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DETERMINATION OF DISPERSE AZO DYES IN INDUSTRIAL TEXTILE WASTEWATER

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ABSTRACT

In the present work qualitative and quantitative determination of synthetic azo dye compounds containing with complex mixtures in textile based industrial wastewater is proposed. Study has been carried out in a three different stage: 1. Sample handling 2. Extraction 3. Measuring. Samples were collected by traditional methods. Because of low solubility of dispersed dyestuff in water, for the extraction of analyte different techniques were applied i.e. liquid-liquid extractions, acid-base extractions and solid phase extractions. Better recovery was achieved with CH_2CI_2 liquid-liquid extraction 99.89%. Determinations were performed using analytical techniques: TLC, UV-VIS, and HPLC-UV. Disperse Red 73 called dyestuff was determined in wastewater both qualitative and quantitative.

INTRODUCTION

A great number of synthetic organic chemicals have been released to the environment via industrial activities. Dye classifications is based on the major functionality of the dye, the main classes being azo, anthraquinone, polymethine, phthalocyanine, sulphur, aryl-methane, stilbene and coumarine dyes [1]. Azo dyes are used by a wide number of industries. Textile industry predominantly use them, this class of compounds can also be present at pharmaceutical, paper and printing, leather and cosmetic industries. Diverse application areas give them majority in wiev of environmental health. Because of these compounds have recalcitrant nature and structural integrity under relative mild environmental conditions such as sunlight, pH, bacteria, and microbial degradation [4]. According to recent information the textile industry is the largest consumer of these products and there is continual demand to develop more applicable dyes. The development of synthetics fabrics such as nylon, lycra, rayon and polyester has required the production of new dyes that can effectively bond to these materials. The U.S Department of Commerce has predicted a 3.5 fold increase in textile manufacturing between 1975 and 2020.Investigations indicates that approximately 12% of the textile dye used each year is lost to waste stream during manufacturing and processing operations and that of those losses will

enter the environment through effluents from wastewater treatment plants. The determination of dyes in environment poses special problems because of their structural diversity. These products are consisting of different chemical compounds with much chemical functionality. In case of azo dye effluents exist in natural and wastewater it cold be carry potential health risk due to carcinogenic aromatic amines (Toluidines, Benzidines, Anilines) as a reduction products of dyes. Azo dyes have been known to resist effective biodegradation in aerobic conditions, and the recalcitrance of azo dyes has been attributed to azo bonds. Therefore, the detection, identification and quantification of azo dyes in wastewater at low levels is important for the protection of environment.

MATERIALS AND METHODS

Disperse azo dyestuffs used as a standard during measurements were purchased from Setas - Chemical Co.Ltd./Turkey. (Disperse Red 1, Disperse Red 13, Disperse Red 73, Disperse Red 167, Disperse Blue 79). Commercial grade dyes were purified with Soxhlet extraction using toluene solvent for 24h before using then 100 mg/ml stock standards were prepared in methanol.

Sample handling

Samples were taken from textile effluent streams down to discharge pipes open (Industrial region Çorlu-Çerkezköy).

Separatory funnel Liquid-Liquid extraction and acid base extractions were performed, better recovery efficiency 99.89% was achieved with methylene chloride (6×30 ml) for Disperse Red 73 determined in study. Solid phase extraction performed with Amberlite XAD-2 non-ionic resin (co-polymer divynil-benzene) show no significant result. To eliminate matrix interferences cheap and simple separation method was employed. Extracted samples were eluted through silica gel bed chromatographic column with solvents having different polarity (n-hexane, diethyl ether, methylene chloride, methanol) in order of increasing polarity. Formed colored fractions then separated and saved.

Measurements

• Qualitative analysis: Saved fractions and stock standards were applied on TLC and most suitable solvent mixture was found as a (n-hexane; methylene chloride; diethyl ether, 2:4:1). Similarity between Rf values of sample fraction and Disperse Red 73 standard was pointed out using TLC. Sample spot was digged and dissolved in methanol and verified again standard on dual-beam UV-VIS spectrophotometer Shimadzu UV-1601 (10 mm cell length, methanol solvent).

• Quantitative analysis was performed using HPLC-UV under conditions: Reverse phase C_{18} Hypersil column, Mobil solvent CH_3OH/H_2O (60%: 40%) with gradient elution. Flow rate: 0.8 ml/min. Detection wavelength 254 nm. Disperse Red 73 standards at concentration 3 ppm and 10 ppm from stock solutions (Fig. 2) and (Fig.3), water sample (Fig.4) HPLC chromatograms were obtained. To avoid solvent peak overlap in chromatograms, methanol chromatogram was also obtained. (Fig. 1). Concentration of Disperse Red 73 in wastewater sample was determined with major peak area calculation that ranged at Rt (retention time) 3.750-3.770 min for 10 ppm,

3.452-3.732 min for 3 ppm and 3.753-3.769 min for sample. Using area under peak centered at Rt 3.70 min, Disperse Red 73 concentration was calculated 0.091 mg/L.

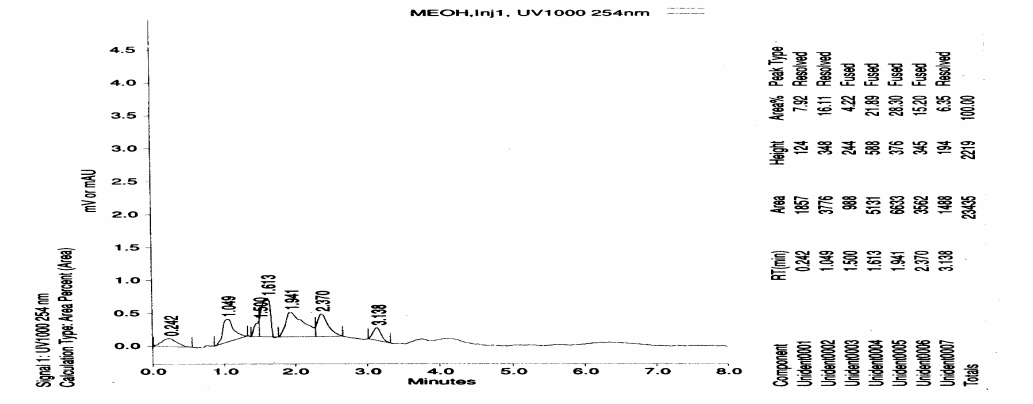

Figure 1. *Solvent (CH_3OH) HPLC-UV chromatogram*

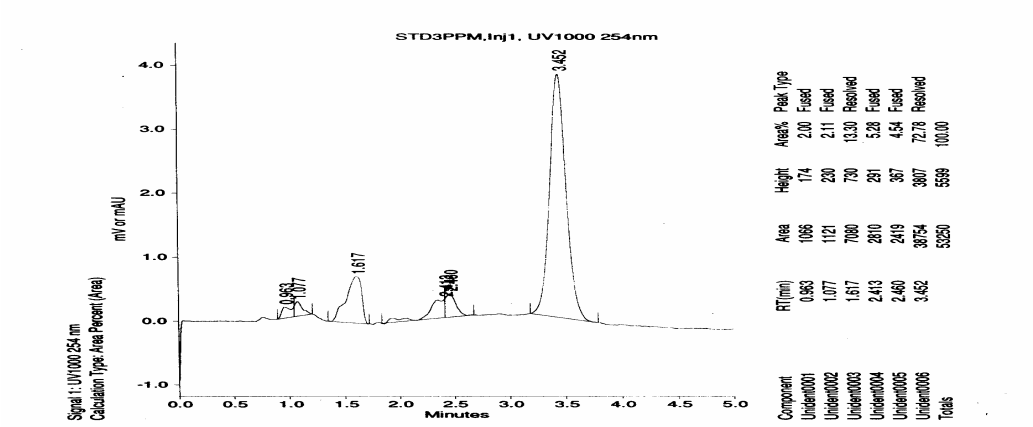

Figure 2.*Standart Disperse Red 73 (3 ppm) HPLC-UV chromatogram*

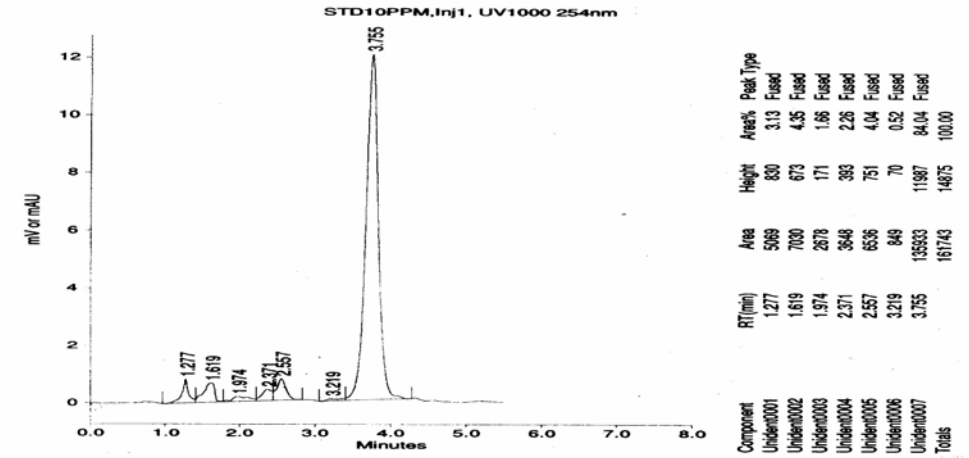

Figure 3. *Standart Disperse Red 73 (10 ppm) HPLC-UV chromatogram*

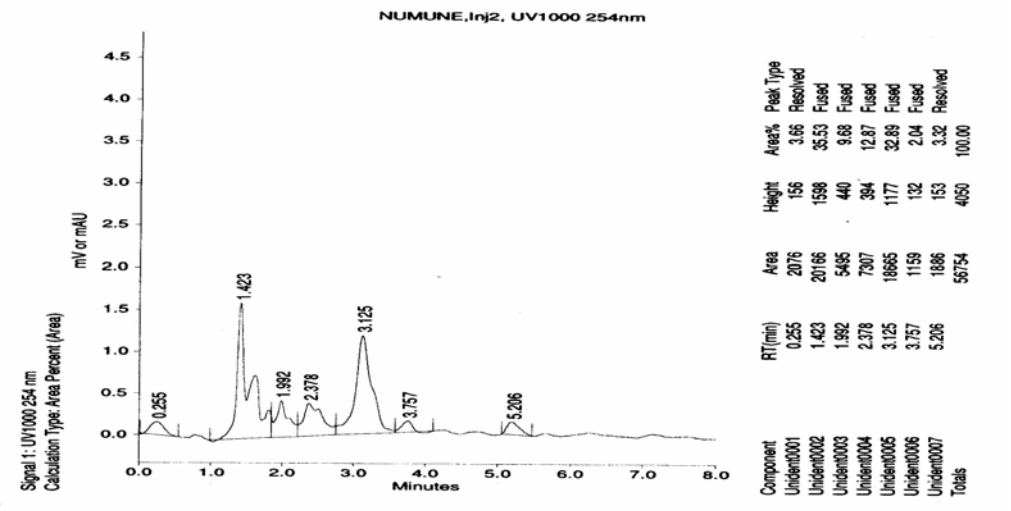

Figure 4. *Water sample HPLC-UV chromatogram*

RESULTS

In evaluation of UV spectrum after applying TLC, narrow absorption band around 200 nm shows that structures have got an aromatic ring, by analyzing composition of the near visible region, spectrum also shows an (-N=N-) azo chromophore at 280 nm. In visible region 506 nm, absorption band proof presence of conjugated system. In the results of HPLC-UV chromatograms, we observed unidentified impurities. The main problem to come across was other pollutants and this matrix was eliminated with useful silica gel column. End of this purification methods, we obtained many colored fraction and these fractions gave us idea about pollution level with dyes.

Although determination of pollution in waste and natural water is made with lower detection using sophisticated instruments such; LC-MS, LC-MS-MS, GC-MS these applications requires experienced stuff and high cost. Despite relative low concentrations were found in wastewater, when huge amount of discharge was taken into consideration seriousness of pollution level can be estimated.

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