paste form, to enhance the stability of colour at different pH values and temperatures, to study any toxicological effect of the extracted red food dye, and to determine the usefulness of the obtained colour in different foodstuffs. The principal objective of the present study was to produce natural food dye that is non-toxic and harmless to human health, since it has been claimed that several artificial colours and flavours used in foods may lead to hyperactivity and learning disability in children (Feingold, 1975). It was estimated that 50% of the hyperactive children could be completely cured by a diet, totally devoid of these chemicals.

Materials and Methods

Instruments used. Freeze dryer (Eyela; FD 550), vacuum oven (Hitachi Yamato; DP 41), hotplate blender (Waring), spectrophotometer (Hitachi; U-1100), atomic absorption spectrometer (Hitachi, 170-10).

Chemicals. Sodium benzoate (Win Laboratories); citric acid, salicylic acid, silicon dioxide, ascorbic acid, disodium hydrogen phosphate (E. Merck, Germany); EDTA (BDH).

Extraction of the colour. The red colour was extracted with 0.125% solution of salicylic acid by blending fine slices of beetroots in a Waring blender at medium speed for 5 min. The extract was filtered through Whatman filter paper# 1. Residues were washed thrice with salicylic acid solution.

Drying techniques. Various drying techniques were used to concentrate the fresh colour extracted from the beetroots, such as waterbath drying, hotplate drying, sun-drying, vacuum oven-
The Effect of Substitution on the Dyeing and Spectroscopic Properties of Some Monoazo Disperse Dyes

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(received December 17, 2005; revised August 6, 2006; accepted August 9, 2006)

Abstract. A range of monoazo disperse dyes has been synthesized. The colour, dyeing and fastness properties of the dyes on polyester, nylon and secondary acetate fibre at 1/1 standard depth have been examined and rationalized in terms of dye structure. The visible absorption behaviour of the dyes was also investigated. In general, substitutions on the diazo component have a significant effect on the visible absorption maxima of the dyes. Increasing the solvent polarity also had a pronounced effect on the absorption maxima.

Keywords: monoazo dyes, diazotization, dyeing, dye migration

Introduction
The disperse dyes arose out of the endeavour of many workers to find an easy and commercially satisfactory way to dye cellulose acetate. The importance of water insoluble disperse dyes has increased to a very great extent with the appearance of synthetic fibres, some of which, such as polyester and triacetate, are much more hydrophobic than cellulose acetate, and therefore very resistant to the conventional water soluble dyes (Trotman, 1984).

As with other classes, diverse properties are expected of disperse dyes according to the dyeing conditions that will be encountered during use. Disperse dyes for acetate are required to have brightness and fastness of shades, good build-up, and levelling properties. Some dyes, otherwise satisfactory, show a tendency to sublime under domestic ironing conditions. Others are sensitive leading to marked deterioration in their shades (Muller, 1970). Research efforts have been accordingly made to overcome these shortcomings and to determine such structural features that would confer improvements in these properties (Clark and Hildreth, 1973). These have been adapted to meet the requirements of polyester fibres and of different dyeing processes, mainly by varying the substituent types of the dye, which have quickly become important for dyeing acetate fibres (Stead, 1970).

Synthesis of some disperse dyes and their dyeing properties have been reported and discussed in the present paper. The findings of this study have been discussed in term of the structural features of the dye molecules. The focus has remained on dyes derived from conventional diazo component and aniline-based coupler.

Materials and Methods

Synthesis of dyes. The dyes were synthesized by coupling the appropriate diazonium ions with N,N-diethylaniline. The amines used in the synthesis were 4-nitroaniline, 2-chloro-4-nitroaniline, 2,4-dinitroaniline, 4-nitroanisole, 2-cyano-4-nitroaniline, 2,6-dichloro-4-nitroaniline. All the amines were diazotized in aqueous hydrochloric acid and then gradually added to a well stirred dispersion of N,N-diethylaniline in a weakly basic system. These have been listed as Ia-If. The parent dye had the general structural formula as given in Fig. 1.

All the dyes were separated from the reaction mixture by filtration and then purified by dimethyl formamide (DMF) and their \( \varepsilon_{\text{max}} \) in the visible region were measured on Nicolet evaluation spectrophotometer (Thermo Electron Corporation, Madison, Wisconsin, USA).

Dyeing of fabric at different concentrations. Dyeing of 0.5 %, 1% and 2% was carried on 5 g fabric at 130 °C for 75 min, using high temperature dyeing machine (Ahiba IR Laboratory Dyeing System, model D400ir/I, SDL Atlas Ltd., London, UK) containing 2 g/l dispersing agent, 3 ml/l acetic acid to maintain pH at 4.5-5.5, and the liquid to goods ratio of 1 : 20. After this period (75 min), the study specimens were removed from the dyeing bath and rinsed with cold water and dried. The dyeings were reduction cleared in an aqueous solution of sodium hydrosulfite (2-3 g/l) and sodium hydroxide (2 g/l), using the liquid to goods ratio of 1 : 20 at 60 °C for 10 min. The samples were then rinsed with water and dried. The prepared dyes exhibited best dyeing properties on polyester and secondary acetate, dyeing on nylon being inferior to those on polyester and secondary acetate.

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Physicochemical Characteristics of Rayon Grade Dissolving Pulp and the Effects of Metallic-Ions on the Viscose Rayon Process

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(received May 5, 2005; revised July 31, 2006; accepted August 2, 2006)

Abstract. Pakistan imports rayon grade pulp from different countries for viscose rayon fibre manufacturing. Samples of imported pulp were collected and analyzed for alpha-cellulose, hemicellulose, calcium, magnesium, silica, copper, manganese, and iron. Moisture, ash content, cuprammonium viscosity, degree of polymerization, alkali absorption, and colour brightness were also determined. The results showed that all these parameters varied from sample to sample. The cotton linter pulp contained high alpha-cellulose content (94-98%) as compared to the softwood pulp (89.7-95%). Degree of polymerization of all samples was above 500 and varied from 500-750 ml/g. The study showed that higher manganese and copper content in cotton decreased the degree of polymerization. Iron above the standard value (7-10 ppm) affected the brightness of fibre, as observed in the case of cotton linter pulp (imported from China). The percentage of ash was less than 0.25% in all the samples studied.

Keywords: rayon pulp, pulp characteristics, metallic ion effects, viscose, rayon fibre, viscose process, dissolving pulp

Introduction

The development and use of a great variety of man-made fibres have created a revolution in textile industry in the recent decades. Rayon is the commercial man-made fibre composed of regenerated cellulose. Pulp is chiefly prepared from wood and cotton linter and is used for the manufacturing of viscose rayon fibre (Shareve, 1977). The term ‘dissolving pulp’ is used for pulp dissolved in the form of alkali soluble cellulose xanthate in the viscose process. Bamboo is being used at present for the manufacture of dissolving pulp. The alpha-cellulose content of the dissolving pulp is important because the rayon yield depends upon it. If it is low, there will be difficulties in processing. The required alpha-cellulose content of dissolving pulp for viscose staple fibre is 89 to 93 %. Higher content of hemicellulose in the pulp spoils the caustic soda lye used for steeping in the viscose manufacture. The hemicelluloses are mostly lower polymers of pentoses and should be less than 4% for the rayon grade dissolving pulp (Mandelia, 1970). Degree of polymerization and cuprammonium viscosity of the pulp is very important for the reduction of molecular weight of the cellulose to get a viscose of right viscosity (Edwin, 1948). The polymerization degree (DP) of the hardwood dissolving pulp for the viscose rayon continuous filaments is generally 550 to 600.

An important quality index for the dissolving pulp is the filterability of viscose made from it. Before spinning, the viscose has to be filtered to avoid the plugging of the spinnerets. Although slow viscose filtration may be due to many causes, the pulp properties influence the viscose filterability to a large extent. Chlorine dioxide helps in increasing the pulp brightness and minimizing the colour reversion. Sulphur dioxide helps in reducing the ash content (Mandelia, 1970). Alkalis are able to swell cellulose at low concentrations and produce dispersion at high concentrations. Certainly, the alkali opens up the fibre structure and leads to enhanced reactivity of the pulp during the xanthation process.

The dissolving pulp, especially for viscose, must be highly purified and uniform in quality (Edwin, 1948). The ash and its constituents are very important in deciding the suitability of the pulp for rayon. Calcium and magnesium are usually found in pulps prepared by the sulphite process. Metallic ions give trouble in the manufacture of viscose and in its filtration (Mandelia, 1970).

The viscose industries convert the dissolving cellulose pulp into products such as staple fibre, cards, films, packing materials, and non-edible sausage casings. The materials are used in the clothing, drapery, hygiene, automobile, food, and packaging industries (Ewing and Stepanik, 2000).

Materials and Methods

Nine rayon grade pulp samples of cotton linter and wood pulp were collected from Chemi Viscose Fiber Pvt., Nawabshah, Sindh, Pakistan. The ash content was determined by igniting the sample of pulp at 580-600 °C in a muffle furnace (ASTM D-586-97, 2002), while silica was determined by heating the sample at 900 °C. The moisture content was analyzed at 105 °C in a drying oven for two h (ASTM D-644-99, 2002). Calcium and
During the recent years, demand of reactive dyes is increasing for the dyeing of cellulosic fibres because of their bright shades and excellent fastness properties. For the dyeing of cellulosic fibres with bifunctional reactive dyes, salts as well as alkalis are added at different stages. During the primary exhaustion stage, the dye is taken-up into the fabric in the presence of added inorganic salts. During the secondary exhaustion stage, alkali is added to the dyebath and the dye-fibre reaction takes place (Imada and Harada, 1992). When the dyeing is performed in an alkaline medium, the electrolytes tend to reduce the charge on the fibre, thus the transfer of dye from solution into the fibre is facilitated (Vickerstaff, 1954). UV-visible spectroscopy is a versatile technique of quantitative analysis for dye concentration, either in the dyebath or on the fabric. Measurements can be performed by absorbance spectrophotometry of the dye solution. The quantity of dye, which disappears from the bath during the dyeing process, may be determined by taking the absorbance of the solution (Venkataraman, 1995).

The present study was conducted to assess the influence of electrolytes on the dye uptake of a bifunctional reactive dye on the cellulosic substrate (cotton K-68), which is a very low-grade cotton of Pakistan. Five electrolytes were used in order to assess their effectiveness in the dye uptake. Sodium chloride, lithium chloride, potassium chloride, caesium chloride...

\[ T = (1-A_s / A_b) \times 100 \]

where:

- \( T \) = dye uptake
- \( A_s \) = the maximum absorbance of the bath solution at dyeing
- \( A_b \) = the absorbance of bath after stripping with 25% aqueous pyridine

In this connection it is further significant to refer to the studies of alkali metal electrolytes on the dye uptake of cellulosic fabrics. The results obtained by taking absorbance, at different electrolyte concentrations (Guo et al., 1993), leads to the conclusion that sodium chloride was the most efficient salt for a short dyeing time. At an electrolyte concentration of 100 g/l, the dye uptake decreased in the order NaCl > KCl > CsCl > LiCl. It is well known that cellulosic fibres, when immersed in aqueous alkaline media, acquire a negative charge because their dielectric constant is lower than that of water. Due to a decrease in the negative surface potential of the fibre, the relative fibre-dye potential remains negative and involves a repulsive effect. By the addition of electrolytes, the adsorption of dyes on cellulosic fibre is influenced by the cations present in the dyebath (Peters, 1975). These cations influence the dye adsorption by disrupting the structure of hydrated water around the hydrophobic parts of the dye molecules and the structure of water bound to the surface of the fibre. This enables the dye anions to come closer to the surface of the cellulosic fibre thus making adsorption easier by virtue of their strong affinity for cellulose (Noah and Braimah, 1986).

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