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# INVESTIGATION OF DIFFERENT REDUCING AGENTS OF AZO DYES FROM TEXTILE MATERIALS

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***Abstract:*** *Toxicology of textiles is a subject of increasing interest, because of the presence of dangerous compounds in clothes generated from dyeing and finishing processes. In order to protect human health, numerous regulations (Oeko Tex Standard 100, REACH Regulation) limit the presence of dangerous chemicals, such as aromatic amines, generated by reductive cleavage of azo dyes, by no more than 30 mg/kg of textile material. The objective of this work was to investigate different methods of azo dyes reduction from colored textile specimens, in order to determine the procedure with the highest selectivity and sensibility. Aromatic amines are generated by chemical degradation achieved by the cleavage of the azo linkage using reducing agents.Different alternatives to sodium dithionite, reducing agent recommended by standard method ISO/FDIS 14362-1 were tested, such as: sodium sulfite and tin chloride. Also, xylene extraction, the common procedure for synthetic fibers was also performed for cotton, dyed with azo dye Direct Blue 6, in order to assess the reliability of common simultaneously extraction and reduction of direct dyes from natural fibres. Sodium ditionite remains the popular choice for reducing agent, since it provides efficient cleavage of azo linkage, generating specifically carcinogenic amines. Both liquid and gas chromatography analytical techniques were used for precise quantitative determination of generated compounds.*

***Key words:*** *carcinogenic amines, azo dyes extraction, ecotoxicology, liquid and gas chromatography*

## 1. INTRODUCTION

Worldwide consumer standards have changed over the years, due to continuous improvement of people's living standards. Even in textile industry, the preferences are headed towards ecological, non-toxic and environmentally friendly textile products. The focus regarding ecotextiles is primarly on materials that may come into direct or prolonged contact with the human skin or oral cavity, such as clothing, bedding, towels, wigs, hats, nappies and other sanitary products, etc. Regulations as Oeko Tex Standard 100 [1] and REACH [2] limit the usage of azo dyes in textile and leather products due to their risk associated with tumours of the urinary bladder and carcinoma of the renal pelvis [3]. The maximum limit established in textile materials for aromatic amines, generated by reductive cleavage of azo dyes, is 30 mg/kg. The main goal of this paper was investigation of different methods of azo dyes reduction from colored textile specimens, in order to determine the procedure with the highest selectivity and sensibility. Aromatic amines are generated by chemical degradation achieved by the cleavage of the azo linkage using reducing agents [4]. Different alternatives to sodium dithionite, reducing agent recommended by standard method ISO/FDIS 14362-1[5] were tested, such as: sodium sulfite and tin chloride [6, 7]. Also, xylene

extraction, the common procedure for synthetic fibers was also performed for cotton, dyed with azo dye Direct Blue 6, in order to assess the reliability of common simultaneously extraction and reduction of direct dyes from natural fibres.

## 2. EXPERIMENTAL PART

### 2.1 Materials

**Textile material**: knitted cotton 188g/m2 weight; 0.927 mm thickness.

**Chemical reagents**:

- Xylene, mixture of izomers (Sigma Aldrich)
- Sodium sulfite (Merck)
- Tin chloride (Merck)
- Acetonitrile, ultrapure water, methanol form Sigma Aldrich (Germany).
- Analytical standard of 24 aromatic amine from Sigma-Aldrich and Dr. Ehrenstorfer GmbH (Germany) -> for quantitative determination using calibration curve.

### 2.2 Method

The cotton knit was dyed using equipment RedKrome REDP - Ugolini. Dyeing recipe is described as follows: Direct Blue 6 dye, 3% mass concentration and NaCl solution 20 g/L were maintained at 98ºC for 60 min (**Fig.1**);

- the material was rinsed as follows: at temp. 70ºC- for 15 min
  at temp. 40ºC- for 15 min
  at temp. 20ºC - for 15 min

***Fig. 1:*** *Cotton knit dyed with azoic dye Direct Blue 6*

For aromatic amines determination from textile azo dyes, standard method ISO/FDIS 14362-1 has been applied, alterations of this method being specified in the following. Four textile samples were cut into narrow strips and weighed, as to obtain about 1 g of material/each sample; they were treated as follows:

Sample 1: dye extraction in xylene (although the procedure is specific only to synthetic fibres, we were interested to determinate the extraction products obtined in case of a natural fibre).

Textile material was hung by a inert hook to a refrigerent and introduced into 50 mL round-bottom flask; dyed textile sample was kept in a refrigerent above 25 ml extraction solvent (xylene) for 40 minutes, droplets leaking from the fabric became colorless; the organic extract was allowed to cool down to room temperature, and then the solvent was evaporated in a rotary evaporator for extract concentration (**Fig. 2**); the azo bond cleavage was performed using reducing agent sodium dithionite, 200 mg/mL.

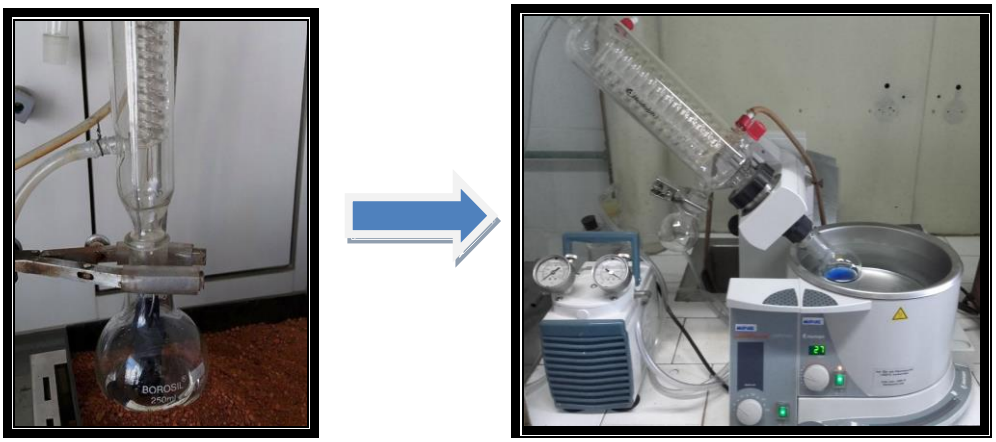

***Fig. 2**. Extraction unit for the extraction of dye and rotary evaporator*

Sample 2: direct dye reduction and cleavage of azo bond, using sodium dithionite, 200 mg/mL
Sample 3: direct dye reduction and cleavage of azo bond, using tin chloride, 200 mg/mL
Sample 4: direct dye reduction and cleavage of azo bond, using sodium sulfite, 200 mg/mL

### 2.3 Qualitative and quantitative determination of aromatic amines

**Instrumentation**

HPLC separation was performed on Agilent 1100 LC System using an Agilent Zorbax Eclipse XDB C18 column with detection on Agilent MWD 1100. GC separation was performed on Agilent 6890 GC System coupled with Agilent 5973N transmission quadrupole mass spectrometer, using standard method ISO/FDIS 14362-1.

## 3. RESULTS

Sample 1

In case of Sample 1, that was subjected to extraction procedure, no aromatic amines were obtained (**Fig. 3, Table 1**), only radicals of azo dyes (alpha-methyl-benzenemethanol, 2-methyl-benzaldehyde) were generated, which means that for natural textiles there is no need for dye extraction, this type of samples can be directly subjected to reductive cleavage of azo bonding.

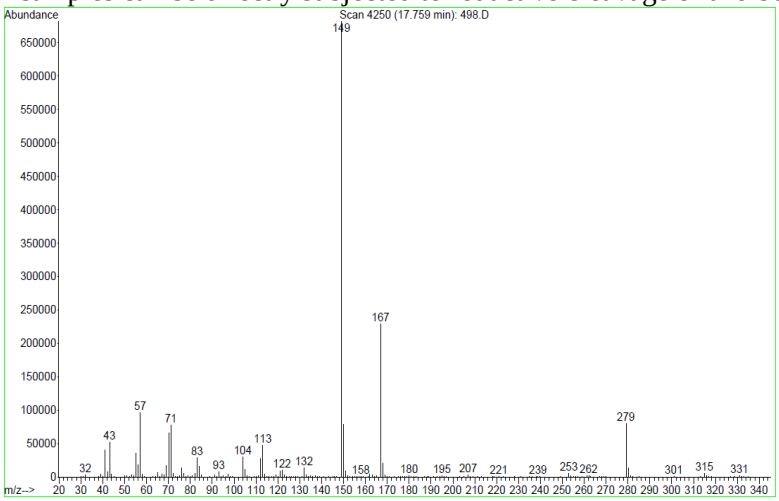


***Fig.3:** Mass spectrum of Sample 1*

***Table 1:*** *Compounds identification using NIST database*

| Compound | Area (%) | Name | CAS # |
|---|---|---|---|
| 1. | 22.88 | alpha-methyl-benzenemethanol | 001445-91-6 |
| 2. | 67.04 | 2-methyl-benzaldehyde | 000529-20-4 |
| 3. | 10.07 | 3-methylbenzyl alchool | 000587-03-1 |

Sample 2

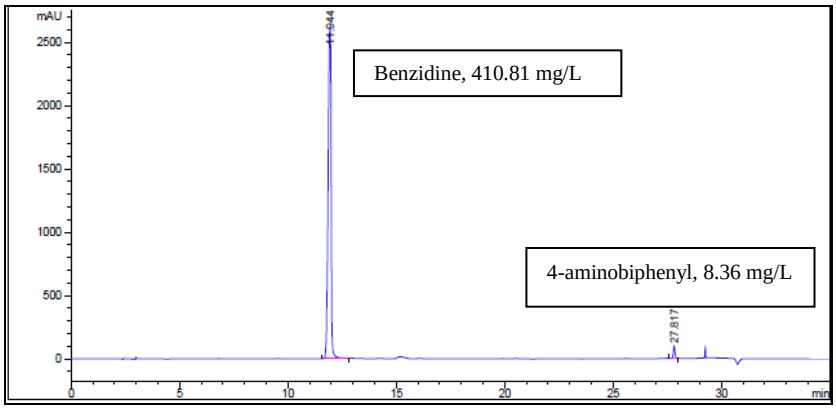


***Fig. 4:*** *HPLC chromatogram of Sample 2*

For sample 2, results indicate a high amount of aromatic amines resulted from degradation of azoic dye, benzidine and 4-aminobiphenyl (Fig. 4); HPLC quantitative results were also confirmed by GC-MS technique (Fig. 5).

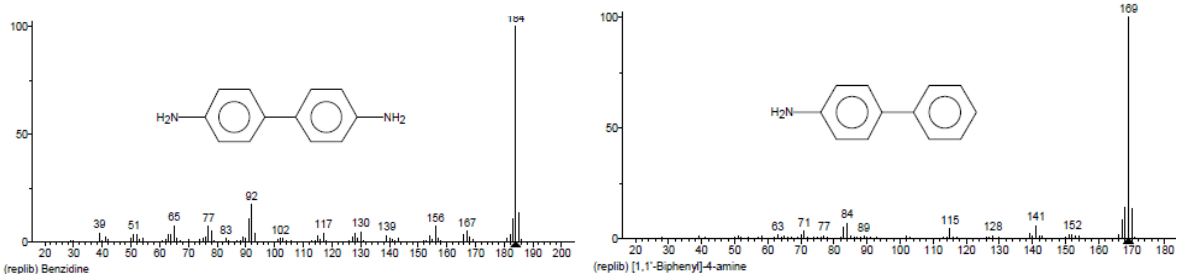


***Fig. 5:*** *NIST confirmation by GC-MS of benzidine and 4-aminobiphenyl*

Sample 3

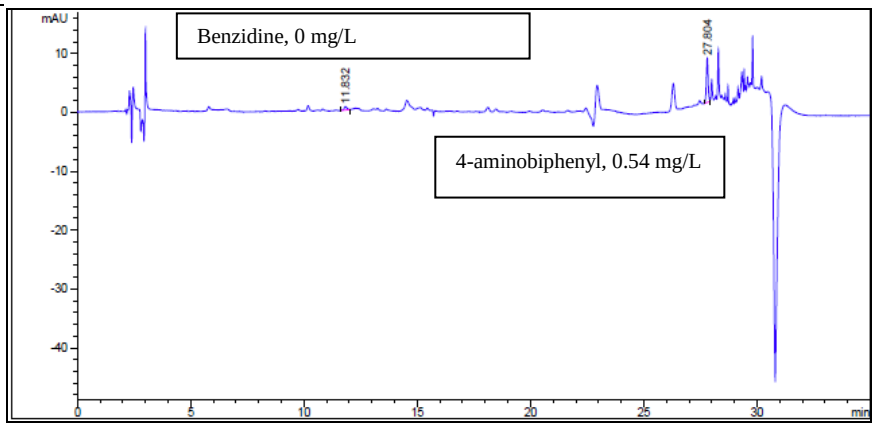


***Fig.6:*** *HPLC chromatogram of Sample 3*

Tin chloride, reducing agent used for cleavage of azo bonding proved to be inefficient in degradation of Direct Blue 6 in aromatic amines (Fig. 6).

Sample 4

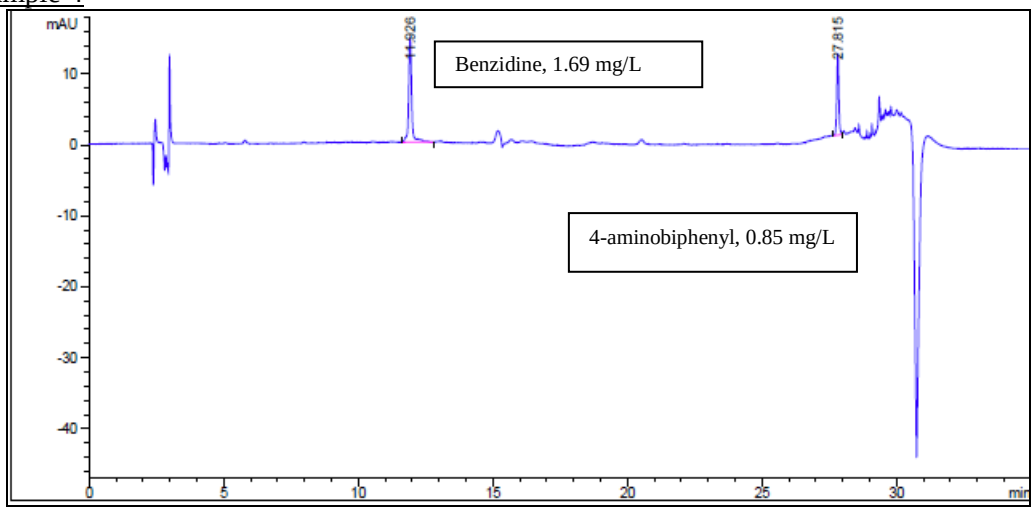


***Fig.7:*** *HPLC chromatogram of Sample 4*

Sodium sulfite, however, managed to reduce the colorant to benzidine and 4-aminobyphenil, but in smaller quantities compared to sodium dithionite (Fig. 7).

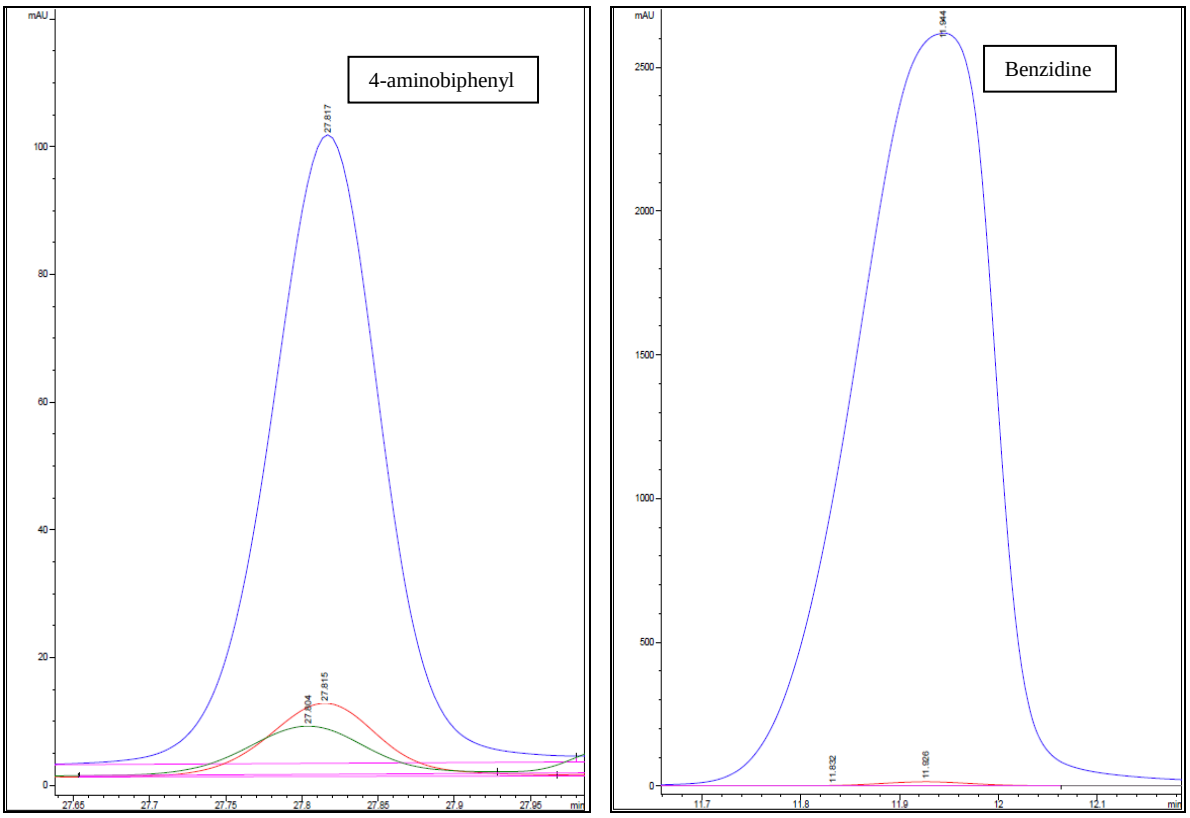


***Fig.8:*** *Overlaid HPLC chromatograms of 4-aminobiphenyl (left) and benzidine (right) in samples 2 (blue), 3 (red) and 4 (green)*

## 4. CONCLUSIONS

Detection of right amount of carcinogenic amines can be made if complete degradation of azo dye is realized, cleavage of azo bonding being possible only with efficient reducing agents; sodium dithionite proved to totally degrade dye solution and form easily detectable aromatic amines.

## ACKNOWLEDGEMENTS

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