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# A Fast and Robust Analytical Method Based on QuEChERS Technique using UPLC- PDA for Quantification of Carcinogenic Arylamines in Consumer Goods inclusive of Leather

by

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## Abstract

Arylamines present in leather and textile products are reduced in vivo by cleavage of azo groups to form highly mutagenic and carcinogenic products that pose consumer's health risk. The major textile and leather products that are offered to consumers need to be safe. In order to ensure safety as per the global regulations, the allowed limit of carcinogenic amines in textile and leather products cannot be more than 20 mg/kg. There are several methods that have been used for extracting the azo dyes and analyzing them in textile and leather products. Most of these methods are polluting from high solvent usage, time consuming, laborious, and have lower recovery rates. In the present study QuEChERS method, (dispersive solid phase extraction-dSPE) method was utilized for extraction of carcinogenic arylamines from dyed leather and textile products. The released arylamines are extracted into acetonitrile using QuEChERS salt and analyzed by Ultra Performance Liquid Chromatography-Photo Diode Array (UPLC-PDA). The extracted product was further confirmed by Gas Chromatography-Mass Spectrometer (GC-MS). The method proposed in this study is novel as it eliminates all significant concerns associated with the official ISO-17234-1 &14362-1 test methods, such as use of solvents like tert-butyl methyl ether (MTBE) and the long duration of analysis. The sample preparation time is minimized from 120 min to 20 min. The developed method is easy to adopt with efficient recovery rate of arylamines in comparison to the official ISO method.

## Introduction

Azo dyes are the primary class of dyes, which find extensive usage in various products like food, garments, cosmetics, drugs, leather and toys. Arylamines are chemically synthesized and find extensive usage in pesticides, fungicides, explosives, adhesives and hair dyes. Arylamines are generated from azo dyes by azo reduction (bioreduction) in skin, intestine, environment by many of the microbes. Azo reductase present in human skin converts the azo dyes.[1-4] Most of the arylamines are considered carcinogenic, mutagenic or known to induce malformations in the human body. The European Union regulation has identified 24 different arylamines, which are extremely dangerous for human health. These are banned by EU regulation authority.[5-8] The hazardous nature of these arylamines has already been reported.[1-4]

Various studies have been carried out for determining arylamines in leather and textiles,[9-15] dyes,[16] toys,[17] water[18] and food.[19-20] The separation and estimation of arylamines is routinely performed by using High Performance Liquid Chromatography (HPLC) with a wide variety of detectors which include UV,[15,18] DAD,[13,16,17,21] electrochemical detectors[22] and mass spectroscopic techniques used in both HPLC and GC.[14,19,23-25] Apart from these techniques, Capillary Electrophoresis,[20,21] UV-VIS Spectrophotometer [26] and TLC [27-29] are also used to identify the arylamines.

Several methods have been reported for the release of arylamines from dyes by the use of chemical [13,14,28] biological[16] and microwave reduction.[13] The released arylamines have been extracted by several techniques such as Liquid-liquid Extraction (LLE),[22,28,30] Supercritical Fluid Extraction (SFE),[13] Microwave-assisted Extraction (MAE)[13] and Solid-phase Extraction (SPE).[14,21-23,31,32] The standard testing procedure [33-34] for detection of arylamines is based on chemical reduction by heating the samples followed by column purification.

The dispersive SPE also known as QuEChERS[35-38] technique is commonly used in food testing for screening pesticides, antibiotics, polynuclear aromatic hydrocarbon (PAH), etc. Commonly used test methods are the unbuffered method, EN 15662, and AOAC 2007.07. The same approach has been used to extract arylamines from leather and textile matrix in the present study.

The QuEChERS method is an effective method for removal of matrix constituents. The QuEChERS method allows for preparation of samples for analysis from a wide range of compounds, as it is not analyte specific. The QuEChERS method achieves a clean matrix by eliminating numerous matrix components while ensuring the analyte enrichment. The method is highly suitable for analysis of solids, semi-solids, viscous liquid mixtures, and liquid samples. The QuEChERS method reduces the usage of hazardous solvents and thus cuts down the cost. At the same time, analyte enrichment is attained with a much better clean-up of the samples. Magnesium

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sulphate ($MgSO_4$) and sodium acetate (CH3COONa) salts increase the ionic strength of the aqueous mixture and induces phase separation with acetonitrile this is called the salting out effect**.** The salting out effect enriches analyte during the extraction procedure. The mixture is shaken in order to provide better extraction. The phase separation of the organic and aqueous phase is well achieved by centrifugation thus allowing the easy sub-sampling of the extract.

The EN ISO 17234-1[33-34] method is the standard method for analysis of azo dyes. The method utilizes MTBE, which is a hazardous solvent and a significant polluter of the environment. The methods also involve heating of arylamines to 70°C. This could result in generation of artifacts. The recovery of arylamines by official method does not exceed 25% for most of the arylamines. To address these snags a simple, rapid and effective technique for estimating arylamines from consumer goods like leather and textile matrices using dispersive SPE technique was developed. This technique was widely used for extraction of pesticides from fruits and vegetables. The present study adopts a novel approach for reduction of azo dyes. In the present method, use of MTBE is eliminated and the heating step of arylamines to 70°C is avoided. Thus, the present method avoids the formation of any artifacts. This study has reduced the extraction process time to 20 minutes. The developed method thus helps in ensuring the integrity and recovery of the analytes and eliminating any matrix interference during extraction. This is a much easier method than the previously proposed SPE method.[39]

## Experimental

### Chemicals and reagents

The various arylamine compounds, which were used as reference for the study, were obtained from Sigma - Aldrich Corporation, St. Louis, MO, USA. The list of arylamine reference compounds obtained include 4-aminobiphenyl, benzidine, 4-chloro-o-Toluidine, 2-naphthylamine, p-chloraniline, 2,4-diaminoanisol, 4,4'–diaminodiphenylmethane, 3,3'-dichlorbenzidine,3,3'-dimethoxybenzidine,3,3'-dimethylbenzidine, 3,3'-dimethyl-4,4'- diaminodiphenylmethane, p-cresidine, 4,4'-methylen-bis-(2-chloraniline), 4,4'-oxydianiline, 4,4'-o-toluidine, 2,4-toluylendiamine, 2,4,5-trimethylaniline, o-anisidine, 2,4-xylidine, 2,6-xylidine and p-phenylenediamine and clean-up materials of Supelclean LC-18, particle size-45 µm (C18 SPE). Another reference material 4,4'-thiodianiline was procured from Acros organics, Geel, Belgium. Analytical grade sodium dithionite was procured from Merck KGaA, Frankfurter Str, Darmstadt, Germany. Analytical grade magnesium sulphate, sodium acetate, sodium chloride (NaCl), sodium hydroxide, citric acid, ammonia and HPLC grade acetonitrile were procured from Avantor Performance Materials, Thane, Maharashtra, India. Tert-butyl methyl ether was procured from Merck Life science, Vikholi (East), Mumbai, India

### Instrumentation

Ultra-Pressure Liquid Chromatography- Photo Diode Array (UPLC-PDA) used for analysis was procured from Waters Corporation, Milford, Massachusetts, USA. The instrument was equipped with AQUITY 'H'class quaternary solvent manager, AQUITY – FTN sample manager and an AQUITY eλPDA detector. Raw data from the instrument was analyzed using the Empower 3 software version 3.0 from Waters Corporation, Milford, Massachusetts, USA. Purospher STAR RP18e column was used to separate arylamines. The column included an integrated guard column with dimensions of 125 mm x 3 mm, particle-size of 5.0-micron. The column was purchased from Merck KGaA, Frankfurter Str, Darmstadt, Germany. Water used for Mobile-phase and other applications was produced in the laboratory using Type I grade water purifier. The water purifier was a Flex 3 model purchased from ELGA, Lane End, High Wycombe, U.K. The Gas chromatography-Mass spectrometric (GC-MS) operations were performed using Agilent Technologies, Stevens Creek Blvd, Santa Clara, United States. The GC model used was 7890A equipped with 7823B auto sampler and MS model used was 5975 C. DB -5MS analytical column was used for various operations. The dimensions of the column were 30 m × 0.25 mm with a film thickness of 0.25 µm. The carrier gas used for the study was helium which was 99.99% pure and pumped at a rate of 1 mL $min^{-1}$. Ultrasonication was performed using Ultrasonicator Model LBS2-10 purchased form FALC Instruments, G. M. Compagnoni, Treviglio BG, Italy. The operating temperature of the instrument was up to 50˚C with operating frequencies of 40 Hz and 60 Hz. Centrifuge model Z366 from Hermle Labortechnik, Siemensstraße, Wehingen, Germany was used for various centrifugation operations. Sample grinding was done using a mill obtained from Fritsch, Idar-Oberstein, Germany. PTFE filter was procured from Pall Corporation Port Washington, NY, USA.

### List of banned arylamines

A complete list of banned arylamines includes 4-aminobiphenyl (ABP), benzidine(BEN),4-chloro-o-toluidine(COT),2-naphthylamine(NAP), 2,4-toluylendiamine (DAT), O-aminoazotoluene and 2-amino-4-nitrotoluene are further reduced to OTD or DAT, p-chloraniline (PCA), 2,4-diaminoanisol (DAA), 4,4-diaminodiphenylmethane (DDM), 3,3'-dichlorbenzidine (DCB), 3,3'-dimethoxybenzidine (DOB), 3,3'-dimethylbenzidine (DMB), 3,3'-dimethyl-4,4'-diaminodiphenylmethane (DDD), p-cresidine (KRE), 4,4'-methylen-bis-(2-chloraniline) (MOCA), 4,4'-oxydianiline (DDE), 4,4'-thiodianiline (TDA), o-toluidine (OTD), 2,4,5-trimethylaniline (TMA), o-anisidine (MOA), 2,4-xylidine (24XD), 2,6-xylidine (26XD), 4-aminoazobenzene is converted to p-phenylenediamine (PPDA) and aniline(ANI).

### Preparation of reference standard for analysis

The various banned arylamines were used as reference standards. Stock of 1000 µg/ml was prepared for each amine in acetonitrile. The twenty-four banned arylamines were grouped as four different mixes using acetonitrile. The concentration of each arylamine in the mix was 15 µg/ml. These mixes were used as reference standards in UPLC-PDA. However, for GC-MS 5 µg/ml of reference standard was injected to confirm arylamine detected in the sample.

**The official procedure, ISO 17234-1 and ISO 14362-1 for extraction of arylamines**

Leather and natural textile samples were ground using a laboratory mill such that the final particle size was 100 to 200 microns. For samples that could not be ground to such a small size, they were cut into small pieces of approx. 1 to 2 mm. One gram of leather or textile samples were weighed and were degreased with about 20 ml of hexane using an ultrasonic bath at 40˚C for 20 min with frequency of 40 Hz. After repeating the degreasing step once again, the sample was left to dry in air overnight. Textile samples are directly taken for extraction. The sample was then transferred to a 50 ml amber-colored glass bottle with a tight closure bearing a silicone septum at the top. A quantity of 17 ml of 0.06 M Citric acid buffer (pH 6.0) was added to the bottle and the contents were heated to 70°C over a sand bath in a hot air oven. Once the temperature was stable, 1.5 ml of aqueous sodium dithionite (200 mg/ml) was added to the bottle using a syringe and kept at 70°C for 10 min. Another 1.5 ml was added similarly and maintained at 70°C temperature for 10 more minutes. Then the contents were cooled to room temperature within two min using running water.

The reaction solution was decanted on an Extrelut column. The column was made of diatomaceous earth. The absorption step was performed for 15 min. To the residual mixture in the bottle 5 ml of MTBE and 1ml of 20% methanolic NaOH was added. The mixture was shaken vigorously, and the solution was transferred to the Extrelut column. The residual mixture in the reaction bottle was washed using 15 ml of MTBE following an additional wash with 20 ml of MTBE. The contents were transferred to the Extrelut column to start eluting the amines. Afterward, 40 ml of MTBE was flushed on the column directly. The eluate was collected in a 100 ml rotary evaporator flask. The ether extract was concentrated to 1 ml by rotary vacuum evaporator using low vacuum at a temperature not more than 50°C. The remaining ether was evaporated to dryness by an inert gas like Nitrogen. Immediately the residue was dissolved with methanol and volume made up in a 2 ml volumetric flask. This solution was filtered through a 0.2 µm PTFE filter for further chromatography analysis.

In case of man-made textile due to the presence of disperse dye, the arylamines were extracted with xylene. After extraction, xylene was evaporated, and the residue was further processed as explained above.

## Chromatographic Condition

**UPLC-PDA condition followed for the arylamine separation**

Water (pH 8, adjusted with ammonia) and acetonitrile were used as mobile phases to separate the arylamines with the following gradient program: The system's total flow rate was 0.5 ml per minute. Gradient at 60% of water and minimised down to 20% in 5 min, further minimised to 0% at 5.5 min, then increased to 60% in 6 min, held for 8 min equilibration. The injection volume of the sample was 1 µl. The detector›s wavelength range used for collecting the spectrum of analytes was 220 nm to 400 nm. The chromatograms collected at 230 nm, 280 nm and 305 nm.

**GC-MS condition followed for the arylamine confirmation**

The temperature programme for GC was as follows: initial temperature, 70°C held for 2 min, linearity to 280°C at 10°C/min, held for 7 min. The injector temperature was 250°C, and injection of 1 µL sample was performed in split less mode. The interphase between GC and MS was maintained at 280°C. The quadrupole and source temperature were maintained at 230°C and 250°C respectively. The analyte was analyzed on the GC-MS in the full scan mode; quantification was carried out by Selective Ion Monitoring (SIM) mode using specific ions as shown in Table I. Mass spectra were obtained in electron impact mode (70eV) in the range between 45 and 300 m/z. The total GC-MS analysis time was about 30 min.

**Table I**

**The list of specific mass ions (SIM) of arylamines for GCMS analysis**

| Arylamines | SIM (amu) | Arylamines | SIM (amu) |
|---|---|---|---|
| 4-aminobiphenyl | 169 | p-cresidine | 122 |
| Benzidine | 184 | 4,4'-methylene-bis-(2-chloroaniline) | 231 |
| 4-chloro-toluidine | 141 | 4,4'-oxydianiline | 200 |
| 2-naphthylamine | 143 | 4,4'-thiodianiline | 216 |
| o-aminoazotoluene[a] | 225 | o-toluidine | 106 |
| 4-nitro-toluidine[a] | 152 | 4-methyl-m-phenylenediamine | 121 |
| 4-chloroaniline | 127 | 2,4,5-trimethylanilne | 120 |
| 4-methoxy-m-phenylenediamine | 123 | o-anisidine | 108 |
| 4,4'-diaminodiphenylmethane | 198 | 4-aminoazobenzene | 92 |
| 3,3'-dichlorobenzidine | 252 | 2,4-xylidine | 121 |
| 3,3'-dimethoxybenzidine | 244 | 2,6-xylidine | 121 |
| 3,3'-dimethylbenzidine | 212 | 1,4-phenylenediamine | 108 |
| 4,4'-methylenedi-o-toluidine | 226 | Aniline | 93 |

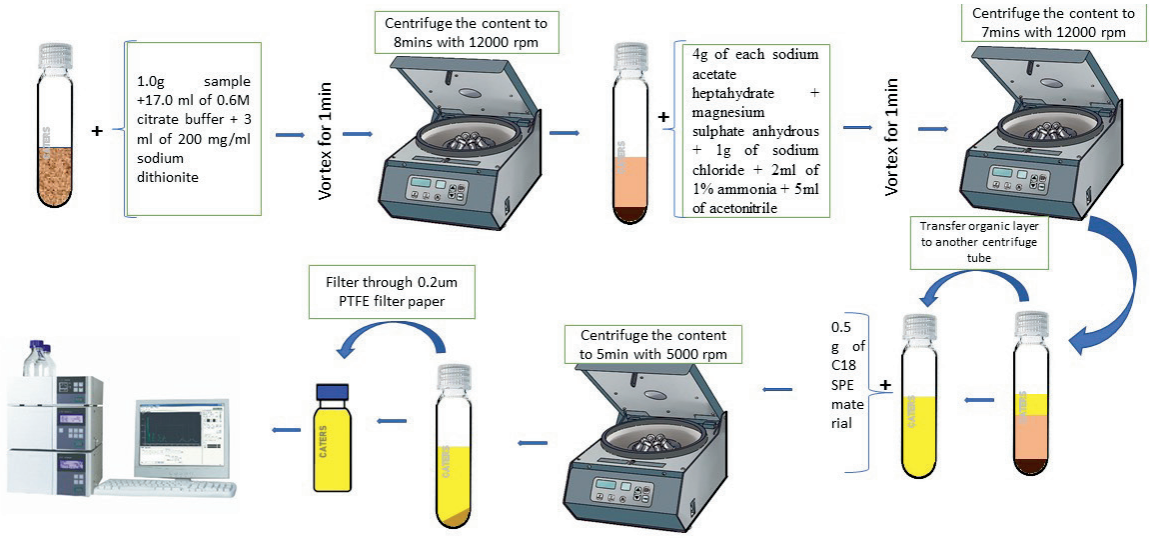


**Figure 1.** Schematic diagram of proposed method

**Sample preparation of the proposed QuEChERS method**

The initial sample was cut into small size of about 2 to 3 square mm. As directed in the official method, leather samples were degreased while textile sample were proceeded with as such. One gram of sample was weighed into a 50ml centrifuge tube with a lid. To the tube 17.0 ml of 0.6 M citrate buffer, 600 mg of sodium dithionite was added. The mixture was vortexed for 1 min and centrifuged for 8 min at 12,000 rpm. Then 4 g each of CH3COONa and $MgSO_4$, 1 g of NaCl, 2 ml of 1% ammonia, along with 5 ml of acetonitrile were added and lid closed. The tube with contents was vortexed for 1 min. The contents were centrifuged at 12,000 rpm for 7 min. Then, the top acetonitrile layer was transferred to another centrifuge tube with 0.5 g of $MgSO_4$ and 0.5 g of clean-up C18 SPE materials. Centrifugation was done at 5000 rpm for 5 min, and then the organic layer (acetonitrile) was collected and filtered through a 0.2 µm PTFE filter. The filtrate was subjected to chromatography analysis. For man-made textiles, the sample was extracted with xylene and after evaporation of the residue it was further processed using the proposed method (Figure 1).

## Results and Discussion

**In-situ reduction**

It is the first ever study for the reduction of dyes by chemical means under room temperature conditions with help of centrifugal force. When hot condition reduction of dyes is done the release of unrealistic, and artifacts of chemical compounds are suspected. Whereas the ambient reduction is close to realistic release.

**QuEChERS for analysis of arylamines**

Magnesium sulphate concentration when varied from 4g to 6g, it was observed that the recovery of arylamines varied from 45% to 60%. In case of highly polar analytes such as PPDA and DAA resulted in a lowered recovery of 19.9% and 24.8%. Hence, it was planned to increase the ionic strength by adding CH3COONa at varying concentrations from 1 g to 4 g, to increase recovery of arylamines. The recovery of arylamines improved in the range of 90% to 106% (Figure 2) when 4 g of MgSO4 and 4 g of CH3COONa were used at pH 8.0 to 9.0. Magnesium sulphate and sodium acetate were used for liquid-liquid extraction of arylamines in the solvent system of acetonitrile and water. Sodium chloride was added to increase the ionic strength further and mainly to serve as emulsion breaker if any. The C18 SPE materials was added in the system to remove fatty compounds, sterols, and other non-polar interferences like hydrophobic compounds. In order to further refine the study, the effect pH on the extraction of analytes was assessed.

**Effect of pH on recovery of arylamines**

For further study, eight arylamines were identified in the range of highly polar to nonpolar. These include PPDA, DAT, BEN, DDM, PCA, DDD, 4ABP and DCB. At pH below 6.0, which is acidic in nature, arylamines form ionic ammonium salts. The ammonium salts have a low solubility in organic solvents. The phase transfer of ionic forms of these analytes to acetonitrile from an aqueous solution becomes difficult. This affects the recovery rate of arylamines as recoveries were found to be less than 60%. At pH 8-9 which is alkaline in nature, the arylamines are neutral. This facilitates the transfer of arylamines from the aqueous phase to the organic phase. The recovery of all the analytes improved to be more than 80% at this alkaline pH. (Figure 3).

**Optimization of Centrifugal speed for extraction and recovery of arylamines**

The centrifugal force plays a vital role in transferring arylamines from the aqueous layer to the organic layer. An intricate study to

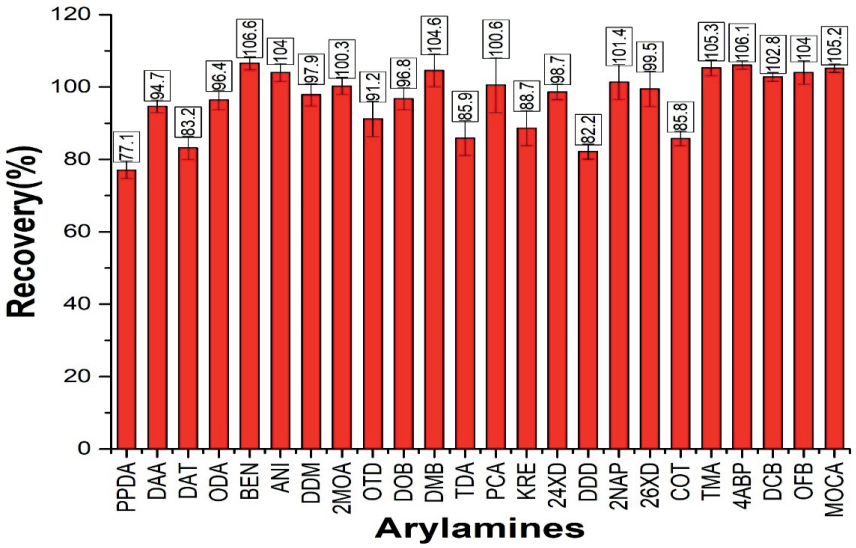


**Figure 2.** Recovery of complete arylamines

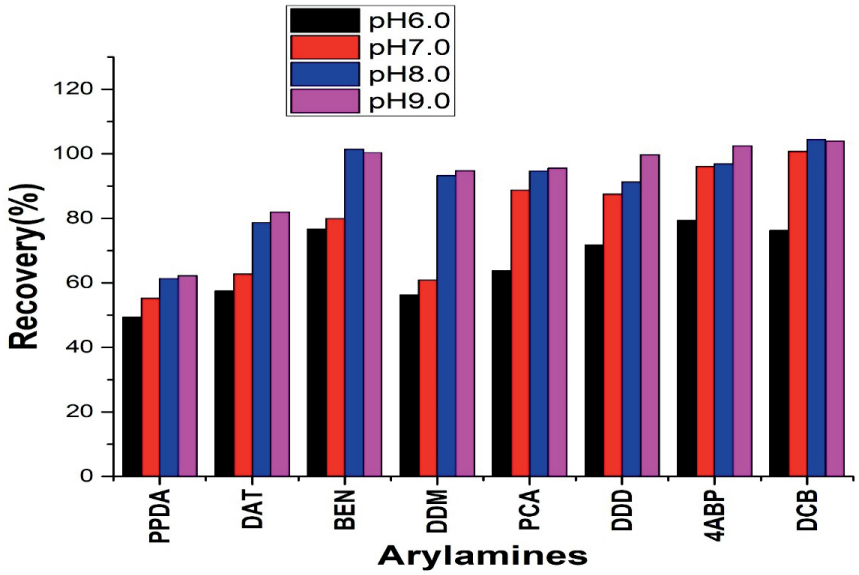


**Figure 3.** Recovery of arylamines by various pH

monitor its influence on the recovery rate at varying speeds was done. Centrifugal speed was varied from 5000 rpm to 12,000 rpm. At 5000 rpm, the effective transfer of arylamines was less because the recoveries of many arylamines were less than 60%. But at 12,000 rpm, the recoveries were more than 90%. When the speed of centrifugation was increased above 12,000 rpm it did not show any considerable further change in the recovery of arylamines. (Figure 4). The enhanced recovery at higher speeds is mainly associated with effective separation of the organic layer which helps in better recovery of the analyte.

**Optimization of centrifugal time for extraction and recovery of arylamines**

This study focused on the optimal time required for the centrifugal force to accelerate the transfer of arylamines from the aqueous to organic layer at 12,000 rpm. Centrifugation for shorter durations such as 5 minutes resulted in lower recovery rates of 14% to 68%. However, when centrifugation was done for 15 to 20 minutes the recovery rates were found to be 80% to 104%. (Figure 5). Longer periods of centrifugation enhanced the extraction of arylamines into the acetonitrile phase resulting in better recoveries of all the analytes.

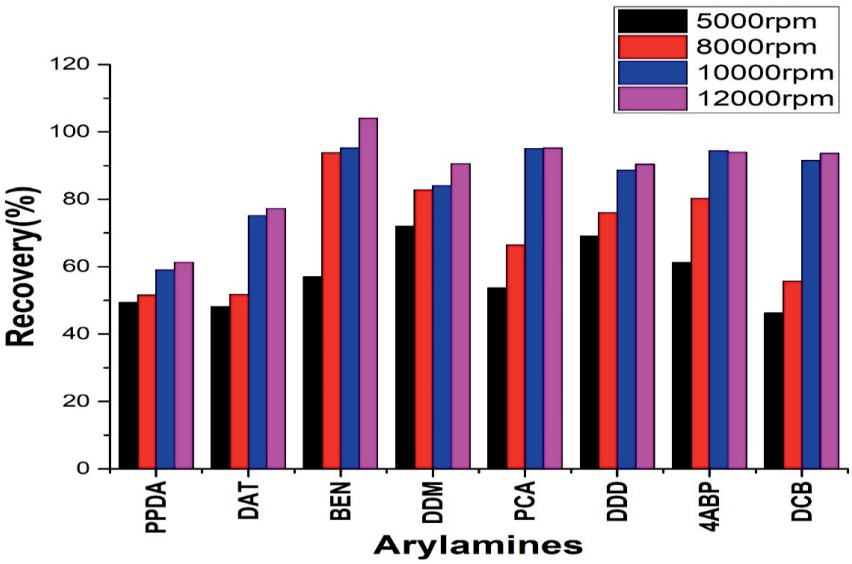


**Figure 4.** Recovery of arylamines by various centrifugal speed

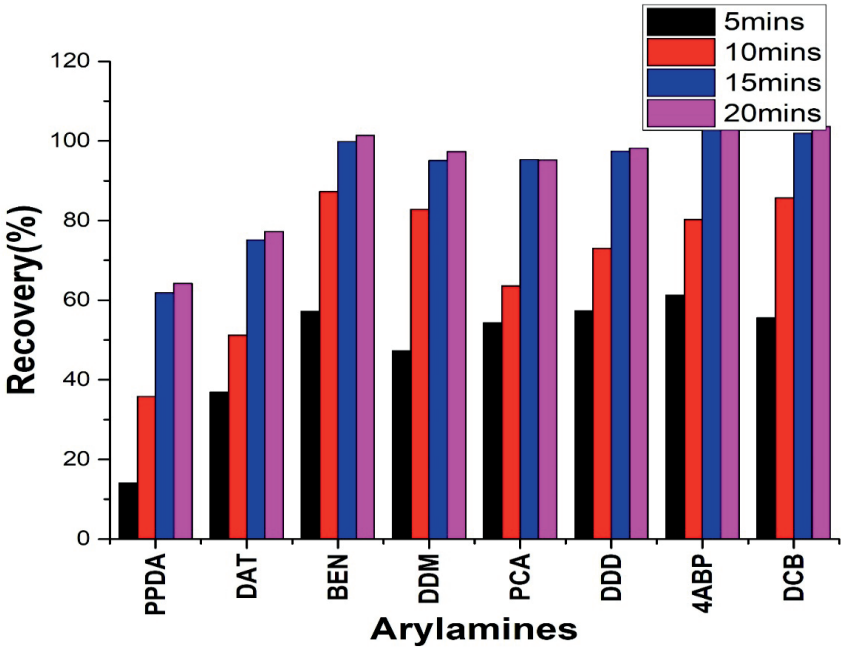


**Figure 5.** Recovery of arylamines by various centrifugal time

**Validation of the method**

The performance characteristics of the method such as Limit of Detection (LOD), Limit of Quantification (LOQ), Linearity, Accuracy, Method precision, Reproducibility and Robustness were studied. LOD of the proposed method was found to be between 1.2 to 2.0 ppm for all arylamines. LOD was determined by injecting the analyte at 10 times lower concentration than normal. Based on the values obtained from the experiment the standard deviation was calculated. LOD was determined by multiplying the standard deviation by 3. LOQ was determined by multiplying the standard deviation by 5. LOQ of the method for all arylamines varied from 2.0 to 3.4 ppm. Linearity ranging from 1 to 15 ppm for 24 arylamines mixture was performed. The experiment showed a correlation coefficient ($R^2$) ranging from 0.9914 to 0.9997. Accuracy of the method was measured with the matrix blanks or test samples un-spiked and spiked with the analyte of interest over a range of concentrations. Each level of concentration (i.e. 30% of LOQ, 100% of LOQ and 150% of LOQ) was injected three times. The difference between mean spiked value X and mean value XI with the added concentration X spike was compared. The relative spike recoveries for accuracy and precision at various concentrations i.e., 30% LOQ, 100% LOQ and 150% of LOQ were calculated.

Acceptance criterion for accuracy was within the range of 80-120% and precision was within range of ≤ 20.0%. The robustness of the method was within range of ≤ 20.0% (Table II).

**Table II**

**Method validation data for proposed method**

| Parameter | | Arylamines | Acceptance criteria |
|---|---|---|---|
| LOD | ppm | 0.4 – 0.6 | — |
| LOQ | ppm | 0.7 – 0.9 | — |
| LINEARITY | $R^2$ | 0.9914 -0.9997 | ≤ 0.990 |
| ACCURACY 30% LESS LOQ | Recovery (%) | 81.1 – 101.1 | 80 – 120% |
| ACCURACY 100% LOQ | | 92.0 – 101.3 | 80 - 120% |
| ACCURACY 150% LOQ | | 91.6 – 100.7 | 80 – 120% |
| PRECISION 30% LESS LOQ | RSD (%) | 4.3 – 9.6 | ≤ 20.0% |
| PRECISION 100% LOQ | | 4.3 – 8.5 | ≤ 20.0% |
| PRECISION 150% LOQ | | 3.9 – 10.6 | ≤ 20.0% |
| METHOD PRECISION | | 3.7 – 8.9 | ≤ 20.0% |
| ROBUSTNESS | | 3.7 – 8.9 | ≤ 20.0% |

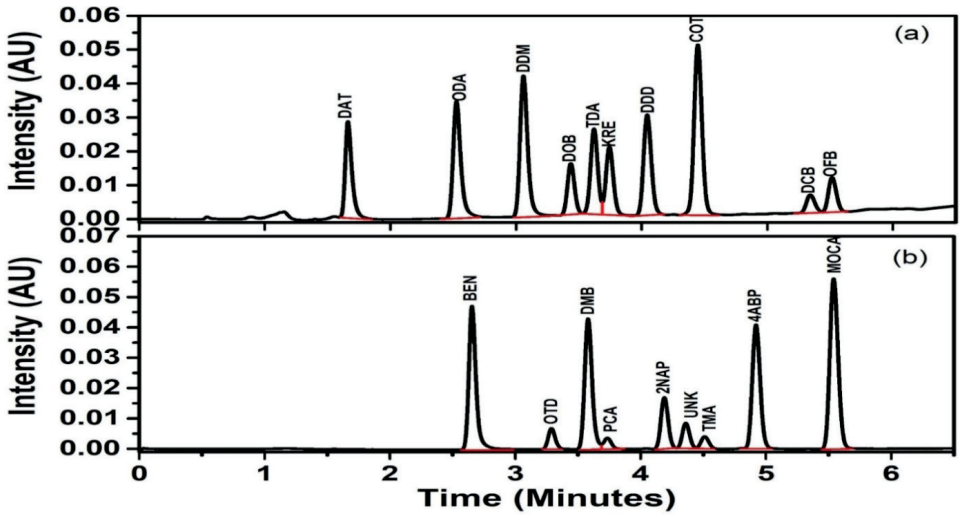


**Figure 6.** Chromatogram for arylamines reference standards **(a)** MIX-1 **(b)** MIX-2

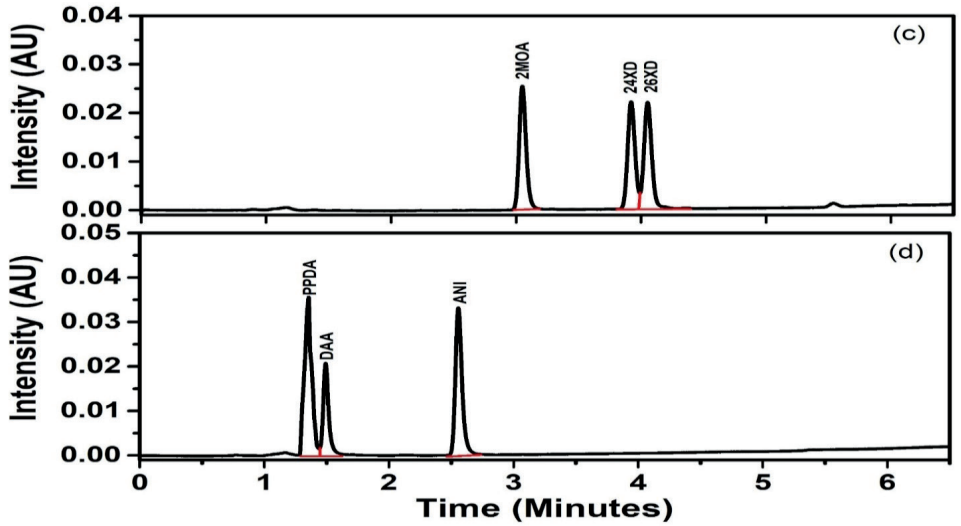


**Figure 7.** Chromatogram for arylamines reference standards **(c)** MIX-3 **(d)** MIX-4

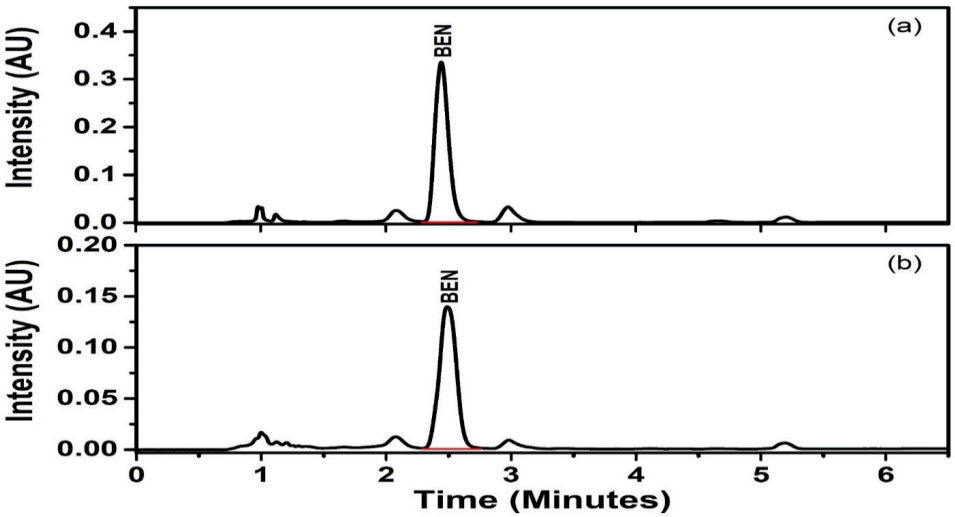


**Figure 8.** Chromatogram for real samples analysed in both **(a)** Official method **(b)** Proposed method for comparison.

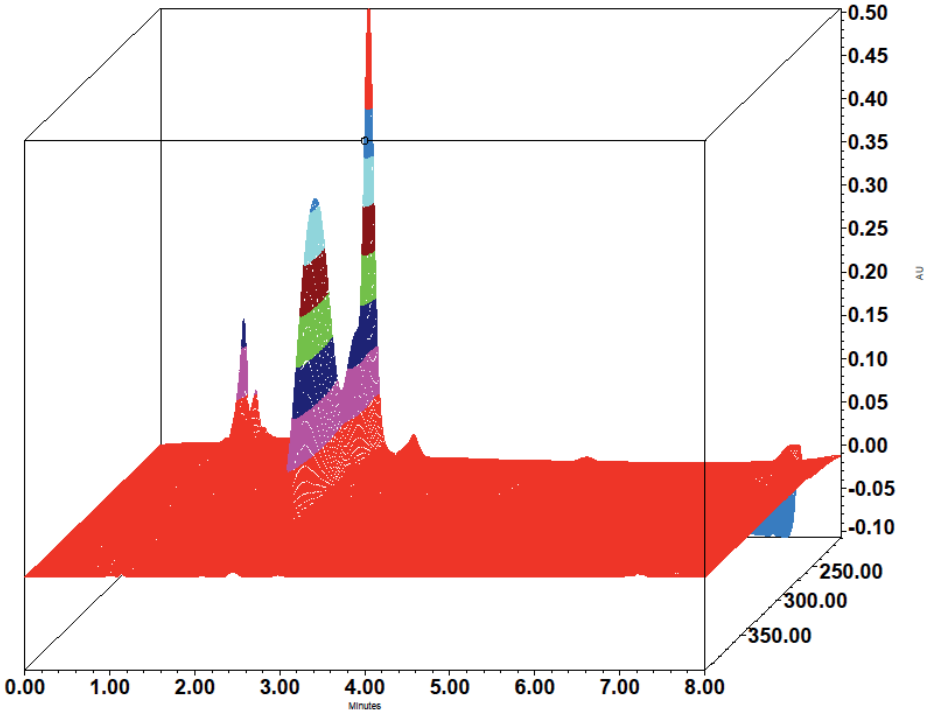


**Figure 9.** 3D spectral view of the real time sample analysis in PDA

**Analysis of Real samples**

Several leather, textile and dye samples were screened by the proposed method UPLC-PDA (Figure 6, 7, 8 & 9) and further confirmed by GC-MS technique (Figure 10). Samples of leather, textile and dye, which were originally found to contain the banned arylamines benzidine (by the official protocol), were chosen for the comparison with the proposed method. Benzidine %RSD found in leather, textile and dye in the proposed method is shown in Table III. The %RSD obtained from benzidine by the proposed method was found to be well within the acceptable limits.

## Discussion

QuEChERS method was primarily developed for detection of pesticides in food materials. The method is simple and easy to adapt. This proposed method has minimised solvent usage and is a green analytical method for arylamines. Although earlier, a SPE method was reported[39] with much improved recoveries for most of the arylamines in the banned list, that method claimed to be successful and used the same reduction of azo dyes at hot condition as that of the official method. Compared to that study, present approach

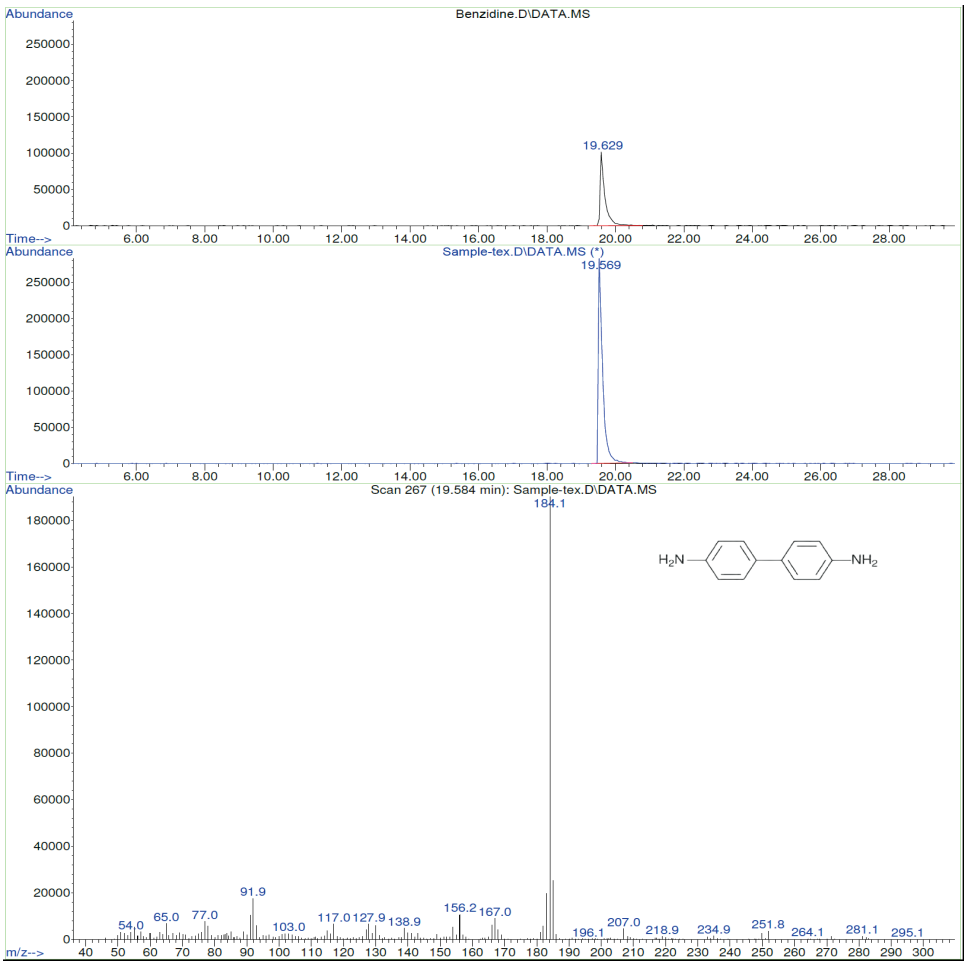


**Figure 10.** Chromatogram and mass spectrum for real time sample analysis in GCMS

**Table III**

**Real sample analysis data for leather, textile and dyes by the proposed method with RSD**

| Material | Benzidine (mg/kg) | | RSD (%) |
|---|---|---|---|
| | Official method | Proposed method | |
| Leather | 126.4 | 128.4 | 5.3 |
| Textiles | 613.3 | 642.6 | 3.8 |
| Dye | 2161.4 | 2160.7 | 2.7 |

followed a reduction step in ambient condition and secondly the solvent extraction is almost simultaneous along with the release of the arylamines. Many of these arylamines are suspected to be unstable and lost especially when the procedure steps are long and spaced with long intervals for successive steps. The proposed work is also greener approach as use of MTBE from 80 ml in the official method is completely eliminated. This proposed procedure is very speedy, requiring only 20 minutes versus 180 minutes for the official method. More importantly, all the analyte recoveries improved in the range 80% to 108% while the official method claimed recoveries from 20% to 70%.

## Conclusion

This proposed method is considered to substitute all tedious parts of the analysis namely the exchange of the analytes into a solvent layer. A great enrichment of the analytes by introducing the QuEChERS method was observed with matrices of samples found to be cleaner as observed from those cases of long official procedures involving multiple steps in its approach. The solvent reduction happened from 80 ml to 5 ml. Multiple steps were consolidated into two short simple steps, which helped to gain time in sample preparation alongside minimization of transfer loss from

considerable change over the vessels. This proposed procedure for arylamines can determine the range of 7-2500 mg/kg of consumer goods comprising leather, textile and dye /pigments. This proposed method ensured a greener approach, ensures good recoveries (80% to 108%), ambient reduction for releasing arylamines, relatively speedy approach for sample preparation (from 180 minutes to 20 minutes) along with advantage of cutting out the transfer loss as proceeded with only 2 vessels.

## Acknowledgement

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# Root Cause Analysis of Color Migration in Footwear: A Case Study

by

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## Abstract

The phenomena of migration and/or bleeding of colorants are one of the major concerns for the footwear and leather goods industries. The migration/bleeding of the colorants from one component to the other has been observed in many cases that spoil the aesthetics of the product, which in turn leads to economic loss for the industries. In this research article, a typical case of color migration in leather footwear has been studied in depth for root-cause analysis of the migration problem. The leather used in the shoe upper (affected due to migration), the lining fabric, and the adhesive used in making the footwear were characterized by microscopic and spectroscopic techniques. The FTIR-ATR study revealed that the leather was finished with polyurethane-based coating, the lining fabric used was an aromatic polyester and the adhesive was natural rubber-based adhesive. Though the lining fabric was colorfast to rubbing, it released color in all the organic solvents generally used in natural rubber-based adhesive. Migration studies showed that migration of the colorant (black) from the lining material to the leather (white) happened only in the presence of the adhesive. In conclusion, the organic solvent present in the adhesive used in making the footwear was responsible for the color migration from the lining material to the attached leather. Finally, recommendations have also been made to avoid such problems of color migration in products made from a variety of multiple fabrics.

## Introduction

The phenomena of migration and/or bleeding of chemicals and colorants are one of the major concerns for the consumer products such as garments, shoes, bags, etc.[1,2] The migration of colorants spoils the aesthetics of the products and therefore faces rejection, which in turn leads to economic loss for the industries.

Footwear and leather goods are such industries that often face the problem of migration and/or bleeding of chemicals[3–5] and colorants[6–8] from one component to the other damaging the physical-mechanical properties and aesthetics of the product. Leather goods are made with leather along with synthetic (polymeric)/ natural (textile) fabrics, adhesives, threads, etc. The migration of dyes, chemicals, residual solvents, and even fatty matter, from one component to another affects the product quality.[7] These chemicals from any of the components of the product may migrate to the adjacent component and sometimes crosses the adjacent component to reach the next component affecting the product quality. This may also lead to false positive or false negative results specifically for restricted chemicals (phthalates, azo dyes) when tested individually in various components of the product. The presence of solvent-soluble matters including adhesives, and environmental conditions like elevated temperature and humidity, are the essential accelerators of migration.[9–11] In a recent research report by Mandal et al., (2022), the migration of phthalate from PVC sole to the leather insole under various environmental conditions has been shown experimentally.[5] Most of the reported literature in this area talks about the problem of migration and its impact on the product. However, very few research reports are available on the migration issues in leather goods and leather-based footwear.

In this typical case of color migration in footwear, the white finished leather used in the "tongue" of the footwear exhibited a bluish stain from the black colored lining. The colorant used in the lining was migrated to the attached leather (white finish) spoiling the aesthetics of the whole footwear. The primary objective of the present study was to understand the root cause of the migration of the colorant in order to find its solution. The present article describes a systematic study of the physicochemical characteristics of the materials used in making the footwear through spectroscopic and microscopic techniques. To study the migration/bleeding and to understand the root cause of migration, experiments were performed under various chemical and environmental conditions.

## Experimental

### Materials

The leather, lining fabric, and adhesive used in making the original product (the case) were provided for the study by the same industry that faced the problem of color migration in footwear. Figure 1a shows the section of the footwear affected by the migration of colorant, and the fresh samples of the leather and the lining fabric are presented in Figures 1b and 1c. Standard cotton lawn (rubbing)

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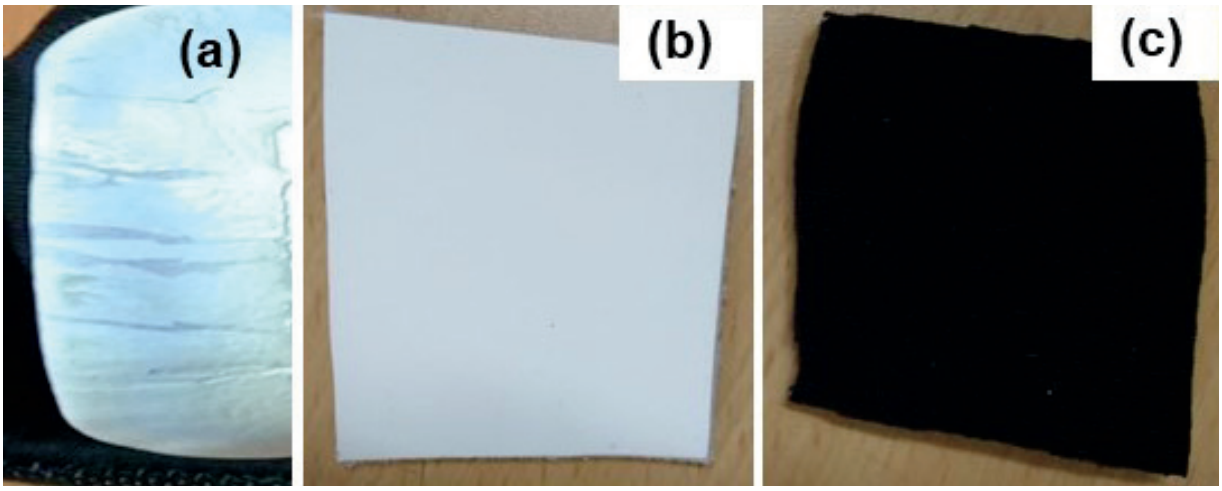


**Figure 1. (a)** Part of the footwear showing migration of the colorant from the lining material to the white finished leather, and fresh samples of **(b)** the finished leather (white), and **(c)** the lining fabric (black).

fabric (5 cm × 5 cm) complies with ISO 105-F09 was obtained from SDC Enterprises, UK. Standard white pigmented plasticized poly(vinyl chloride) (PVC) sheet (50 mm × 30 mm) complies with ISO150701 / IUF 442 was obtained from James Heal, UK. Solvents used in natural rubber-based adhesive namely, ethyl acetate, toluene, dichloromethane (DCM), tetrahydrofuran (THF), methyl ethyl ketone (MEK), cyclohexane, and acetone[12] were laboratory grade chemicals from Merck, India.

**Characterization techniques**

Microscopic images of the leather after removing the coating/finishing were captured using a modular stereo microscope model: DZ.5040 from Euromex, Holland. FTIR spectra of the samples were recorded in ATR mode using 4700 ATR-FTIR spectrometer, JASCO, Japan.

The lining material was tested for colorfastness to rubbing by following the test method SATRA TM 167:2017[13] (SATRA TM 167:2017, Color fastness to rubbing – Crockmeter test, SATRA Technology Centre, UK). Here, the test sample was rubbed against a standard cotton lawn in a crock meter (10 times) in dry and wet conditions. After rubbing, the test sample and standard rubbing fabric (cotton lawn) were graded as per grey scale rating on a scale of 1-5. Test for colorfastness to migration was performed by following the standard test method ISO 15701 IULTCS/IUF 442 (Leather — Tests for color fastness - Color fastness to migration into polymeric material).[14] The primary materials used in making the migration-affected section of the footwear were the leather (white finished), the lining fabric (black), and the adhesive. The experiment for colorfastness to migration was performed with the above-mentioned three materials and with the standard PVC sheet (complies with ISO 150701 / IUF 442). The leather, lining fabric, and the PVC sheet were cut into pieces of dimension 3 × 10 cm. The lining fabric was attached to the leather/PVC sheet with and without the adhesive and kept under controlled temperatures (28±2 and 50±2 °C). The color migration was visually assessed after 2 hours. The color bleeding test of the lining fabric was performed by adding 0.2 g (cut pieces of dimension 2-5 mm) of the lining fabric in 5 ml of the solvent taken in a glass test tube and stirring with a vortex mixer of 2 minutes. The UV-Visible spectra of the solution of the colorant from the lining fabric in various solvents were recorded using UV-visible spectrophotometer, model Cary 300, from Agilent Technologies, USA.

## Results and discussion

**Microscopic and FTIR-ATR study**

The microscopic images of the grain side and cross-section of the leather sample after removing the finishing layer are presented in Figure 2. The microscopic image (Fig. 2a) shows the characteristic grain pattern of cow origin leather.[15] The cross section of the leather sample (Fig. 2b) shows that it is made of closely packed fibrous collagen.

The FTIR-ATR spectra of the leather sample before and after removing the coating/finishing layer, lining fabric, and the adhesive are presented in Figure 3a-d. The FTIR-ATR spectrum of the finished leather sample shows all the peaks corresponding to the water-based polyurethane coating (Figure 3a). The characteristic –NH bond stretching and bending vibrations corresponding to the urethane linkage of the PU are observed at 3325.6 and 1529.3 $cm^{-1}$, respectively.[16] The characteristic stretching vibrations of the carbonyl (–C=O) group of the urethane linkage appear at 1727.9 $cm^{-1}$. The absorption bands between 1000-1250 $cm^{-1}$ match well with the water-based polyurethane coating.[17] The C–H symmetric and asymmetric stretching vibrations of $CH_2$ groups can be observed at 2922.6 and 2855.1 $cm^{-1}$, respectively. The absorption bands at 1459.8 $cm^{-1}$ and 1372.1 $cm^{-1}$ are due to the $CH_2$ and $CH_3$ bending vibrations.

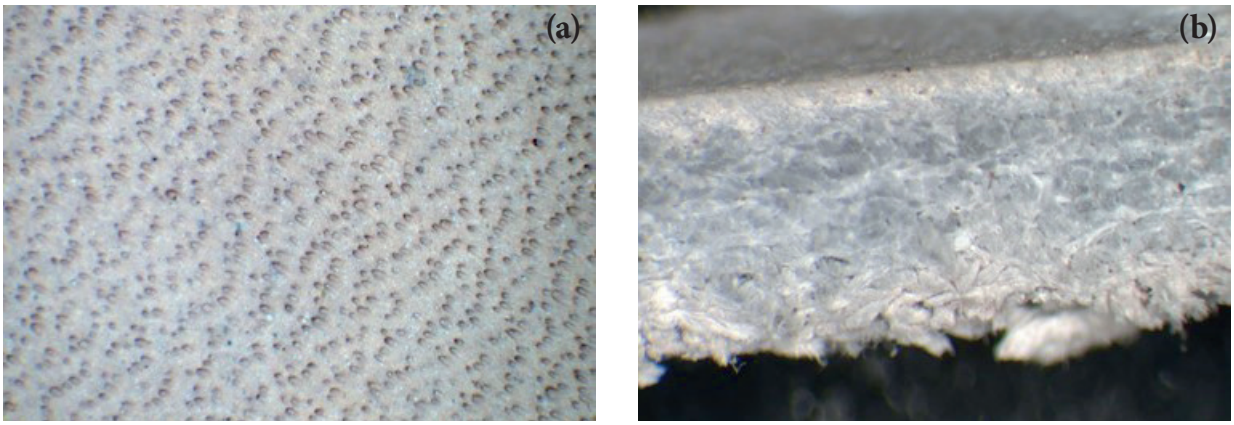


**Figure 2.** Optical microscopic images of the leather **(a)** grain pattern, 20× magnification and **(b)** cross-section, 40× magnification.

The FTIR-ATR spectrum of the unfinished leather shows distinct peaks characteristic of leather at 1635.3, 1529.3, and 1237.1 $cm^{-1}$ corresponding to the amide I, amide II, and amide III bonds of collagen structure, respectively.[18] The absorption band for amide A of collagen can be seen between 3250-3350 $cm^{-1}$ (Figure 3b).

The FTIR-ATR spectrum of the lining fabric shows that it is made of polyester (Figure 3c). The characteristics bands at 1711.5 $cm^{-1}$ can be assigned to the C=O bond of an ester group. The peaks at 1407.8, 1015.3, and 869.7 $cm^{-1}$ can be attributed to the vibration of aromatic ring.[19] The peak at 1338.3 $cm^{-1}$ is characteristic of -$CH_2$ groups bending vibration. The peaks at 1239.4 and 967.1 $cm^{-1}$ are due to the characteristic stretching vibration of C-O bond.[19] Peaks at 1463 and 1376 $cm^{-1}$ are identified as C–H bending and C–H deformation of methylene, respectively. The peak at 719 $cm^{-1}$ can be attributed to C-H bending vibrations.[20]

The FTIR-ATR spectrum of the adhesive shows that it is a natural rubber-based adhesive (Figure 3d). The characteristic absorption bands of natural rubber (polyisoprene) are observed at 2955.4, 2944.7, 2866.6, 1660.4, 1449.2, 1375 and at 838.8 $cm^{-1}$ wavenumbers.[21] The strong and sharp absorption band between 2860-2960 $cm^{-1}$ is due the C-H stretching vibrations. The absorption band at 1660.4 $cm^{-1}$ is due to the C=C bond stretching vibrations. The sharp absorption peaks at 1449.2 and 1375 $cm^{-1}$ can be attributed to $CH_2$ and $CH_3$ deformation vibrations.[22] The absorption band at 838.8 $cm^{-1}$ is due to the out of plane bending of $CH_3$ group. Additionally, the broad peak at 3270.7 $cm^{-1}$ due to -OH group indicates that the adhesive used here is hydroxy terminated natural rubber.[23]

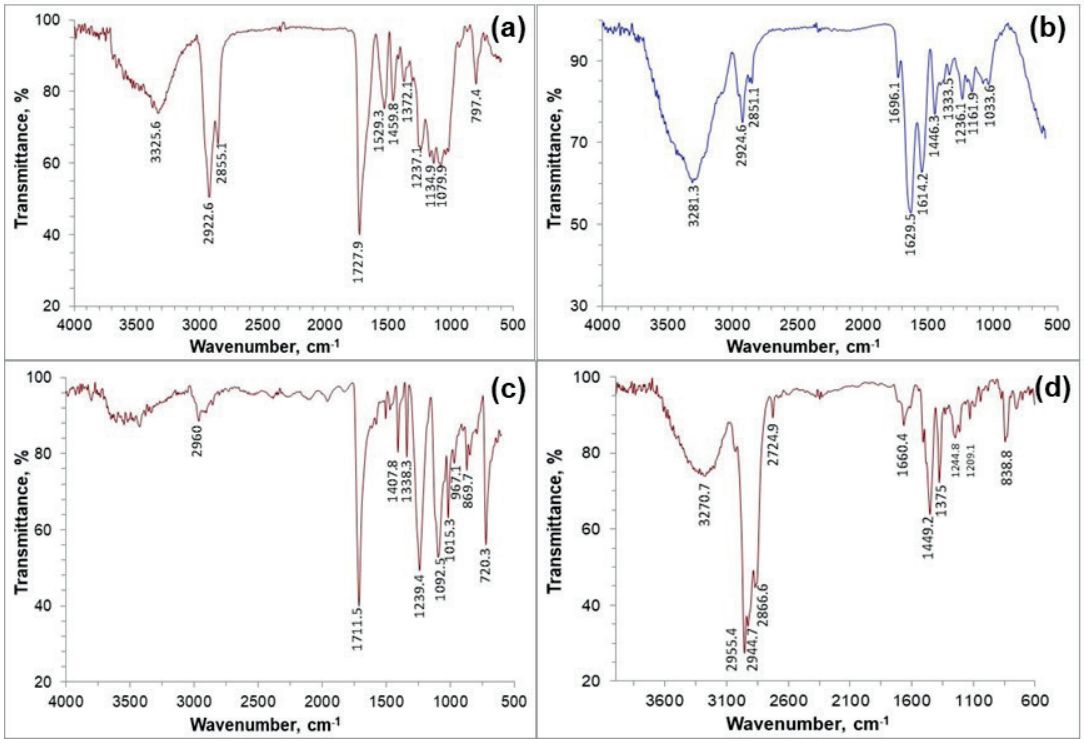


**Figure 3.** FTIR-ATR spectra of the **(a)** leather sample (as obtained), **(b)** leather sample after removing the finished layer, **(c)** lining fabric, and **(d)** adhesive.

**Table I**

**Values of grey scale rating for the lining and the standard cotton lawn.**

| Dry rub | | Wet rub | |
|---|---|---|---|
| Standard rubbing fabric | Lining sample | Standard rubbing fabric | Lining sample |
| 4/5 | 4 | 4/5 | 4 |

**Color fastness to rubbing of the lining fabric**

The lining fabric was tested for color fastness to dry and wet rubbing and the values are presented in Table I. The rub fastness values between 4 and 4/5 for both the lining fabric and the rubbing fabric indicate the lining fabric released very small stain to the rubbing fabric and a very little fading of the color of the lining fabric was observed. This signifies that the lining fabric has very good color fastness to rubbing.

**Color migration/bleeding tests of the lining fabric**

The migration of the colorant from the lining fabric to the leather and standard PVC sheet when they are kept attached with or without the adhesive has been shown in Figure 4. It can be seen that the colorant is migrated to the attached leather/PVC sheet when they were attached through adhesive. However, no migration of colorant is observed when no adhesive was used between the lining and the leather/PVC sheet. Moreover, it can also be seen that color of the staining on the leather is different from that on the standard PVC sheet.

The leaching out of the colorant from the lining fabric in various solvents used in industrial adhesives are tested. The colorant from the lining fabric is leached out in all the solvents except in water (Figure 5).

The UV-visible spectra of the colorant solutions obtained from the lining fabric in various solvents are shown in Figure 6. The colorant is insoluble in water and the corresponding UV-visible spectrum is overlapped with the abscissa (X-axis) in the whole visible region of the spectrum. The colorant of the lining fabric is highly soluble in all the organic solvents. All the UV-visible spectra of the colorant in organic solvents (except cyclohexane) show that the colorant absorbs the light radiation in the whole visible light wavelength range (390-700 nm) and hence looks black. However, in cyclohexane, the

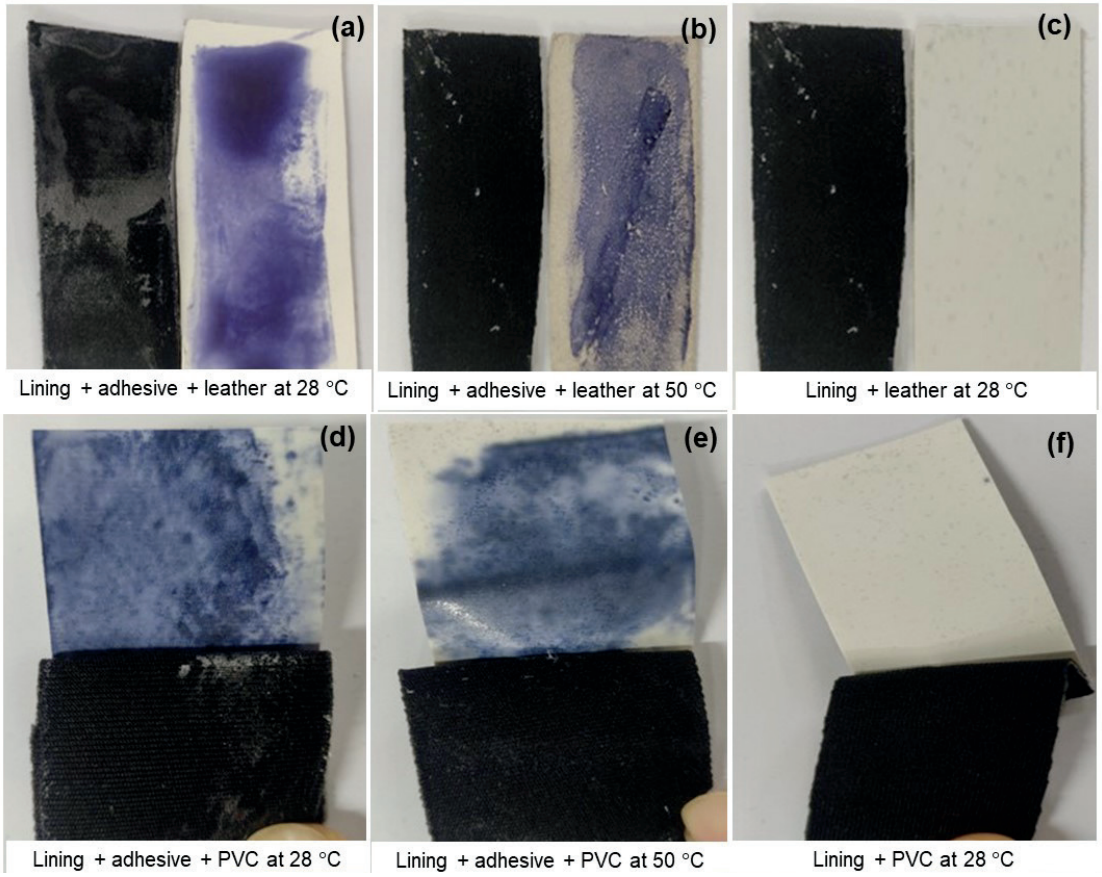


**Figure 4.** The lining kept attached to the leather **(a, b)** and PVC sheet **(d, e)** using adhesive for 48 hours **(a, d)** at 28°C, **(b, e)** at 50°C, and **(c, f)** lining kept attached to leather/PVC sheet without adhesive for 48 hours.

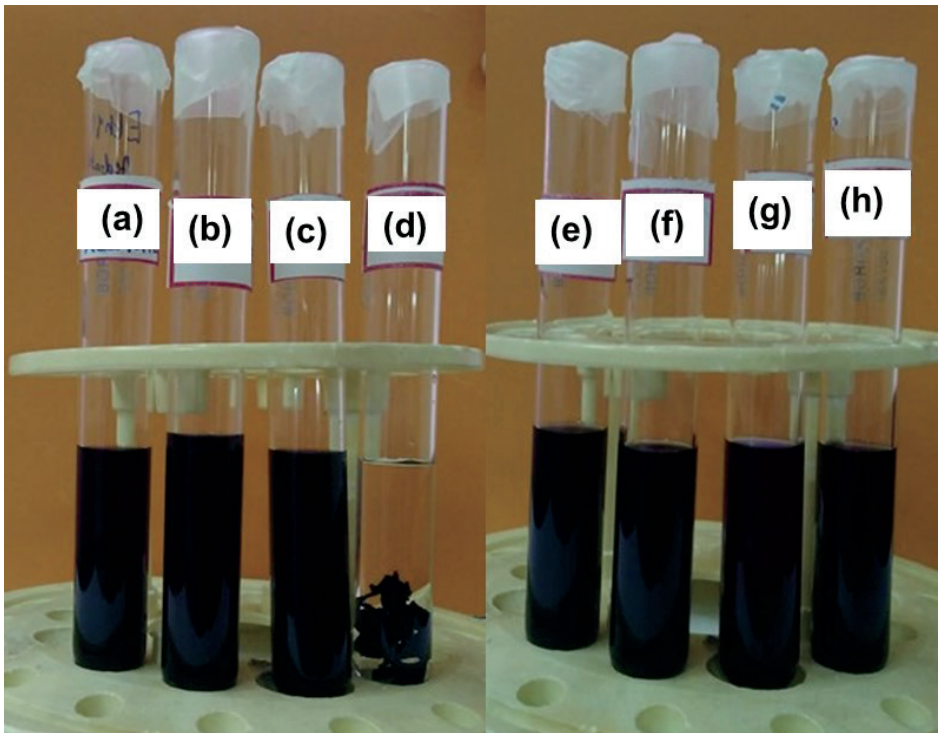


**Figure 5.** Leaching of the colorant from the lining fabric to various solvents **(a)** Ethyl acetate, **(b)** Toluene, **(c)** Dichloromethane (DCM), **(d)** Water, **(e)** Tetrahydrofuran (THF), **(f)** Methyl ethyl ketone (MEK), **(g)** Cyclohexane, and **(h)** Acetone.

spectrum shows an absorption maximum at 570 nm, which gives a violet coloration. This can be correlated with the color released by the lining fabric to the attached leather shown in Figure 4a-b. This indicates that cyclohexane might have been used as a solvent in the adhesive.

## Conclusion

In this specific case of color migration in footwear, the leather, lining fabric and the adhesive used were characterized. The lining material which is a black colored polyester fabric was colorfast to rubbing, however it released color in the organic solvents that are generally used in natural rubber-based adhesives. The adhesive used in this case was identified as organic solvent based hydroxy-terminated natural rubber. Migration studies showed that migration of the color from the lining material to the leather / PVC sheet happened only in the presence of the adhesive. The color migration was very fast and happened within hours even under normal environmental conditions. Therefore, it may be concluded that the organic solvent in the adhesive used in this case was responsible for the color migration from the lining material to the attached leather.

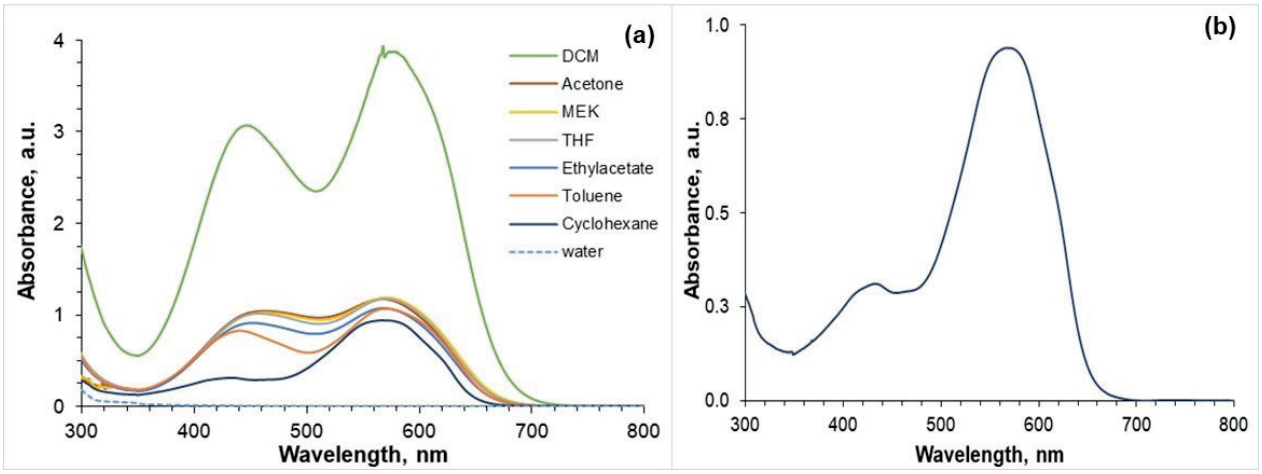


**Figure 6. (a)** UV-visible spectra of the colorant leached out from the lining fabric in different solvents, and **(b)** projected view of the UV-visible spectrum of the leached-out colorant in cyclohexane.

In the present case of the affected footwear, the colorant from the lining fabric leached-out in the solvent of the adhesive (most probably cyclohexane) and adsorbed on the finished surface of the attached leather. The adsorbed colorant slowly migrated from the edge to the middle of the leather spoiling the aesthetics of the footwear. The solvent in the adhesive is responsible for this migration. Moreover, the solubility of the colorant of lining in the adhesive's solvent contributed to the migration. Therefore, it is recommended to check the solubility of the fabric's colorant in aqueous and non-aqueous solvents, and thereafter select appropriate adhesive to avoid such migration of colorants in products specifically those made from various types of fabrics.

## Acknowledgment

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## Conflict of interest

The authors declare that there is no conflict of interest.

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# Studies On the Kinetics of Oil Oxidation Using Benzoyl Peroxide and Its Synergistic Effect in Fish Oil Tanning

by

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## Abstract

The oxidation of oil is an unavoidable process during oil tanning which aids in the forming of aldehydes that subsequently interact and react with amino groups in collagen. Oxidizing agents are commonly used to catalyze a faster reaction, thereby reducing days required for oil tanning. Fish oils are widely and regularly used for oil tanning. The oxidation of fish oil depends on its content of unsaturated fatty acids. In the current research, we focused on the kinetics of fish oil oxidation using Benzoyl Peroxide [BPO]. To assess the catalytic behavior of BPO, the kinetic study of the oil oxidation was carried out by determining the peroxide and p-Anisidine values. The maximum peroxide and p-Anisidine values were obtained on the 4th day. This is in accordance with our earlier studies.

## Introduction

Fish oil is highly unsaturated, which makes it readily susceptible to the various chemical reactions associated with double bonds, especially addition reactions of oxidation. The oxidation of unsaturated oil is one of the most important and studied reactions where its double bonds play an essential role. The two most common methods associated with the oxidation of oils are autoxidation and photo-oxidation of fatty acids present in fish oil. Catalysts such as metals, oxidizing agents, and enzymes accelerate the rate of oxidation.[1-3]

The high unsaturation content in fish oil makes it vulnerable to the various chemical reactions associated with double bonds, especially addition reactions. After that, the final product of oxidation reactions can be utilized in different applications.[4,5]

Several studies describe how oil oxidation depends on its fatty acid composition. The autoxidation of monounsaturated acid (oleic acid) can be achieved at high temperatures, while polyunsaturated fatty acids such as linolenic and linoleic acids undergo rapid oxidation even at room temperature.[5] Due to the free radical chain reaction, the primary oxidized products, such as allyl hydroperoxides and hydroperoxide, would be further oxidized to secondary products such as saturated and unsaturated aldehydes, short-chain ketones, alcohols, acids, esters, ethers, and hydrocarbons.[6] The use of oxidizing agents is to accelerate the rate of production of primary and secondary products.[7,8]

In principle, the standard oxidative quality parameters are based on measurements of primary and secondary oxidation products which are determined by Peroxide Value (PV) and p-Anisidine value (AV) respectively by Fourier transform infrared (FTIR) Spectroscopy,[9] 1H Nuclear Magnetic Resonance (NMR) Spectroscopy[10] and Dynamic Headspace Gas Chromatography-Mass Spectroscopy (GC-MS) techniques.[11]

In the present study, the effect of different percentages of BPO on the rate of oxidation of fish oil has been investigated. The current research predominantly focuses on reducing the oxidation period to understand fish oil oxidation. The effect of oxidants and the kinetics of the fish oil oxidation have been evaluated by its Peroxide and p- Anisidine values. Further, this can be confirmed by the previous study[14] where fish oil tanned leathers made within four days by using BPO (1%).

## Materials and Methods

### Materials

Fish oil was purchased from a local supplier, Chennai. BPO was procured from Sigma-Aldrich, Chennai. All the other chemicals were obtained commercially and of analytical grade.

PV measurements by Iodometric titration: Acetic acid (glacial) 99.7%, Isooctane, Potassium Iodide, Distilled water. AV measurements: p-Anisidine reagent, Acetic acid (glacial) 100%, Iso-octane

### Methods

In order to determine the chemical kinetics of fish oil oxidation, the first set of experiments corresponds to the determination of Peroxide and p-Anisidine values of fish oil (2g) without an oxidizing agent [blank]. Another set of experiments was carried out in the presence of 1 % of BPO (0.02g) for the determination of the experimental Peroxide and p-Anisidine values.

### Auto oxidation of fish oil

Fish oil [20mL sample] was added in a beaker and exposed to air for ten days. The resultant autoxidized oil was sampled at predetermined intervals to assess its oxidation state.

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**Peroxide value determination**

Peroxide Value [PV] measures peroxides contained in the oil and is determined by measuring iodine released from the oxidation of potassium iodide. The determination of PV was performed as per standard method.[12]

A fish oil sample (2 ±0.01 g) was dissolved in 30 mL iso-octane/acetic acid solution (2:3). The saturated Potassium Iodide [KI] solution and distilled water were added, followed by vigorous shaking to liberate iodine into the extracting chloroform layer. The mixture was titrated with 0.1 N sodium thiosulphate using starch solution as an indicator until the dark blue color disappeared. As per the kinetic studies of the auto-oxidation of oil, it is indicated that the rate of formation of the fatty acid hydroperoxides and the rate of degradation of polyunsaturated fatty acids is low at the start of the process.

The peroxide value was calculated from the following formula:

$$\text{Peroxide Value} = (\text{mEq peroxide kg–1 oil}) = [C(Va–Vb)/m] \times 1000$$

Where C represents the concentration of Titrant (mol/L), Va is the volume of Titrant (mL), Vb is the volume of blank, m is the mass of the oil sample (g), and 1000 is the unit conversion factor.

The analysis was performed in triplicate, and the experiments were carried out again in the presence of 1% of BPO. The results were reported in mEq peroxide $kg^{-1}$ oil in Table I.

**p-Anisidine value determination**

The Anisidine value is defined as the spectroscopic absorbance of a solution of 1g of oil dissolved in 100mL of solvent (iso-octane) and added reagent (0.25% p-Anisidine, dissolved in glacial acetic acid). Aldehydes derived from the secondary oxidation of the oil matrix react with p-Anisidine, determining a variation in the absorbance measured at 350 nm. The p-Anisidine value was determined according to the protocol from AOCS Official Method.[13]

The 0.25% p-Anisidine reagent was prepared every working day. p-Anisidine [0.25 grams] was dissolved in 100 mL of 100% acetic acid, and the absorbance was measured to ensure a value below 0.2. To analyze the samples, about 0.1 grams of oil were weighed directly in test tubes and dissolved in 5 mL of iso-octane. An aliquot of 2.5mL of this sample was transferred to a cuvette, and the absorbance was measured at 350 nm against pure iso-octane as blank. Then, 0.5 mL of p-Anisidine reagent was added, and the cuvette was shaken by hand. The cuvette was kept in the dark for 10 minutes before the second absorbance measurement was made. The measurements were performed in triplicate. The analysis was performed again in the presence of 1% of BPO and the results are reported in the Table II.

Peroxide value (PV) and p-Anisidine value (p-AV) were used to measure the level of peroxide/hydroperoxide and secondary by-products formed during the oil oxidation. To measure the peroxide value (PV) and p-Anisidine value (p-AV) of the oil with 1% of BPO, the oxidation property of fish oil is studied and compared with that of fish oil without the oxidizing agent.

The p-AV was calculated using the following formula:

$$\text{p-Anisidine Value (p-AV)} = V \times \{[1.2 \times (ES2–B2) – (ES1–B1)]/m\}$$

Where V is the volume (mL) of iso-octane used to dissolve the oil sample, ES1 is the first spectrophotometric reading of the experimental sample, ES2 is the second spectrophotometric reading of the experimental sample, B1 is the first spectrophotometric reading of blank, B2 is second spectrophotometric reading of blank and m is mass (g) of oil sample.

## Results and Discussion

**Peroxide value determination**

The official method for Peroxide value determination is based on an iodometric titration technique. During the process, the peroxides in the oil sample oxidize Iodide ion ($I^-$) to Iodine ($I_2$). Iodine then complexes with starch, resulting in the development of a dark blue color. Iodine is then reduced by thiosulfate, as indicated by the disappearance of the dark blue color. Therefore, it is concluded that the amount consumed of sodium thiosulfate solution can be directly related to the milliequivalents of hydroperoxides present in the oil sample.

During the course of the oxidation of fish oil with and without an oxidizing agent, the peroxide value (PV) was steadily increasing for three days. The actual rate of accumulation of peroxides was uneven over time and during storage, there were a series of maxima and minima. The presence of maxima at the beginning of oxidation (the 1st day) indicates the free-radical nature of oil oxidation. The highest rate of accumulation of peroxides was observed for the fish oil due to the presence of high unsaturation therein. Peroxides being unstable, primary products of fat oxidation quickly form new radicals or stable secondary products.

From Figures 1 and 2 it is concluded that, the PV values for fish oil with and without oxidizing agents shows appreciable changes. The PV values are measured with a time interval of one day. The fish oil without an oxidizing agent shows a gradual increase in PV values in the initial stage, reaching to maximum by the 6th day. The PV values start decreasing from the 7th day till the 10th day. This is due to the non-availability of driving force for further oxidation of oil where Peroxide stopped oxidizing iodide ion ($I^-$) to Iodine ($I_2$). But in the case of oil with an oxidizing agent, the initial 1st day gives a too high value of PV compared with oil without an oxidizing agent. This indicates the formation and enhancement of peroxide molecules in the oil to undergo an accelerated oxidation

**Table I**

**PV values with and without oxidizing agents**

| SI. No | Time in days | PV value without Oxidizing Agent (meq/kg) | PV value with Oxidizing Agent (meq/kg) |
|---|---|---|---|
| 1 | 1 | 1.573 ± 0.05 | 3.081± 0.05 |
| 2 | 2 | 1.886± 0.05 | 4.491± 0.05 |
| 3 | 3 | 2.221± 0.05 | 4.575± 0.05 |
| 4 | 4 | 3.123± 0.05 | 1.002± 0.05 |
| 5 | 5 | 4.266± 0.05 | |
| 6 | 6 | 4.133± 0.05 | |
| 7 | 7 | 3.699± 0.05 | |
| 8 | 8 | 2.418± 0.05 | |
| 9 | 9 | 1.054± 0.05 | |
| 10 | 10 | 1.005± 0.05 | |

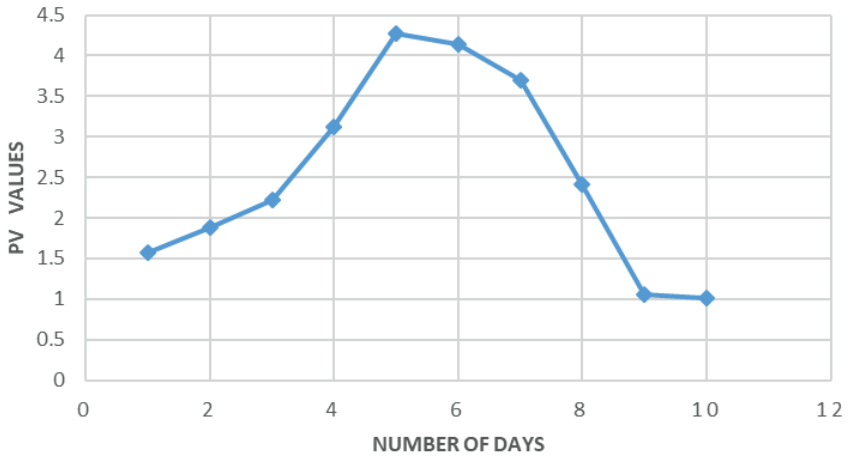


**Figure 1.** Peroxide values without oxidizing agent

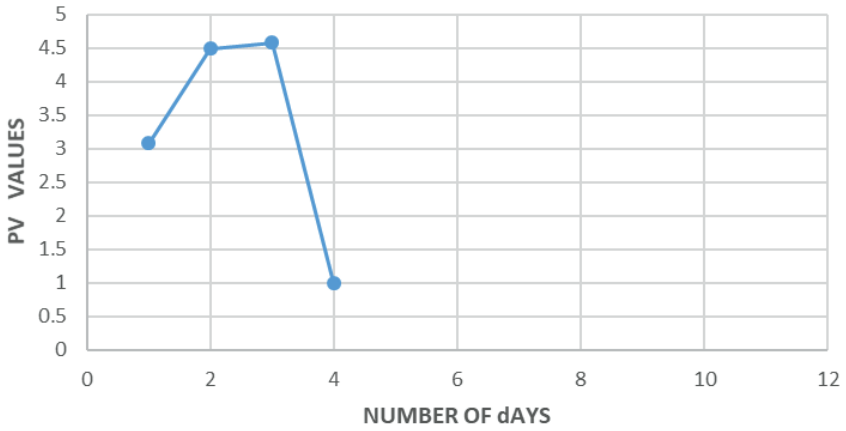


**Figure 2.** Peroxide values with oxidizing agent

**Table II**

**p- Anisidine values with and without oxidizing agents**

| Sl. No | Time in days | p-AV value without oxidizing agent | p-AV value with oxidizing agent |
|---|---|---|---|
| 1 | 1 | 0.11± 0.05 | 2.081± 0.05 |
| 2 | 2 | 0.23± 0.05 | 19.491± 0.05 |
| 3 | 3 | 1.52± 0.05 | 19.575± 0.05 |
| 4 | 4 | 2.52± 0.05 | 19.175± 0.05 |
| 5 | 5 | 4.69± 0.05 | |
| 6 | 6 | 19.235± 0.05 | |
| 7 | 7 | 19.089± 0.05 | |
| 8 | 8 | 18.135± 0.05 | |
| 9 | 9 | 17.175± 0.05 | |
| 10 | 10 | 17.063± 0.05 | |

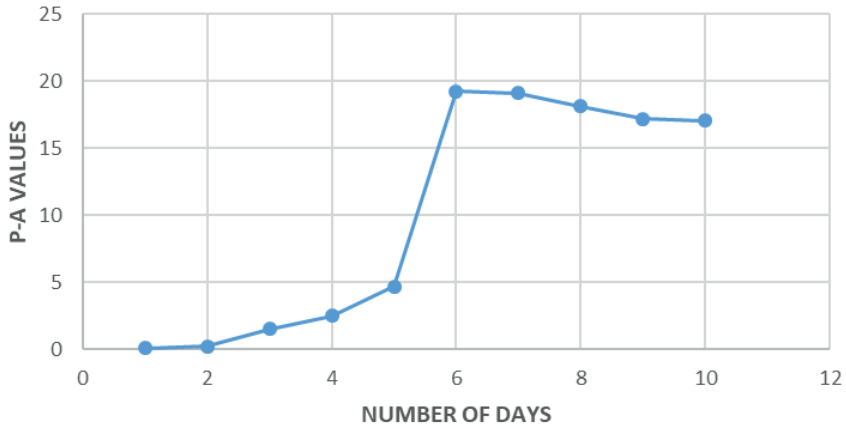


**Figure 3.** p- Anisidine values without oxidizing agent

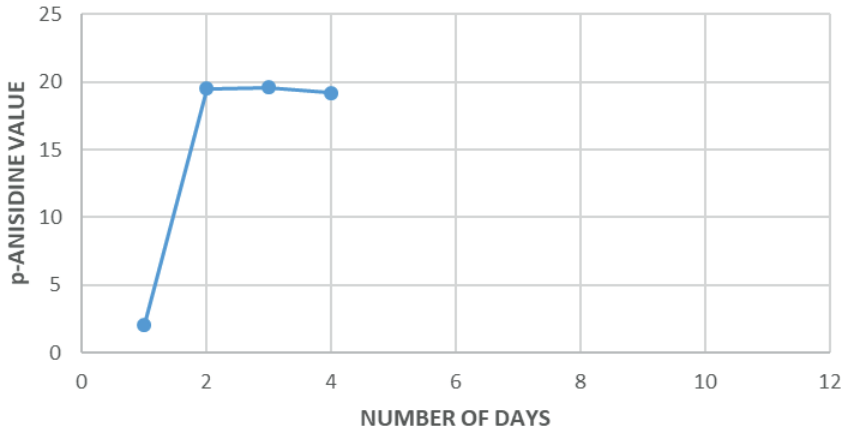


**Figure 4.** p- Anisidine values with oxidizing agent

process by the oxidizing agent. In this case, the oxidizing agent drives peroxide/hydroperoxide molecules to participate in the reaction with KI actively. For the subsequent days, the PV value for the sample with oxidizing agent increases gradually. In contast the 4th-day sample shows less PV due to the lower concentration of peroxide/hydroperoxide molecules. Therefore, the oxidizing agent in the initial stage speed up the reaction rate for the formation of required peroxide/hydroperoxide for the tanning process. It indicates that the oxidizing agent enhances the rate of peroxide formation and enables the long-term stable intermediate for higher PV values. It suggests that the sample without oxidizing agent will take up to 6 days to complete the oxidization reaction. In contrast, the sample with an oxidizing agent takes just 3 days.

**p-Anisidine values determination**

p-Anisidine values are essential for the complete study of secondary oxidation products of oxidized fish oil with and without an oxidizing agent.

The secondary oxidized products of fish oil without an oxidizing agent (BPO) were reported in less concentration initially from day one to day four and only increased from day 5 to day 7. The concentration of the same starts decreasing from day 8 till day 10 and stands nearly constant. This may be due to the slow and steady production of secondary by-products initially. After reaching maxima again, the production starts decreasing.

In contrast, fish oil with an oxidizing agent (BPO) exhibited high p-Anisidine values from day 2 to day 4. It is presumably due to the reaction of p- Anisidine reagent with the secondary by-products of fish oil oxidation such as aldehyde, acetone, and their derivatives.

**Significance of the rate of oil oxidation**

The present research establishes the synergistic effect rate of oil oxidation has in oil tanning using fish oil. The core objective was to explore the catalytic behavior of oxidizing agent towards accelerating the rate of oxidation of fish oil which in turn speeds up the oil tanning processes. Conventional oil tanning takes about 10-12 days and is labor intensive depending on environmental condtions. To accelerate the oil tanning process, oxidizing agents are preferred due to the reduction in manufacturing days. Several oxidizing agents have reported to achieve the completion of tanning in shorter duration. In our earlier studies,[14] we have reported the use of benzoyl peroxide as an oxidizing agent for chamois leather manufacture and documented that the fish oil tanning can be completed within 4 days and physical strength characteristics of the experimental leathers found to be as comparable to the conventionally processed chamois leather. The mechanism of oil tanning is based on the oxidation of oil leading to carbonyl groups that interact/react with the Ɛ-amino groups of collagen to form covalent bonds. The interaction of oil with collagen primarily depends on the rate of oil oxidation. To understand the behavior of benzoyl peroxide on fish oil, kinetics studies have been carried out in the present research work and discussed the peroxide and p-anisidine values. Peroxide and p-anisidine values are the tangible measurements to ascertain the rate of oil oxidation and the values are directly correspondent. Concentration of oil and benzoyl peroxide are simulated as mentioned in our earlier research article with 1% concentration of oxidizing agent and the values are calculated to understand the oil tanning mechanism. It has been found that the oxidation of oil completed within 4-5 days as inferred from peroxide and p-anisidine values which is in accordance with the leather manufacture, as reported in our prior research article. Comprehensively the study provides an insight on the importance of the kinetics of oil oxidation and its relevance in leather manufacture. The exploration also provides a tool to identify and screen new or other oxidizing agent for leather manufacture with p-anisidine and peroxide values, which is a direct indictor for the completion of oil tanning based on the choice of oxidizing agent and oil substrate.

## Conclusion

The oxidation pattern of fish oil is confirmed by the study[14] whereas 1% of BPO was used to make fish oil-tanned leather (chamois). According to our studies, the use of 1% of BPO completed the fish oil tanning within four days with improved water absorption and physical properties of the experimental leathers. The chemical kinetics also confirms the completion of fish oil oxidation within four days.

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# Development of Nano Bio Aldehyde Tanning Agent for Sustainable Leather Manufacture

by

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## Abstract

Exploring the application of natural biopolymers in leather manufacture is a need of the hour to achieve sustainability. The present research work explores the possibility of using modified biopolymer nanoparticles as a tanning agent. Starch, a polysaccharide with high functionalization, is converted into Nano Bio Aldehyde (NBA) through periodate oxidation as water-in-oil microemulsion method. The synthesized product was characterized by its physico-chemical nature. The prepared NBA shows an aldehyde content of 85%, which endorses its application as a tanning agent. Experimental leather trials were carried out to assess the tanning efficacy and found that NBA tanned leathers show a shrinkage temperature of 90°C. Physical characteristics of the experimental leathers were found to be 24 N/mm$^2$ and 90 N for tensile and tear strength, respectively. The study provides a holistic understanding of modified biopolymer as a nano tanning agent to manufacture leather.

## Introduction

The tanning process improves the thermal and enzymatic stability of leather.[1-2] Among organic tanning systems, aldehyde tanning agents have gained prominence in the global leather industry because of their crosslinking ability.[3] Aldehydes, aliphatic aldehydes, aldehydic agents, and dialdehyde polysaccharides have been studied as crosslinkers for stabilizing native collagen.[4] Polysaccharides such as starch, alginate, and cellulose are modified based on their functionality to increase their crosslinking ability as tanning agents.[5] Such modified biopolymers show profound changes in properties and enhanced functionalities. Dialdehyde Starch (DAS) as oxidized starch exhibits biocompatibility, biodegradability, alkali-solubility, crosslinking and strong bonding ability.[6] DAS also has higher reactivity associated with the aldehyde functional groups in each oxidized monomeric unit, which provide the basis for a more effective application of DAS as a tanning agent.[7] The enzymatic degradation of collagen is significantly reduced by DAS crosslinking with an increase in thermal stability. Functionalized starch-based nanoparticles have recently drawn more attention due to their versatile and multi-functional properties. The most salient feature is the profuse functional groups and high surface area (surface/volume ratio) ascribed to their submicron sizes allowing higher reactivity and solubility.[8-9] The present study focuses on converting SS to NBA (NanoBioaldehyde) for its possible application as a tanning agent in leather manufacture. The tanning properties of NBA are characterized by their morphological, thermal and physical properties, viz., SEM images, shrinkage temperature, tensile strength and tear strength properties. The studies provide an insight into process technology towards developing sustainable leather manufacture using natural biopolymeric agents.

## Materials and Methods

### Materials

Soluble Starch (SS) powder, Span 80, acetic acid, sodium periodate, chloroform, and toluene were obtained from SRL Chemicals, India. Wet salted goat skins were procured from Slaughterhouse, Chennai, India. The chemicals used for the leather process were of commercial-grade. All other chemicals used were of analytical grade and purchased from SRL Chemicals, India.

## Methods

### Preparation of Nanobioaldehyde Particles

SS solution (1%) was heated at 70°C with constant stirring (1000 rpm, 30 min) and hydrolyzed using 4 N sulfuric acids ($H_2SO_4$) until it reached a proper solution and then sonicated for 1 h. 2% Span 80 was dissolved in toluene, and chloroform solvent mixture (3:1 ratio) at 1500 rpm stirring condition and hydrolyzed SS was added dropwise to form micro-emulsion to the solvent mixture. For this micro-emulsion, 1.49g sodium periodate ($NaIO_4$) was mixed to form a micro-emulsion to the solvent mixture and stirred for about ~2.5 h. The pH was adjusted to ~3-3.5 using 4 N sulfuric acid. The oxidation reaction was carried out in the dark at 27°C for 2.5 h under constant stirring (500 rpm). Five milliliters of 0.25% of sodium tripolyphosphate was added with continuous stirring for about 45 min. As a continual process, the micro-emulsion was treated with ethanol and dilute acetic acid. Finally, acetone and

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water wash were repeated until no white depositions appeared. The resultant solution was centrifuged (10000 rpm, ~25 min), and the residue was lyophilized to obtain NBA particles.[10]

**Characterization of the product NBA**

**Determination of Aldehyde Content**

The amount of aldehyde present in the prepared NBA particles was estimated by the quantitative alkali consumption method.[11]

Aldehyde content was calculated with the following formula,

$$\% \text{ of Aldehyde content} = \frac{(C_1V_1 - 2C_2V_1)}{(W/161 \times 1000)} \times 100$$

Where W is the mass of NBA in grams (g), and 161 is the average molecular weight of repeat unit in NBA.

- $C_1$ and $C_2$ are the concentrations of NaOH and $H_2SO_4$ respectively in mol/mL
- $V_1$ and $V_2$ is the volume of NaOH, and $H_2SO_4$ added respectively in (mL)

**Fourier Transform Infrared (FTIR) Analysis**

FTIR measurements of SS and NBA were measured by JASCO 4200 FTIR spectrometer. Entire spectrum was recorded by absorption mode at 4 $cm^{-1}$ resolutions with a wavenumber range from 4000-400 $cm^{-1}$.[12]

**Particle Size Analysis**

Particle size was measured at 25°C using a dynamic light scattering (DLS) analyser (Malvern Nano-Zetasizer ZS, Malvern, UK). The SS and NBA samples were dispersed with distilled water to form a solution of 0.01% (w/v) concentration.[13]

**Thermogravimetric Analysis (TGA)**

TGA Q50 V200.5 Build 30 model Thermogravimetric analyser was used for thermal decomposition studies. Approximately 1.9 mg (dry basis) of samples were loaded into a platinum pan and heated under a steady flow of dry nitrogen maintained at a flow rate of 40 mL/min from 25° to 800°C at 10°C/min.[14]

**Differential Scanning Calorimetric (DSC) Analysis**

The DSC measurement was performed for SS and NBA to understand the thermal stability using Evo Robot gas option (DSC 2A - 00837) in $N_2$ atmosphere.[15]

**Preparation of DAS and NBA tanned Leathers**

Wet salted goat skins were processed through conventional method till pickling. Pickled pelt was divided into two halves, left side skin was used as control and the right side was processed for the experimental trials. pH of the pickled pelt was adjusted to the required pH by sodium formate and sodium bicarbonate and tanned with different concentrations of NBA viz., 1, 2, 3, 4, and 5% (based on the pickled pelt weight) for 4 h. The process and recipe formulation is given in Table I. The next day, post-tanning process (Table II) was carried out to evaluate the physico-chemical properties of the crust leathers.

**Characterization of DAS and NBA Tanned Leathers**

**Hydrothermal stability measurement**

Hydrothermal stability of DAS and NBA tanned leathers were measured. Hydrothermal stability of leather samples was measured using SATRA STD 114 Testing apparatus. Samples taken from official sampling positions.[16]

**Mechanical strength**

The tensile and tear strength were determined using the standard IULTCS methods.[17-18] Mechanical properties of DAS and NBA

**Table I**

**Experimental NBA tanning process**

| Process | Chemicals | % | Duration | Remarks |
|---|---|---|---|---|
| **Tanning** | Pickle liquor | 50 | | pH 2.8 |
| | NBA | *X | 120 min | Check for penetration |
| | Water | 50 | | |
| | Sodium formate | 1 | 3×15 min | |
| | Sodium bicarbonate | 1.5 | 3× 10 +60 min | pH Adjusted to 4.0; Drain |
| **Washing** | Water | 100 | 15 min | Drain; aged for 24 h; sammed; shaved for thickeness1.0-1.1 mm |

*X: 1%, 2%, 3%, 4% and 5% for tanning trial experiments. Piled overnight

Percentage (%) is based on the pickled pelt weight of the goat skins

**Table II**

**Post tanning process**

| Process | Chemicals | % | Duration(min) | Remarks |
|---|---|---|---|---|
| **Wetting** | Water | 200 | | |
| | Wetting agents | 0.1 | 60 | Drain |
| **Neutralization** | Water | 150 | | |
| | Sodium bicarbonate | 1 | 30 | pH adjusted to 5 |
| **Washing** | Water | 150 | 15 | Drain |
| **Retanning** | Water | 100 | | |
| | Acrylic syntan | 2 | | |
| | Phenolic syntan | 2 | 30 | |
| | Melamine syntan | 8 | 45 | |
| **Dyeing and fatliquoring** | | | | |
| | Synthetic fatliquor | 10 | 60 | |
| | Acid dye brown | 2.5 | 60 | Penetration of dye checked |
| **Fixing** | Formic acid | 1 | | |
| | Water | 10 | 3×10+30 | Drain |
| **Washing** | Water | 100 | 10 | Drain, leathers were piled O/N, set, dry, stake, trim and buff |

tanned leather were determined using Instron series II Automated Materials Testing System.

**Subjective evaluation of processed leathers**

DAS and NBA tanned leathers were assessed for organoleptic properties. Functional properties of the leathers were rated on a scale of 0-10 points by three experts.

**Morphological Evaluation**

The morphological features of the prepared particles and tanned leathers were examined using scanning electron microscope (Tescan Clara, Newzeland).[19]

## Results and Discussion

Starch is a biodegradable and biocompatible polysaccharide having varied applications in the field of translational research. As a cost-effective material, it has gained profound interest as an independent bi-functional material. Through micro-emulsion technique NBA is prepared by acid hydrolysis and periodate oxidation method.[20] Prepared NBA showed 85% of aldehyde content with 99% solubility at a minimal ratio (1:1.5) of periodate oxidation.

**Structural alterations in NBA**

Vibrational spectroscopy of SS and NBA are shown in Figure 1. From the spectrum it can be observed that the characteristic peak of O-H stretching and vibration is around 3481 $cm^{-1}$, C-H asymmetrical stretching and vibration is exerted at 2932 $cm^{-1}$ and O-H vibration of physically absorbed water is at 1651 $cm^{-1}$ respectively, which correspond to starch. The absorbance peak around 1000-1200 $cm^{-1}$ is attributed to C-O stretching in starch.[21] However, when the stretching is compared with NBA; the characteristic peaks at 2897 $cm^{-1}$ and 1735 $cm^{-1}$ are attributed to the bonds of aldehyde carbonyl (C=O) and C-H stretching of aldehyde (–CHO). The FTIR spectrum confirms the presence of anhydrase glucose units having -OH groups

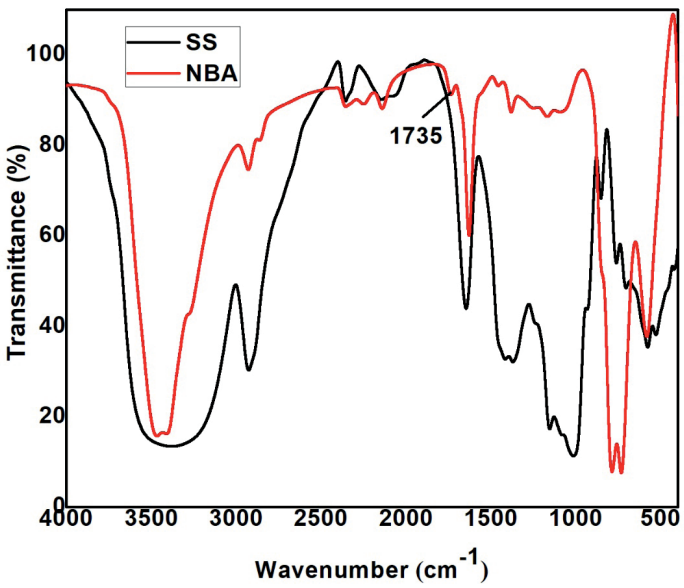


**Figure 1.** FTIR spectra of SS and NBA

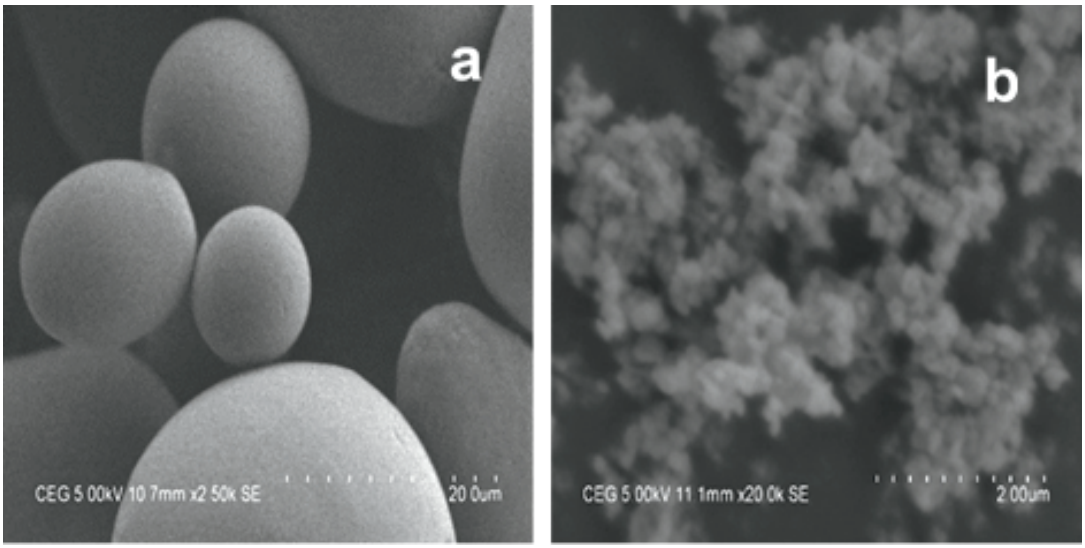


**Figure 2.** Scanning electron microscopy images of **(a)** SS scale bar-20µm and **(b)** NBA scale bar-2µm.

at 2,3 carbon positions, and the oxidation mainly replaces the 2,3 positions (OH) with the aldehyde group.[22] Moreover, the vibrational spectroscopic studies confirm the presence of dialdehydes which is a pre-requisite for an effective aldehyde tanning system.

**The morphological structure of SS and NBA**

The morphological variation of SS and NBA samples are shown in Figure 2. In Figure 2(a), SS appears spherical with loosely bound grains. Figure 2(b) shows the nano system of SS into NBA, which shows molecular size ~86 nm. SEM images depict the phase transition of the SS to NBA correlated to the size reduction (micron to nano).

**Characteristics of the prepared particles**

The particle size distribution of the prepared particles is shown in Figure 3. The native SS has particle size of ~5.4 µm, and that of NBA is 41 nm, showing significant reduction in size due to hydrolysis of SS prior to oxidation. The prepared NBA resulted in a diameter of 41 nm and a polydispersity index value of 0.997. The PDI value shows that the particle size of NBA has narrow size distribution.

**Thermal properties of SS and NBA**

The thermal degradation of SS and NBA were studied through TGA (Figure 4). Figure 4 indicates thermal degradation of SS and NBA. The results obtained from TGA indicate NBA has enhanced thermal resistance than SS.[23]

The DSC thermogram of SS and NBA is shown in Figure 5. SS resulted in $T_o$ and $T_p$ values between 86°C and 189°C, whereas NBA resulted in one sharp peak value at 134°C. NBA showed increase in gelatinization peak temperature compared to SS, which is due to the decreased crystallinity. In the process of acid hydrolysis and oxidation treatment, the amorphous region of starch has been

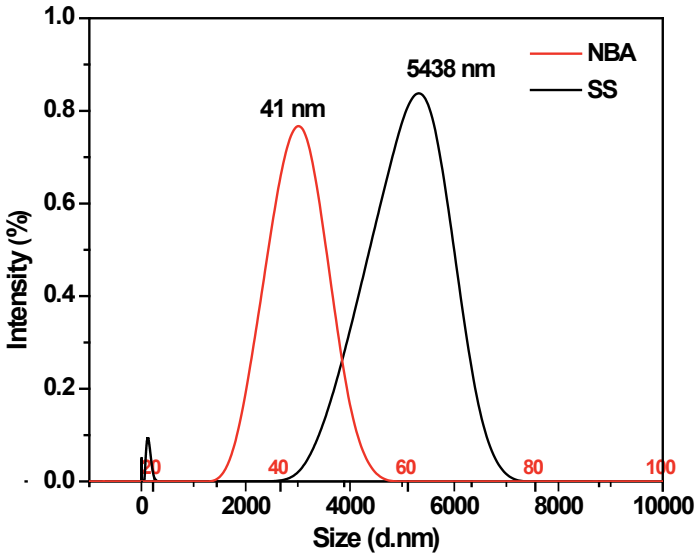


**Figure 3.** Dynamic light scattering measurements of SS (black line) and NBA (red line).

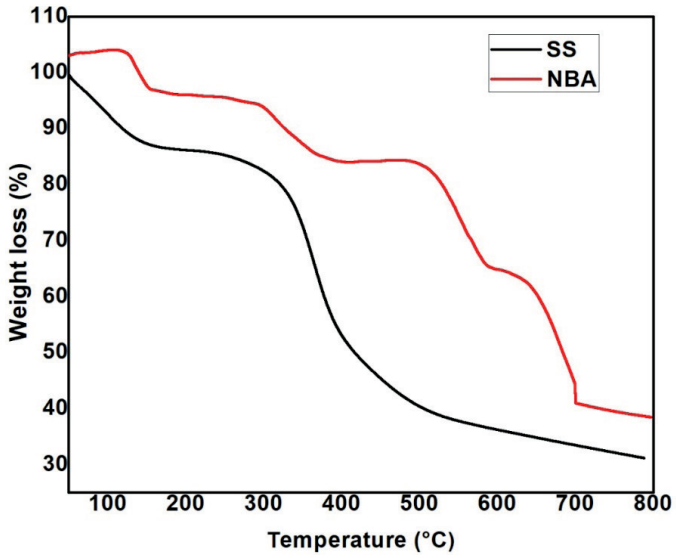


**Figure 4.** TGA analysis of SS and NBA

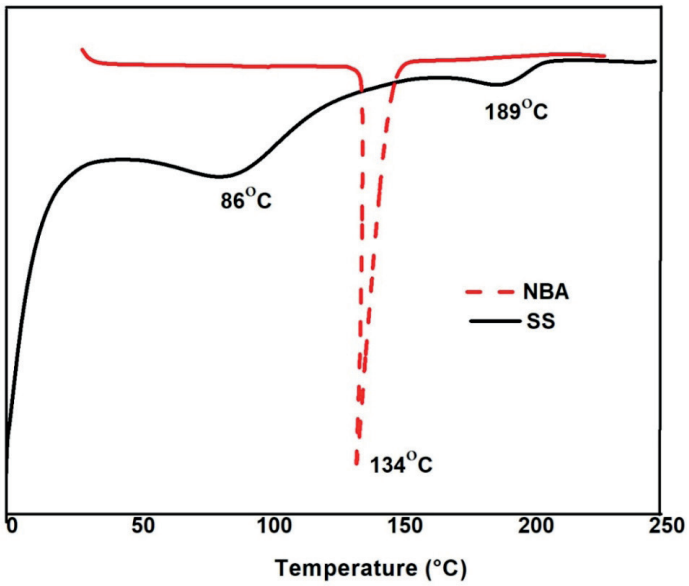


**Figure 5.** Differential scanning calorimeter analysis of SS and NBA

**Table III**

**Physical strength properties of control and experimental NBA tanned leather**

| Sample Tanning | Tensile Strength (N/mm$^2$) | Tear Strength (N) |
|---|---|---|
| DAS tanned | 19.42±1.3 | 51.11±5 |
| NBA tanned | 24.90±1.6 | 90.83±2 |

**Table IV**

**Organoleptic properties of NBA tanned leather**

| Parameters | Control DAS | Experimental NBA |
|---|---|---|
| Grain smoothness | 8.5 | 8.7 |
| Grain softness | 8.1 | 8.2 |
| Fullness | 8.0 | 8.3 |
| General appearances | 8.5 | 8.5 |

destroyed leading to instability in the crystalline and amorphous regions.[24-25]

**Hydrothermal resistance of tanned leathers**

The hydrothermal resistance of experimental NBA tanned leather was compared with DAS tanned leather. The modified skin upon tanning with NBA increased the degree of crosslinking, which eventually led to an increase in shrinkage temperature. The higher shrinkage temperature of the leather indicates better thermal stability, which could possibly be due to a high degree of crosslinking between the tanning agent and the collagen matrix. The hydrothermal stability measurements of native collagen (raw hide) show shrinkage temperature of about 60°±0.26°C. As a function of concentration, the shrinkage temperature of collagen exhibited 65°±0.16°C (@1% NBA), 75°±0.32°C (@2% NBA), 87°±0.25°C (@3% NBA), 90°±0.35°C (@4% NBA) and 90°±0.55°C (@5% NBA) respectively. Experimental NBA tanned leather (5%) showed that the thermal stability of leather measured about 90°±0.55°C when compared with control DAS tanned leather (85°±1.00°C). There is no significant increase in the shrinkage temperature of leather above 4% offer of NBA, and hence the same has been considered to be the optimum offer for tanning.

**Physical strength characteristics of the crust leathers**

The physical strength of DAS and NBA tanned leather is given in Table III. From the results it can be observed that the physical strength viz., tensile strength, and tear strength of the experimental NBA tanned leathers are found to be better when compared to the minimum requisite values.

**Subjective evaluation of the tanned crust leathers**

The results of the organoleptic assessment of the crust leather are given in Table IV. From the results, it can be ascertained that the fullness characteristics of NBA tanned leathers are slightly better than DAS tanned leathers. NBA crust leathers were observed to have reasonably good strength and organoleptic characteristics than DAS. The overall appearances of the NBA crust leathers are comparable to that of the conventionally processed crust leather samples from DAS tanning system. Hence, NBA as a tanning system may suit the requirement for processing wide range of leathers.

**Morphological structures of control and experimental tanned leathers**

Surface morphology of NBA and DAS tanned leathers are shown in Figure 6. Figure 6A shows the SEM images of the control leathers (DAS tanned leather) and Figure 6B shows the experimental leathers (4% NBA tanned leathers). DAS tanned leather at 800x shows some physical deposition in the surface (Figure 6A (a)) and cross-sections (Figure 6A (b)). Whereas in experimental NBA tanned leather, there is no physical deposition and observed compact grain and cross-sections (Figure 6 B (c, d)).

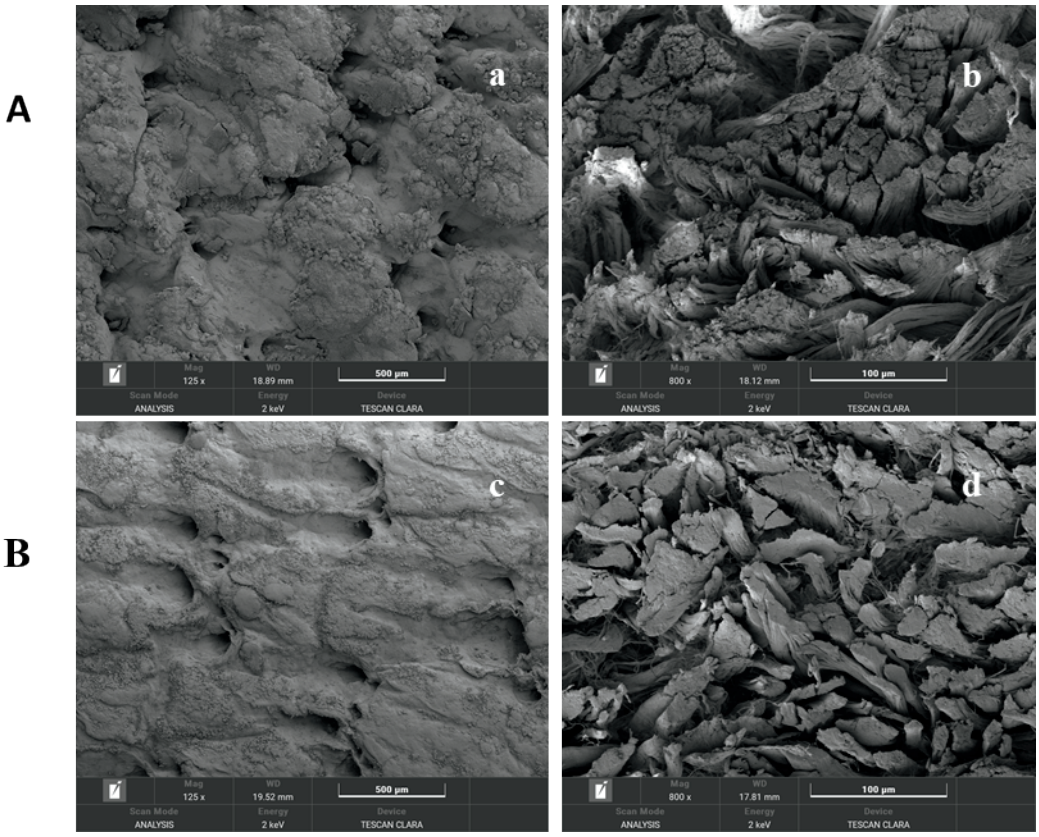


**Figure 6.** SEM images of DAS tanned leather surface and cross-section **A (a, b)** and NBA tanned leather surface and cross section **B (c, d)**

## Conclusion

The present work aimed to develop a biologically eco-benign tanning system using NBA. The current study looked upon using nano tanning system using dialdehyde starch. The NBA as a tanning agent was prepared using water in oil emulsion technique. NBA has proved to be a potential eco-friendly tanning material for leather tanning process. NBA was synthesized from soluble starch. NBA can be a novel aldehyde tanning agent in leather making. A maximum shrinkage temperature of about 90°±0.35°C was achieved with 4% NBA. The tanned leather met the standards norms of physical characteristics of upper leather. The present study resulted in a sustainable solution for metal free tanned leathers using nano-tanning system.

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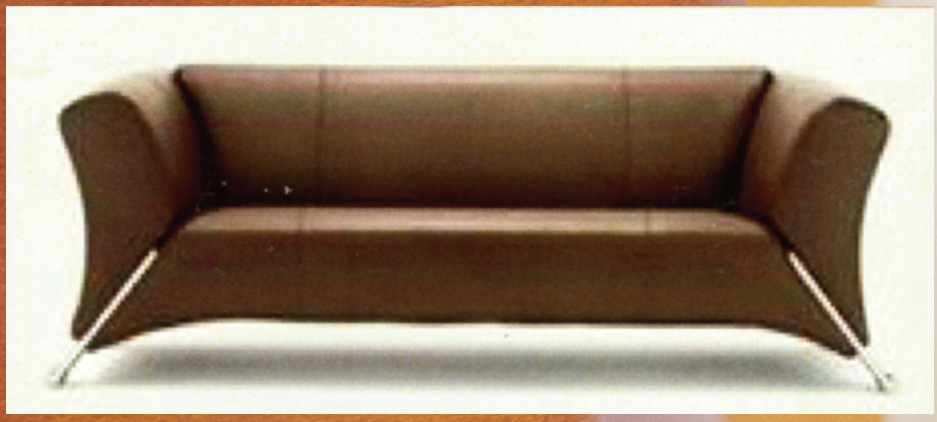

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**N. Priya** is a post graduate in Chemistry and with over 12 years of experience in Analytical chemistry of Leather and in particular specialized in the area of Hazardous Chemicals analyses. An expert in various Chromatography and Spectroscopic techniques.

**R. Kunjitham** is a post graduate in Chemistry and with over 33 years of experience in teaching and 10 years of research experience in crystal growth and electrochemistry.

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**Bindia Sahu**, see JALCA 114, 359, 2019

**A. Yasothai** is a Research Scholar, Department of Chemistry, CEG Anna University, Chennai, India. She has expertise in the field of leather and leather chemical analysis. Her research interests include synthesis of polymer nanomaterials and characterisation, leather and biomedical applications.

**GC Jayakumar** is currently working as a Senior Scientist at Centre for Academic and Research Excellence, CSIR-Central Leather Research Institute, Chennai, India. His research interests include cleaner leather processing technologies and utilization of tannery wastes for developing by products.

**S. Angyarkanny** is currently working as an Assistant Professor, Department of Chemistry, CEG Anna University, Chennai, India. Her research interests are surface science, nanocarriers, drug delivery, polymer synthesis and characterisation, biopolymers and plastic waste management.

**Swara V. Kanth** is currently head and Senior Principal Scientist, Centre for Human and Organizational Resources Development (CHORD), CSIR-Central Leather Research Institute, Chennai, India. Her research interests include Leather biotechnology, enzyme technologies applicable for environmental applications, cleaner leather production, human resource development and skill development.

# Industry News

## Winners of three 2023 IULTCS Young Leather Scientist Grants for research announced

The Executive Committee of the IULTCS is pleased to announce the winners of the 2023 IULTCS Research Commission (IUR) Young Leather Scientist Grants. The research grants are awarded to three young scientists, under the age of 35. The monetary awards help support the work of young talent in the leather sector.

This is the ninth year of the grants which have been generously supported by industry. The Selection Committee of IUR, chaired by Professor Dr Michael Meyer, is pleased to announce the following recipients:

**Tyson Foods: Young Leather Scientist Grant 2023**
**Basic Research**
Tyson Foods has provided the sponsorship of a €1,500 grant for Basic Research to **Dr Ilaria Quaratesi** from the Leather and Footwear Research Institute (ICPI), Bucharest, Romania. The title of the project is 'Non-toxic and biodegradable supramolecular additive with flame retardant and antimicrobial properties for the tanning industry'.

The project's main objective is to develop an antimicrobial flame retardant, which can as well be used in the leather industry basing on hydroxyl apatite and cyclodextrines using an ultrasound assisted continuous flow process. Flame retardancy and antimicrobial activity will be tested according to standardised procedures.

**Erretre: Young Leather Scientist Grant 2023**
**Machinery / Equipment**
Erretre has provided the sponsorship of a €1,000 grant for Machinery / Equipment research to PhD candidate **Vasanth Swaminathan** from SRM Institute of Science and Technology, Chennai, India. The title of the project is 'Reduction of carbonization and gas emissions using mechanotronics based intelligent laser beam machining, with machine learning, for cutting leather with better environmental measures for operator health'.

The project's main objective is to optimise leather cutting by variation of the distance and pulse width of a laser diode assisted machining. Effects on different parameters as carbonization, rate of material removal, kerf width and emission rate will be investigated, and carbonization will be followed by using image processing.

**Dr Mike Redwood: Young Leather Scientist Grant 2023**
**Sustainability / Environmental Award**
Leather Naturally has provided the sponsorship of a €1,000 grant for Sustainability / Environment research to **Dr Yue Yu** from Sichuan University, Chengdu, China. The title of the project is 'Controllable oxidation and degradation of lignin via $H_2O_2/O_3$ from biomass into a retanning agent for sustainable leather manufacturing'.

The project's main objective is to develop a light-coloured, lignin-based retanning agent which can be used as a green substitute for aromatic syntans using $H_2O_2/O_3$ synergistic oxidation technology. The oxidation mechanism has to be investigated, followed by research about the interaction mechanism between oxidized lignin and Cr-tanned leather. Finally a new retanning process is to be developed and its environmental impact will be evaluated.

The grants have been very successful and well received by industry. Referring to the awardees of the 2023 grants Dr Meyer said "All three project proposals show technological knowledge at a very high level and demonstrate the competitiveness of the leather industry with other industries worldwide. We are very happy that the profile of the Young Leather Scientist Grants continues to grow and thank our sponsors for the support that they continue to give. It will enable our young scientists to contribute their scientific knowledge, to the benefit of the leather community. We look forward to seeing the research outcomes of the projects we are supporting and wish them every success as they contribute to expanding our industry knowledge."

# 117th ALCA ANNUAL CONVENTION June 20-23, 2023 Grand Geneve Resort & Spa Lake Geneva, Wisconsin

***Featuring the 62nd John Arthur Wilson Memorial Lecture***

***Retelling "Viewing Leather Through the Eyes of Science"***

***A Century On***

***By Mike Redwood, Leather Naturally,***
***Teacher at University of Bath School of Management,***
***and Trustee of the U.K. Leather Conservation Centre***

**Tentative Schedule**

**Tuesday, June 20**
***Golf Tournament, Opening Reception and Dinner***

**Wednesday, June 21**
***John Arthur Wilson Memorial Lecture***
***All Day Technical Sessions, Fun Run, Dinner***
***Boat Cruise***

**Thursday, June 22**
***All Day Technical Sessions, Annual Business Meeting***
***Activities Awards Luncheon***
***Social Hour, Awards Banquet***

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