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This Journal is indexed/abstracted in Biological Abstracts and Biological Abstracts Reports, Chemical Abstracts, Geo Abstracts, CAB International, BioSciences Information Service, Zoological Record, BIOSIS, NISC, NSDP, Current Contents, CCAB, Rapra Polymer Database, Reviews and Meetings and their CD-ROM counterparts etc.

Subscription rates (including handling and Air Mail postage): Local: Rs. 2000 per volume, single issue Rs. 350; Foreign: US$ 400 per volume, single issue US$ 70.

Electronic format of this journal is available with: Bell & Howell Information and Learning, 300, North Zeeb Road, P.O. 1346, Ann Arbor, Michigan 48106, U.S.A; Fax.No.313-677-0108; http://www.umi.com.

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Printed and Published by: PCSIR Scientific Information Centre, PCSIR Laboratories Campus, Shahrah-e-Dr. Salimuzzaman Siddiqui, Karachi-75280, Pakistan.

EDITORIAL ADDRESS
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Pakistan Journal of Scientific and Industrial Research, PCSIR Scientific Information Centre, PCSIR Laboratories Campus, Shahrah-e-Dr. Salimuzzaman Siddiqui, Karachi-75280, Pakistan
Tel: 92-21-34651739-40, 34651741-43; Fax: 92-21-34651738; Web: http://www.pjsir.org, E-mail: info@pjsir.org
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Pakistan Journal of Scientific and Industrial Research, a bimonthly sponsored by the Pakistan Council of Scientific and Industrial Research, started publication in 1958. It has been bifurcated in 2011 into:


- *Pakistan Journal of Scientific and Industrial Research Series B: Biological Sciences* (issues of March-April, July-August and November-December)

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(Dr. Kaniz Fizza Azhar)
Executive Editor

February 10, 2011
Deposition and Characterization of ZnS Thin Films Using Chemical Bath Deposition Method in the Presence of Sodium Tartrate as Complexing Agent

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(received October 21, 2010; revised January 21, 2011; accepted January 22, 2011)

Abstract. ZnS thin films were deposited on indium tin oxide glass substrate using the chemical bath deposition method. The deposited films were characterized by X-ray diffraction and atomic force microscopy. The influence of bath temperature on the structure and morphology of the thin films was investigated at three different bath temperatures of 60, 70 and 80 °C in the presence of sodium tartrate as a complexing agent. The XRD results indicated that the deposited ZnS thin films exhibited a polycrystalline cubic structure. The number of ZnS peaks increased from three to four peaks as the bath temperature was increased from 60 to 80 °C based on the XRD patterns. From the AFM measurements, the film thickness and surface roughness were found to be dependent on the bath temperature. The grain size increased as the bath temperature was increased from 60 to 80 °C.

Keywords: chemical bath deposition, thin films, zinc sulphide, atomic force microscopy

Introduction

Zinc sulphide thin films are wide band gap semiconductors which have been used in phosphors, catalysts, solar cells, electro-luminescent devices and many other optoelectronic devices. The ZnS thin films have been deposited using various methods such as RF reactive sputtering (Shao et al., 2003), chemical bath deposition (Goudarzi et al., 2008; Noikaew et al., 2008; Antony et al., 2005), atomic layer epitaxy (Oikkonen et al., 1998), pulsed-laser deposition (Yano et al., 2003) and electrodeposition (Lokhande et al., 1998). Chemical bath deposition method is considered a cheap method for producing large area thin films. Up-to-date, chemical bath deposition method has been successfully used to deposit various thin films including FeS₂ (Anuar et al., 2010), PbS (Raniero et al., 2010), CdTe (Gataridak et al., 2010), CdS (Li et al., 2005) and As₂S₃ (Mane et al., 2004). Chemical bath deposition method is based on controlled precipitation from solution of a compound on a suitable substrate. The substrate is immersed in either alkaline or acidic solution containing the metal ion, chalcogenide source and a complexing agent. Several complexing agents have been utilized in the deposition of thin films such as ammonium sulphate (Soundeswaran et al., 2004), sodium citrate (Esparza-Ponce et al., 2009), triethanolamine (Gumus et al., 2005), disodium ethylene diamine tetra-acetate (Anuar et al., 2009), nitrilotriacetic acid (Khallaf et al., 2008) and sodium tartrate (Anuar et al., 2004).

The present work reports preparation and physical characterization of ZnS thin films onto indium tin oxide glass substrates using chemical bath deposition method. The chemical bath contains zinc sulphate and sodium thiosulphate which provide Zn²⁺ and S²⁻ ions, respectively. It is the first time that the influence of bath temperature ranging from 60 to 80 °C on the ZnS thin film in the presence of sodium tartrate solution is reported. Thin films were analyzed by X-ray diffraction and atomic force microscopy.

Materials and Methods

All the chemicals used for the deposition were analytical grade reagents and all the solutions were prepared in deionised water (Alpha-Q Millipore). Zinc sulphide thin films were prepared from an acidic bath using aqueous solutions of zinc sulphate (ZnSO₄) and sodium thiosulphate (Na₂S₇O₃) as a source of Zn²⁺ and S²⁻ ions, respectively. Sodium tartrate (Na₂C₄H₄O₆) was used as complexing agent to chelate with Zn²⁺ for obtaining Zn-tartrate complex solution. Indium tin oxide (ITO) glass was used as the substrate for deposition of ZnS thin films. Before deposition, indium tin...
Rapeseed Lipase Catalyzed Synthesis of Butyl Butyrate for Flavour and Nutraceutical Applications in Organic Media

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(received September 1, 2010; revised January 26, 2011; accepted January 27, 2011)

Abstract. Butyl butyrate, a short chain ester with fine fruity pineapple odour, is a significant flavour compound. Recent investigations show that butyrate esters also have anticancer activity. Factors influencing the synthesis of butyl butyrate by organic phase biocatalysis were investigated. Maximum ester yield of 89% was obtained when 0.25 M butanol and butyric acid were reacted at 25 °C for 48 h in the presence of 250 mg rape seed lipase acetone powder in hexane. Addition of water did not affect synthesis, while a water activity of 0.45 was found optimum. Of 15 different alcohols evaluated, isoamyl and (Z)-3-hexen-1-ol were esterified most effectively with molar conversion yields of 92.2 and 80.2%. Short chain primary alcohols such as methanol and medium-long chain alcohols, such as heptanol and octanol were esterified more slowly. The results show that rape seed lipase is versatile catalyst for ester synthesis with temperature stability range 5-50 °C.

Keywords: flavour, butyl butyrate, rape seedling, biocatalysis, esterification, anticancer agent

Introduction

Esters of butyric acid are important as flavour compounds (Leblanc et al., 1998). Ethyl butyrate and isoamyl butyrate are found in the aroma of strawberry and banana. The butyrate ester of isoamyl alcohol is a valuable, high demand flavour and fragrance compound widely used in the food, beverage and pharmaceutical industries. The world market for flavours is thought to account for a quarter of the total food additive market. An emerging area of application of butyrate esters is as nutraceutical agents. Naturally occurring butyrate esters such as tributyrin as well as synthetic esters have been shown to possess antiproliferative action against a wide variety of cancer cell lines. Anti-tumour activity was also demonstrated in-vivo (Kuefer et al., 2004).

Direct synthesis of esters from fatty acids and alcohols by enzymatic methods has been suggested as a good alternative route to industrial catalysis. Butyrate esters and other short chain flavour esters can be synthesized by organic phase biocatalysis (OPB) to satisfy commercial demands (de Baros et al., 2009; Pires-Cabral et al., 2009; Torres et al., 2009; Ben Salah et al., 2007; Romero et al., 2005). Fungal lipases are preferred for organic phase biocatalysis (OPB) owing to their ready availability and low cost (Abbas and Comeau, 2003; Krishna et al., 2000; Langrand et al., 1999). Lipases from higher vegetative plants including wheat germ (Xia et al., 2009), papaya (Miyazawa et al., 2008; Caro et al., 2000) and rapeseed lipase (Mukherjee and Jachmanian, 1996; Neube et al., 1993; Hills et al., 1990) have also been used for various purposes in OPB. The cost of biocatalyst remains an important consideration in OPB as purified enzymes are expensive. Crude seedling powder is potentially inexpensive alternative form of biocatalyst for OPB. Procedures for preparing acetone powder are simple, making it quite suitable for technical use (El et al., 1998). Earlier, we had evaluated various plant seedlings in OPB and results showed that acetone powder obtained from day 4 germinated rape seed was potentially useful biocatalyst for the synthesis of low molecular weight flavour esters (Liaquat and Apenten, 2000). Butyl butyrate was amongst the esters formed in a good yield.

In the present study, the impact of several parameters on synthesis of butyl butyrate catalyzed by crude rape seedlings powder was carefully investigated first time, which included effect of added water, water activity, substrate concentration, temperature and incubation time. The ability of enzyme to catalyze the synthesis of

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Effects of Storage and Packaging Materials on Some Physicochemical Properties and Sensory and Microbiological Parameters of Pineapple Juice (*Ananas comosus*)

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(received February 12, 2010; revised August 23, 2010; accepted September 3, 2010)

Abstract. Physicochemical, microbiological and sensory parameters of concentrated pineapple juice stored in cans and glass bottles were studied over a period of ten weeks. There was slight increase in pH from 4.2 to 4.7 and to 4.8 and decrease in titratable acidity from 8.1 to 5.1 and to 4.6 mg/100 mL, whereas total solids (%) decreased from 76.23 to 65.47% and to 60.38% in canned and bottled pineapple concentrates, respectively. Over 90% loss of Vitamin C was observed, with the bottled samples retaining more Vitamin C than the canned samples. The microbial counts ranged from $2.0 \times 10^3$ to $2.4 \times 10^4$ cfu/mL whereas fungi and mesophilic bacteria, were not detected to $6 \times 10^3$ cfu/mL. Freshly prepared single strength juices of pineapple were better in terms of taste and colour, while the bottled reconstituted juice concentrate competed favourably with the fresh one in colour. The canned samples lost their colours within 10 weeks of storage. The glass bottled samples had a characteristic desirable aroma. Thus concentrated juice in glass bottles stored at room temperature enhanced the keeping quality of the juice and compared more favourably with the fresh juice than the canned concentrated juice.

Keywords: pineapple juice, packaging materials, physicochemical properties, sensory qualities, microbiological quality, storage

Introduction

Fruits are common food materials, which contribute micronutrients (vitamins and minerals) and natural soluble sugars for energy to support human nutrition (Ihekoronye and Ngoddy, 1985).

Juice is obtained from fruits e.g., orange, pineapples, apple, grape etc., and concentrates can be prepared by partial evaporation of moisture from the juices which are likely to have a longer shelf life than the juices due to lower moisture content (Takahashi et al., 2000)

Pineapple (*Ananas comosus*) is one of the most common non-citrus tropical and sub-tropical fruits. It has pleasant flavour and acceptable taste and is a very rich source of Vitamin C and organic acids. Pineapple contains high level of sugars and other carbohydrates and is, therefore, a major source of dietary fibre and enzymes and can serve as digestion aids (Takahashi, et al., 2000). Pineapple is a member of the Bromiliaceae family (Medina and Garcia, 2005) and is the second largest harvest of importance after bananas, contributing over 20% of the world production of tropical fruits (COVECA, 2002). Nearly 70% of pineapple is consumed as fresh fruit in the producing countries. Thailand, Philippines, Brazil and China are the main pineapple producers in the world, supplying 50% of the total output (FAO, 2004). Other important producers include India, Nigeria, Kenya, Indonesia, Mexico and Costa Rica that account for the remaining 50%.

Pineapple, as a plant is put to a number of uses. One of the best known uses of pineapple juice is as a diuretic in the ailments of kidneys, bladder and prostate. Due to the fibre content of the pulp, pineapple prevents constipation and regularizes the intestinal flora (FAO, 2004). Furthermore, there is evidence of pineapple being an appetite reducer, heat protector and an aid in treatment of fever and sore throats, mouth aches and inflammation. Lightly boiled ground pineapple can be used to clean infected wounds because it eliminates dead tissues without affecting live tissues, acts as a disinfectant and accelerates cicatrisation (Mundogar, 2004).

Unfortunately, this fruit is seasonal, highly perishable and prone to high post-harvest losses. Post-harvest losses
Osmotic Dehydration of Pomegranate (*Punica granatum* L.)
Using Response Surface Methodology

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(received April 28, 2010; revised July 14, 2010; accepted September 6, 2010)

Abstract. For studying osmotic dehydration of pomegranate arils, a mathematical model was developed to quantify the responses of water loss, weight reduction and solute gain using response surface methodology. Under the experimental conditions, 15-32% water was lost, whereas 6-13% solids were gained. The high value (> 0.98) for determination coefficient (R²) and adequate precision (> 38) and a low value for coefficient of variance (< 2.5) was achieved for the developed model. Optimisation of the model with the goal of maximum water loss and minimum solute gain resulted in 24.5% and 9.6% values, respectively, whereas, with the goal of minimum water loss and maximum solute gain resulted in 15.6% water loss and 13.8% solute gain.

Keywords: pomegranate, osmotic dehydration, mathematical modeling

Introduction

Pomegranate (*Punica granatum* L.) is a fruit of tropical and subtropical regions. It is widely cultivated in Iran, Spain, Egypt, Afghanistan and India (Adsul and Patil, 1995). The edible fruit is a berry with a rounded hexagonal shape, and has thick reddish skin and around 400-600 seeds (Al-Said *et al*., 2009). The pulp bearing seeds are called “arils”. Dehydrated arils are known as “Anardana” in local language in India and Pakistan and are used in culinary and traditional medicines. The arils are either consumed as fresh or their juice is extracted. The juice may also be used in processed products like jams and jellies.

Drying conditions of pomegranate arils, significantly affect essential functional properties. Pomegranate is usually dried in open environment (sun drying) due to which the resulting product contains dust, insects and other contaminants. Moreover, open environment (sun drying) does not result in consistent product due to varying humidity and temperature conditions (Doymaz and Pala, 2002). Industrial dryers have been proposed (Doymaz, 2004) to avoid these problems. However, industrial dryers are not only expensive but result in low quality product as well due to the use of hot air for drying the product. An alternate drying method is osmotic dehydration.

Osmotic dehydration (OD) is widely used to remove water from fruits and vegetables by dipping them in aqueous solutions of low molecular weight compounds e.g., sucrose at high concentration. During OD, water is lost from the product, whereas solids are transferred from the dipping medium to the product simultaneously (Madamba, 2003). OD thus results in energy saving and improved product quality (Raoult-Wack, 1994).

Rate of OD depends on several variables including temperature, immersion time and solute concentration. Successful application of osmotic dehydration requires mathematical modelling of process variables. Mathematical modelling helps in dealing with multiple factors to optimise the desired outcome by simulating the process variables and allowing the quantification under various conditions (Jalali *et al*., 2008).

Using response surface methodology (RSM), the aim of this work had been to study the effects of temperature, immersion time and concentration on the weight reduction (WR), water loss (WL) and solute gain (SG) during the OD of pomegranate arils. The OD parameters were simulated and optimised using mathematical model.

Materials and Methods

Sample preparation. Pomegranate fruits of approximately same size, weight and maturity level were purchased from the local market. The arils were manually separated from the fruits and the peel was discarded. The arils were then subjected to osmotic treatment.
Effect of Roasting Temperature on the Fatty Acid Composition and Physicochemical Characteristics of Extracted Oil

Carthamus tinctorius Thori-78 of Pakistani Origin Seeds

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(received June 25, 2010; revised October 7, 2010; accepted October 22, 2010)

Abstract. Study of Carthamus tinctorius L. (safflower) oil extracted from unroasted and roasted seeds (at temp 120-180 °C) showed, on roasting, significant increase in free fatty acid, acid value, unsaponifiable matter, rancidity, peroxide value, colour development and oxidative deterioration, while refractive index and density were relatively constant. The iodine value of oil of seeds roasted at 160 and 180 °C was reduced. The concentration of oxidation-sensitive linoleic acid reduced from 75.42 to 73.41% but that of palmitic and stearic acids increased, showing no adverse effect on the nutritional value of the roasted seed-oil. But at higher temperature (180 °C) the browning of seeds occurred.

Keywords: C. tinctorius Thori-78, roasted-seed oil, fatty acids, vegetable oil

Introduction

Carthamus tinctorius L. (safflower) is an annual herb belonging to the family Compositae. It is widely distributed throughout the world such as Asia, USA, Canada, Africa and Australia. India, Africa and USA are the main producers of safflower oil. It has long been extensively grown for obtaining a dye from the flowers as well. This oil crop was introduced into Japan from China, where it became an important source of cooking oil (Oyen and Umali, 2007; Knights et al., 2001; Kaffka et al., 2000; Sastri, 1950). From Middle East, the crop also spread to Europe and then to America and Africa. C. tinctorius flowers, seeds and oil have a wide range of medicinal uses in different countries (Kaffka et al., 2000; Sastri, 1950). In northern America, the plant is cultivated for using as bird seed, animal meal and industrial applications (Oyen and Umali, 2007; Mündel et al., 2004; Oelke et al., 1992).

C. tinctorius seeds are edible and are also eaten after roasting like sunflower seeds (Duke, 1983). The seed is rich in edible oil and oil content is similar to olive, sunflower and peanut oils. The oil content varies from 24 to 36%, depending on the variety of C. tinctorius, soil texture, climate and other conditions (Pritchard, 1991; Swern, 1964). The oil is composed of linoleic acid (67.7-83.2%), the essential fatty acid that the human body is unable to biosynthesize (Hamrouni et al., 2004, Lee et al., 2004). Hence the seeds and seed oil are therapeutically important.

C. tinctorius oil can be used in cosmetics, foods, nutritional supplements, personal care products, soap and shampoos. Developed countries have the most significant market for C. tinctorius oil as salad oil, margarine and cooking oil, as it is non-allergenic and is considered to be one of the healthiest oils for human consumption with a high ratio of polyunsaturated/saturated fatty acids.

Roasting process is the primary step for making condiment oil since the colour, flavour, composition and quality of oil are all influenced by the processing conditions. C. tinctorius oil is used as condiment oil along with sesame, red pepper and perillar oils in Korea (Lee et al., 2004; Kim et al., 2002a; 1998; Yoshida and Takagi, 1997). Recently, use of roasted C. tinctorius safflower seed was investigated as medicinal food for bone formation in Korea and the powder of roasted C. tinctorius seeds was found to help in recovery of bone repair in rats (Kim et al., 2002b; 1998).

In Asia roasted seeds of C. tinctorius are commonly consumed. Hence, the objective of the present study was to investigate the changes in physical and chemical indices of unroasted and roasted seed oil of C. tinctorius Thori-78 and correlate the results of physicochemical parameters of oil to evaluate the
Effect of Moisture Content and Heat Treatment on Peroxide Value and Oxidative Stability of Crude Palm Kernel Oil

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Abstract. Effect of moisture content, roasting time and temperature on peroxide value (PV) and oxidative stability (OS) of unrefined palm kernel oil was studied using response surface methodology at five levels of moisture content (4, 7, 10, 13 and 16% wet basis), roasting time (5, 10, 15, 20 and 25 min) and roasting temperature (50, 70, 90, 110 and 130 °C). Within the studied range, mean PV of palm kernel oil was recorded to be 13.06±5.13 meq/kg. Least PV of 7.3 meq/kg was obtained at 10% moisture content, 15 min roasting time and 130 °C temperature. Maximum stability time of 27.0 h was achieved at 10% moisture content, 15 min roasting at 130 °C. This treatment produced unrefined palm kernel oil stable for 388 days. All the studied parameters significantly influenced flavour rating and shelf life of unrefined palm kernel oil at P < 0.05.

Keywords: palm kernel oil, oxidative stability, peroxide value, moisture, heat treatment

Introduction

Vegetable oil, as a valuable part of a well-balanced diet, contains a range of fat soluble vitamins (A, D, E and K) and essential fatty acids, both necessary for the healthy functioning of the body (Fellows and Hampton, 2003). Good quality palm kernel oil serves the aforementioned nutritional significance. Industrial application of palm kernel oil is also fast increasing. Among the 17 commodity covered in the data provided by Oil World (2009), palm kernel oil occupied eleventh production level, after four major vegetable oils (soy, palm, rape, and sunflower), three animal fats (tallow, lard and butter) and three minor oils (groundnut, cotton seed and coconut).

Palm kernel oil is a yellowish white fat containing 82% proportional weight of saturated fatty acid and 18% unsaturated fatty acid (O’Brien, 2008). It is classified by the nutritional experts as saturated oil and has the advantage of having solid texture at room temperature (Rossell et al., 1985). Chemicals and physical properties of palm kernel oil resemble those of the coconut oil. It belongs to members of a group called lauric oils due to high level of lauric acid (46-52%) present in proportional weight (Tat and Eng, 1985).

Preferences for fat and oil products with fresh bland flavours and odours require keeping quality and rancidity evaluations both during development and processing. Peroxide value (PV) is one of the most widely used chemical tests for the determination of fats and oils quality. Peroxide value is a measure of rancidity in its early stage, this test showed good correlation with organoleptic flavour scores (O’Brien, 2008). Although a linear relationship has been observed between peroxide values and flavour scores during the initial stages of lipid oxidation, this method alone is not a very good flavour quality indicator because the peroxide value increases to maximum and then decreases as storage time increases (Hill, 1994). Hence, oils and fats are subjected to oxidative stability test which is a good quality parameter assessment that complements PV analysis (Shahidi and Naczk, 2004; Holser and Isbell, 2000). Most fat and oil products are tested for flavour stability as part of quality control programmes to assure that customer specifications are satisfied. The purpose of this evaluation is to satisfactorily determine the product shelf life. Studies have been carried out on oxidative stability of edible fats and oils such as sesame oil (Lee et al., 2010), safflower oil (Lee et al., 2004), olive husk oil (Lucas et al., 2002), meadow foam oil (Holser and Isbell, 2000), cotton seed (Hill, 1994) and lard (Kikugawa et al., 1983). In summary, these reports showed oxidative stability of fats and oils dependent on the method used for determination of chemical composition and processing parameters.
Effect of Citric Acid and Storage Containers on the Keeping Quality of Refined Soybean Oil

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(Received February 6, 2010; revised August 31, 2010; accepted September 27, 2010)

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Abstract. Free fatty acids (FFA), acid value (AV), peroxide value (PV) and iodine value (IV) of the soybean oil in tinned cans, transparent white glass and plastic bottles were monitored for one year at room temperature. The results revealed that the oil stored in tin containers had the highest FFA and AV of 0.334±0.054% oleic acid and 0.653±0.104 mg KOH/g oil, respectively, while that in plastic containers had the lowest value of 0.252±0.033% oleic acid and 0.495±0.064 mg KOH/g oil for the FFA and AV. Addition of food grade citric acid (FGCA) at 0.2% level increased the keeping quality of refined soybean oil stored in glass and plastic bottles both with respect to hydrolytic stability of the oil. However, it reduced the peroxide value and slightly increased the iodine value of oil in all the containers. The additive (FGCA) led to a higher reduction in the oxidative rancidity of the oil stored in plastic bottles as compared to that stored in glass and tinned cans. There was significant difference at P<0.05 in FFA and AV of oil stored in tin and glass containers as well as in PV and IV of the oil stored in all the containers. The additive enhanced the shelf life with respect to oxidative stability of the oil the most in plastic bottles and the least in tinned cans.

Keywords: soybean oil, containers, citric acid, free fatty acids, acid value, peroxide value, iodine value

Introduction

Soybean oil remains in high demand due to low cholesterol level making it safer for human consumption (Arawande, 2008). Crude soybean oil is produced from soybean seeds which are cracked, adjusted for moisture content, rolled into flakes and solvent-extracted with commercial hexane. The crude oil is further subjected to refining (Wikipedia, 2007) through degumming, neutralization, bleaching and deodorisation (Arawande and Abitogun, 2009a). Refined soybean oil is the predominant vegetable oil used domestically in edible oil products (Erickson et al., 1980). Application of soybean oil falls into two main categories: edible fat products, meant for human consumption, and industrial fat products, used for technical purposes (ASA, 1996). The oil is unique among vegetable oils due to its high content of unsaturated fatty acids and remains in liquid form much below the room temperature. It contains potential natural antioxidants which are not removed during processing thereby preventing the oxidative rancidity which may occur in the lipids present in the oil (Haumman, 1994). It contains 7-8% linolenic acid which can be reduced during processing. The high content of linolenic acid is responsible for the development of off-flavour and off-odour during degradation of the oil. Nowadays, there is a drastic shift from the consumption of common red palm oil and other edible oils to refined soybean oil (Arawande, 2008). Vegetable oil merchants sometimes purchase the oil when it is cheap and store it in different containers, such as plastic bottles, glass bottles and tinned cans, and later sell it during off season when it becomes expensive, without taking into consideration the deterioration of oil quality.

One of the major problems confronting the producers, sellers and consumers of oil is associated with the deterioration of oil during storage where in the oil turns rancid owing to high content of unsaturated fatty acids. However, the use of antioxidants reduces deterioration during the storage (Arawande and Abitogun, 2009b).

Several studies have been conducted earlier and reported on soybean oil. Carlson and Scott (1991) and Erickson et al. (1980) reported processing and utilisation of soy oil, whereas Abitogun et al. (2009) studied effects of phosphoric acid on physicochemical parameters of soybean oil. Arawande (2008) investigated effects of storage containers on the shelf life of refined soybean oil. The use of soybean oil as insect repellent has been
Soil Micronutrient Status in Hazro Area of District Attock, Pakistan

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(received April 17, 2010; revised July 12, 2010; accepted July 20, 2010)

Abstract. Study of micronutrients in the soil of Hazro area of District Attock (Potohar), Pakistan, revealed micronutrient deficiency in the order of Fe> Mn> Zn> Cu. All the soils were low to medium in Fe and Mn followed by Zn content, whereas only 8% samples had low Cu content. 92% and 18% soils in Hazro area had satisfactory to adequate Cu and Zinc contents, respectively, Thus soils were deficient in Fe, Mn and Zn, whereas Cu was in medium to adequate range.

Keywords: micronutrients, Hazro, soil micronutrients, Attock

Introduction

Micronutrients are as important in plant nutrition as the macro nutrients and plants grown on soils deficient in micronutrients can exhibit similar reduction in growth and yield (Havlin et al., 2004). To get optimum yield, a balance dose of macro as well as micronutrients are required. Deficiency of various micronutrients is related to soil type and crop. The introduction of new high yielding hybrids or cultivars demanding a higher level of soil fertility has further accentuated the incidence of micronutrient deficiencies. Zn deficiency is the most widespread disorder in the country. Soil analyses revealed that > 50% of the cultivated soils of the country are unable to provide sufficient Zn to meet the needs of many crops (Khattak, 1995). The information obtained from 329 soil samples collected from various depths throughout the country during the period of seven months revealed widespread deficiency of Zn and B followed by Fe (Zia et al., 2004b).

District Attock of Potohar comprises of six tehsils, i.e., Attock, Hazro, Fatehjang, Pindi Gheb, Jand and Hasan Abdal. The district lies between latitude 32.35° N and longitude 72.55° E. The climate is sub-humid to semi-arid with 400-700 mm annual rainfall. Hazro tehsil is among the most productive tehsils of Attock with sizeable contribution to agriculture. The soils of Hazro are medium (loam) to light (sandy loam) textured with most of the soils poor in fertility status (Mehmood et al., 2008).

Keeping in view the low fertility, nutritional disorder and importance of micronutrients for successful cropping in Hazro area, a study was conducted to assess the extent of micronutrients viz., zinc, iron, copper and manganese deficiencies in soils of Hazro area of District Attock.

Materials and Methods

Soil samples were collected from different field locations of Hazro area of District Attock, air dried, sieved and stored in plastic bottles. Samples were analyzed by diethylene triamine pentacetic acid (DTPA) extraction method. Twenty (20) grammes of soil were shaken with 40 mL of 0.005 M DTPA solution for 2 h, and double filtered with Whatman filter paper # 42. A series of standard DTPA extraction solutions for micronutrients were also prepared. Zn, Fe, Cu and Mn were measured directly in the filtrate and the standard solutions by atomic absorption spectrophotometer using appropriate lamp for each element (Ryan et al., 2001). The data was subjected to statistical analysis in MS Excel-2007.

Soil micronutrients have been characterized (Table 1) according to the generalized guidelines (Martens and Lindsay, 1990) used for interpretation of soil micronutrient analysis data in Pakistan (Zia et al., 2004a).

Table 1. Guidelines for interpretation of soil micronutrient status

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Abstract. Specimens of nineteen different global varieties of cotton were studied to determine their contribution to water hardness through calcium and magnesium impurities, resulting in various problems during textile pretreatment, colouration and finishing. Pakistani cotton was found to be the second most contaminated cotton in terms of calcium and magnesium impurities, whereas Elisa variety from Uzbekistan was the cleanest.

Keywords. cotton, water hardness, magnesium, calcium

Introduction

Cotton is the backbone of the world’s textile trade. It has many countless end uses, which make it one of the most abundantly used textile fibres in the world (Wilson, 2006; Yafa, 2006; Becerra, 2000; Cook, 1984). It is seed hair of plant of genus Gossypium (Lewin, 2006) and the purest form of cellulose found in nature. Although cotton may be as much as 96% cellulose, there are always some other components present in it as impurities. The level of impurities in cotton is affected by geology of the cultivation area, soil constitution, weather conditions during the maturing period, cultivation techniques, chemicals, pesticide, fertilisers and harvesting techniques. Among the impurities present in cotton, the elements that pose the greatest threat in textile wet processing are alkaline earth and heavy metal contaminants such as iron, manganese, calcium and magnesium.

Textile wet processes comprise of desizing, scouring, bleaching, dyeing, printing and chemical finishing. Water hardness caused by calcium and magnesium impurities in cotton, may cause several problems in each of the textile wet processes. In desizing process, effectiveness of the wetting agents used may be reduced in the presence of calcium and magnesium ions. In scouring processes, calcium and magnesium ions may precipitate the soaps used, forming a sticky insoluble substance which deposits on the cotton fabric (Losonczi et al., 2005). These deposits impair the fabric handle, cause resist-spots in dyeing, attract soil to the material and cause inconsistent absorbency in subsequent processes. Although most synthetic detergents today used in scouring do not precipitate in the presence of calcium and magnesium ions, the fatty acid hydrolysis products formed by the saponification of natural waxes, fats, and oils in the fibres will precipitate. Formation of complexes with alkaline and alkaline earth salts drastically reduces the solubility and the rate of dissolution of surfactants, thus impairing the wash removal ability of the surfactants (Bille, 1987).

Although magnesium produces beneficial effects when present in hydrogen peroxide bleaching solutions, the presence of calcium may result in decreased stability of peroxide bath due to blockage of stabilisers, harsh handle of the fabric due to deposition of insoluble salts and decrease in fabric whiteness due to formation of insoluble products with optical brighteners. In bleaching cotton with hydrogen peroxide, sodium silicate is used as stabiliser, which may be converted to calcium silicate in the presence of calcium impurities. This calcium silicate has poor water solubility and is not washed-off the fabric easily, resulting in harsh fabric handle (Topalovic, 2007).

In dyeing, the presence of calcium and magnesium ions may result in lowering of solubility of dyes and staining due to formation of insoluble products with dye, change in dyeing shades, and difficulties in the removal of hydrolysed reactive dye ensuing in low washing fastness. Most water-soluble anionic dyes are sodium salts of sulphonic acid which, in the presence of calcium and magnesium impurities, may be converted into their respective salts with lower water solubility, and thus staining. In the washing-off stage, the removal of unfixed hydrolysed reac-
Study of Tannery Wastewater Treatability by Precipitation Process

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(received April 14, 2010; revised August 31, 2010; accepted September 28, 2010)

Abstract. A study was conducted for the removal and recovery of chromium from tannery wastewater, using NaOH, MgO, Ca(OH)₂ and Al₂(SO₄)₃.18H₂O as precipitating agents and comparing their effect on pH, total dissolved solids (TDS), total suspended solids (TSS), sludge volume and chromium removal. MgO and Ca(OH)₂ produced least amount of sludge and dewatering of sludge was also easy as compared to Al₂(SO₄)₃.18H₂O and NaOH. The chromium removal of MgO and Ca(OH)₂ was 95% and 96%, respectively.

Keywords: precipitating agents, chromium removal, tannery wastewater, sludge volume

Introduction
Pakistan leather industry is one of the major foreign exchange earners of the country. About 90% of leather products are exported in finished form. However, the operation of tanneries is causing severe environmental degradation due to the disposal of untreated effluent on land and in water bodies. High chromium concentration is harmful for environment and human health (Zayed and Terry, 2003).

In tanning process, chromium compounds are commonly used for processing of hides, 60-70% of which react with the skin and the remaining amount is discharged as effluent (Mant et al., 2005; Sreeram and Ramasami, 2003).

The remaining chromium (about 30-40%) in the solid and liquid waste contributes to the environmental pollution. Considering the high cost of chromium metal, it would be preferable to recover it from the wastewater (Kocaoba and Akcin, 2002; Ludvik, 2000; Fabiani et al., 1997).

Various methods have been used for removing toxic metal ions from aqueous solutions including chemical precipitation, ion exchange, reverse osmosis, evaporation, solvent extraction, electrodialysis, coagulation and adsorption (Dhungana and Yadav, 2009; Rashed, 2008; Kongjao et al., 2007; Esmaeili et al., 2005; Kocaoba and Akcin, 2002). Among these, chemical precipitation is the most commonly used method.

Many factors affect the process of chemical precipitation including the type of precipitation agent, pH, nature, velocity of precipitation, sludge volume, time of mixing and complexing agents (Patterson, 1985). Precipitation can be followed by coagulation and flocculation, in order to enhance sedimentation. The process is very effective for the removal of precipitated solids and is used to treat the industrial effluent before discharging them into receiving water (Noyes, 1994). The precipitation process is not always perfect and chemical characteristics of the treated wastewater may not meet the standards. Consequently, a further treatment is often necessary.

Kasur town is located 55 Km southeast of Lahore in the province of Punjab, Pakistan. The city is well known for its tanning industry with more than 250 tanneries discharging large volumes of untreated tannery waste in the form of wastewater, sludge and solid waste. There is an urgent need for the treatment of tannery effluents prior to their disposal. The main purpose of this research was to compare pH, chromium concentration, sludge volume, colour, TDS and TSS using Al₂(SO₄)₃.18H₂O, Ca(OH)₂, NaOH and MgO in the precipitation process, so as to find the best precipitating agent for chromium removal and recovery.

Materials and Methods
The study was carried out at Pakistan Council of Scientific and Industrial Research (PCSIR) Laboratories Complex, Lahore, in June 2009. Samples were brought from inlet of Kasur treatment plant and
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</table>
Quantitative Status of Heavy Metals in Soils of Quetta Irrigated by Sewage Water

Syed Ishtiaq Hyder**, Muhammad Ayaz Khan Malghani®, Muhammad Maqsood Ahmed®,
Muhammad Arshadullah® and Addal Mir Khan®

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bBaluchistan University of Information Technology & Management Sciences, Quetta, Pakistan

(Received August 24, 2010; revised October 27, 2010; accepted December 06, 2010)

Abstract. In soils of different areas of Quetta city, irrigated by sewage water, the highest concentration of heavy metals was found to be as follows: lead (1.38 ppm), copper (0.86 ppm), chromium (0.036 ppm), cadmium (0.29 ppm), iron (10.50 ppm), nickel (0.74 ppm), zinc (19.45 ppm) and arsenic (0.001 ppm) on average basis. The sewage water contained lead (53.26 ppb), copper (22.5 ppb), chromium (1.33 ppb), cadmium (0.53 ppb), iron (127.7 ppb), nickel (51.14 ppb), manganese (17.08 ppb), zinc (31.38 ppb) and arsenic (0.011 ppb). At each site the concentration of heavy metals and sewage water showed positive relationship.

Keywords: heavy metals, sewage water, bio-accumulation, bio-magnification

Heavy metals in environment affect human life and bio-diversity and ultimately deteriorate sustainable development. Human activities have drastically changed the bio-chemical cycles through discharge of heavy metals into the environment. Heavy metals, being non-degradable, tend to accumulate in soil, sea water, fresh water and sediments and pose risks to human consumers of the sea foods, vegetables and also to many other organisms at the same level.

Nowadays large amount of untreated sewage/industrial water is being discharged into surface bodies for disposal (Saleemi, 1993) which may contain non-essential heavy metals in large amounts and which could be transferred to animal and human beings through food chain (Malla et al., 2007; Ghafoor et al., 1994). Sediments are ready sink or reservoir of pollutants including trace metals (Becker et al., 2001; Muohi et al., 2003).

The main anthropogenic sources of heavy metals are various industrial sources including former and present mining activities, foundries and smelters, and defuse sources such as piping, combustion bio-products, traffic, detergents, welding, batteries and leather tanneries.

For determining the status of heavy metals in soil of Quetta, in summer, soil samples were collected from Habib Nala, Hudda, Samungli and Barori and sewage water samples were collected from Habib Nala, Hudda, Samungli, Mariaabad and Angle Road. Drinking water samples were also collected from Shahbaz town, Jinnah town, Pashtoonabad, Mariaabad and Satellite Town. After removing the stones, drying and grinding, the soil was sieved through 2 mm wire mesh. (MAFF, 1986). The sample were then digested and analyzed using atomic absorption spectrometer.

All the analyzed sewage water samples (40 in number) contained on an average (ppb) lead 53.26, copper 22.5 chromium 1.33, cadmium 0.53, iron 127.7, manganese 17.08, nickel 51.14, zinc 31.38 and arsenic 0.011 ppb (Table 1).

It was observed that the results relating to heavy metals in the sewage water were quite below the National Environmental Quality Standards of EPA for sewage

<table>
<thead>
<tr>
<th>Elements</th>
<th>Average conc. (ppb)</th>
<th>NEQS (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>53.26</td>
<td>500</td>
</tr>
<tr>
<td>Copper</td>
<td>22.50</td>
<td>2000</td>
</tr>
<tr>
<td>Chromium</td>
<td>1.33</td>
<td>1000</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.53</td>
<td>100</td>
</tr>
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</tr>
<tr>
<td>Arsenic</td>
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</tr>
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*Author for correspondence; E-mail: hyder292002@yahoo.com