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Ultrasound assisted enhancement in natural dye extraction from beetroot for industrial applications and natural dyeing of leather

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A B S T R A C T

There is a growing demand for eco-friendly/non-toxic colorants, specifically for health sensitive applications such as coloration of food and dyeing of child textile/leather garments. Recently, dyes derived from natural sources for these applications have emerged as an important alternative to potentially harmful synthetic dyes and pose need for suitable effective extraction methodologies. The present paper focus on the influence of process parameters for ultrasound assisted leaching of coloring matter from plant materials. In the present work, extraction of natural dye from beetroot using ultrasound has been studied and compared with static/magnetic stirring as a control process at 45 °C. The influence of process parameters on the extraction efficiency such as ultrasonic output power, time, pulse mode, effect of solvent system and amount of beetroot has been studied. The use of ultrasound is found to have significant improvement in the extraction efficiency of colorant obtained from beetroot. Based on the experiments it has been found that a mixture of 1:1 ethanol–water with 80 W ultrasonic power for 3 h contact time provided better yield and extraction efficiency. Pulse mode operation may be useful in reducing electrical energy consumption in the extraction process. The effect of the amount of beetroot used in relation to extraction efficiency has also been studied. Two-stage extraction has been studied and found to be beneficial for improving the yield for higher amounts of beetroot. Significant 8% enhancement in % yield of colorant has been achieved with ultrasound, 80 W as compared to MS process both using 1:1 ethanol–water. The coloring ability of extracted beet dye has been tested on substrates such as leather and paper and found to be suitable for dyeing. Ultrasound is also found to be beneficial in natural dyeing of leather with improved rate of exhaustion. Both the dyed substrates have better color values for ultrasonic beet extract as inferred from reflectance measurement. Therefore, the present study clearly offers efficient extraction methodology from natural dye resources such as beetroot with ultrasound even dispensing with external heating. Thereby, also making eco-friendly non-toxic dyeing of fibrous substances a potential viable option.

1. Introduction

There is a growing demand for developing suitable extraction techniques for more efficient and effective extraction of available active matters from the plant materials. In this line, the main objective of the present study is to develop suitable methodology for both extraction of dye from natural resources and for application in the substrate. Highly colored substances, widely known as colorants, can be used to impart color to an infinite variety of materials described technically as substrates [1]. Recent studies have confirmed that azo dyes contain potential colon carcinogens, which is a possible hazard to humans when chronically exposed [2]. During textile/leather processing, inefficiencies in dyeing result in a large amount of dyestuff being directly lost in the wastewater, which ultimately finds way into the environment. It is estimated that 10–35% of the dye is lost in the effluent during the dyeing process, while in the case of reactive dyes, as much as 50% of the initial dye load is present in the dye bath effluent [3]. EU decision on the restriction of azo based dyes with potential breakdown into certain toxic amines (22 in numbers) as well as recent regulation for chemicals i.e. REACH. These factors tend to restrict the use of synthetic dyes due to routine monitoring of these industrial effluent

Abbreviations: EU, European Union; REACH, Registration, Evaluation, Authorisation and Restriction of Chemical substances; FDA, US Food and Drug Administration; US, ultrasonic extraction at 45 °C (without external heating); MS, magnetic stirring extraction 45 °C (with external heating); AR, analytical reagent (grade); OD, optical density; UV–VIS, ultraviolet–visible region; SLTC, Society of Leather Technologists and Chemists; λ_{max}, wavelength of maximum absorbance in UV–VIS spectrum; MEM, maximum extractable material; CIE, Commission Internationale de l'Eclairage; CIELAB, CIE color space; L^*, color lightness variable; a^*, color variable in the red–green axis; b^*, color variable in the blue–yellow axis; *c*, chroma of the color; *h*, hue of the color.

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discharges, which may pose health hazards, viz., carcinogens. Our earlier work focused towards, improving dye uptake by substrates leading to near zero discharge levels with ultrasound in leather dyeing process in detail [4–9] as in-plant control measure rather than end of pipe treatment. Influence of ultrasound in leather processing has been analysed and reviewed in detail as eco-friendly methodology [4]. Our recent paper analyses sono-leather technology as a green method of activation in leather processing [10]. However, growing environmental concern with regard to synthetic dyes, natural dyes offer scope for eco-friendly way of dyeing of fibrous materials such as textiles or leather and for food coloration.

Natural dyes are non toxic and non allergic which are very important for some sensitive applications. The process of release of potential toxic chemicals from substrates during usage attracts worldwide attention such as EU and REACH. There is a growing need for the non-toxic method of coloration for health sensitive applications such as children textile/leather garments as well as toys and for food coloration. Coloration of child garment/toys require a special attention due to the reason that kids have the habit of biting these materials which cause release of the colorant and intake leading to possible health risks. Therefore, there is a need for suitable coloring material from natural vegetation sources and efficient extraction methodology for the same.

1.1. Beetroot as a natural dye source

There is a pressing need for dyeing of fibrous substances such as leather, and textiles for some health sensitive applications. Betalain colorants extracted from red Beetroot (*Beta vulgaris*) provide a natural alternative to synthetic dyes [11]. Beetroot was selected as the topic of the present study because of the good colorant yield and the prominent peak it gave in the visible region of the spectrum for better quantitative analysis. Beetroot colorants are commercialized as juice concentrate and FDA classifies them as vegetable juices, which are commonly spray dried with maltodextrin to obtain beetroot powder [12]. Most varieties of Beetroot contain betalains-red colored cyanins and betanins and yellow colored xanthins. Cyanin represents 75–90% of total color present in beetroot. Betanin is the most prevalent betalain in red beets, which typically contain large quantities of it (e.g. 300–600 mg/kg). According to studies conducted it has been found that 100 g of raw beetroot contain 87.1 g of water, 7.6 g of carbohydrate, 1.7 g of protein and 0.1 g of fat [13]. Betalain, natural food colorant is associated with the antioxidant, antiviral and antimicrobial activities [12]. Therefore, beetroot dye is associated with nutrient value along with non-toxic nature suitable for dyeing application where health aspect is a prime criterion. Beetroot (*B. vulgaris*) is one of the richest sources of betanin and used for imparting a desirable red color. Unlike the synthetic dyes, these beetroot based natural dyes are eco-friendly and pose no environmental problems.

Extraction of coloring matter from beetroot is a solid–liquid leaching process involving mass transfer problem. Since the coloring matter is strongly bound with plant cell membranes, extraction could be better by way of some improved methods such as ultrasound. The gamma ray irradiation technique studied to improve the extraction efficiency led to possible degradation and instability of coloring matter [12]. The use of electric pulse studied for the same [14] may involve operational difficulties. Therefore, the use of power ultrasound to improve the extraction of beetroot dye and application to the substrates such as leather has been studied for the first time and reported in this paper.

1.2. Power ultrasound – sonochemistry

Ultrasound may be broadly classified according to frequency range as power ultrasound (20–100 kHz) and diagnostic ultrasound (1–10 MHz). When a liquid is irradiated by ultrasound, micro bubbles appear, grow and oscillate extremely fast and even collapse violently if the acoustic pressure is high enough. The occurrence of these collapses near a solid surface will generate micro jets and shock waves. Moreover, in the liquid phase surrounding the particles, high micro mixing will increase the heat and mass transfer and even the diffusion of species inside the pores of the solid [10,15]. Our recent studies show significant improvements in solid–liquid myrobalan tannin extraction process due to the use of ultrasound [16].

1.3. Objectives of the present study

The specific objectives of the present study include,

(i) To study the influence of ultrasound on the extraction of natural dye from beetroot compared to magnetic stirring as control process.
(ii) Study the influence of process parameters for extraction such as ultrasonic output power, time, pulse mode, and effect of the solvent system.
(iii) Scale-up possibility study with amount of beetroot as well as two-stage extraction.
(iv) Application beetroot dye extracted with ultrasound for coloration of leather as well as sheet of paper for health sensitive applications.

2. Experimental section

2.1. Experimental setup

Ultrasonic extraction experiments (US) were performed using ultrasonic probe (VCX 400, Sonics and Materials, USA, 20 kHz and 0–400 W) in a glass vessel with provisions to set required output power time and temperature [16]. Control experiments were performed with a magnetic stirrer (MS), which had provision to control the temperature.

Beetroot (*B. vulgaris*) grown in agriculture land in Southern part of India has been procured from Chennai based vegetable market and used for the experiments. Distilled water and Ethanol (AR reagent, SD fine chem. Ltd., India) have been used for the experiments.

2.2. Extraction of beet-dye with ultrasound

Freshly cut cubical beetroot pieces of 5 mm dimension were used for the experiments. Typically, 1 g of sample with 50 ml distilled water was taken in the extraction beaker. The beaker was covered using aluminium foil to prevent loss of solvent by evaporation. The ultrasonic probe was placed in the beaker with pre-selected values of time and power output. The US bath temperature was maintained at around 45 °C in order to prevent potential heat damage to the plant material. Extraction with MS was carried out at 45 °C using thermostat in the stirrer as control experiment for comparison. Hence from here onwards in this paper the term 'US' refers to ultrasonic extraction without any external heating and 'MS' refers to magnetic stirring extraction with external heating both maintained at 45 °C. Samples were taken at every 30 min and the optical density (OD) values were recorded with the help of UV–VIS spectrophotometer. After the extraction time of 3 h, yield and extraction efficiency have been calculated by gravimetric method. The extract was stored at low temperature for future reference.

All the experiments were repeated for duplicate and the average of extraction data was used in plotting the graphs. Standard error has been calculated for the data.