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The effect of perspiration on photo-induced chemical reaction of azo dyes and the determination of aromatic amine products

Haiyan Li [a,b,*], Zhongduo Xiong [b], Xibin Dai [b], Qinqfu Zeng [b]

[a] College of Chemical Engineering, Wuhan Textile University, Wuhan 430073, China
[b] Engineering Research Center for Clean Production of Textile Dyeing and Printing, Ministry of Education, Wuhan 430073, China

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ABSTRACT

In order to investigate the impact of perspiration on photo-induced chemical reaction of azo dyes and the carcinogenic aromatic amine products produced from the reaction, we have carried out experimental studies on the photochemical reaction of C.I. Reactive Red 2 mixed with American Association of Textile Chemists and Colorists (AATCC) standard artificial perspiration. UV–vis spectroscopic technique was employed to monitor the reaction processes, and the reaction products were analyzed by hollow fiber protected liquid-liquid-liquid phase micro-extraction with capillary electrophoresis (HF-LLLME-CE). The results showed that perspiration had remarkable influence on the photochemical reaction of azo dyes. Aromtic amines formed during the photochemical process as a result of reduction of azo dyes by organic components in perspiration. The HF-LLLME-CE methodology was validated in analyzing aromatic amines produced from the photochemical degradation of azo dye C.I. Reactive Red 2 and C.I. Acid Red 35 mixed with artificial perspiration.

1. Introduction

Synthetic azo dyes are among the largest and most versatile classes of synthetic dyes with the greatest variety of colors. One side effect of extensive use of these chemicals is the production of potentially carcinogenic compounds [1]. The problem has arisen from the end use of azo dyes as many azo dyes with excellent light fastness show extremely low stability under simultaneous exposure to light and perspiration. The photochemical reactions between metabolic products of human sweat and dyestuffs on garments may produce toxic substances such as carcinogenic aromatic amines, which will directly contact with skin and possess potential harm to human health [2].

In terms of photo-induced chemical reaction of azo dyes, the stability of azo dyes under perspiration-light condition is influenced by three main factors, namely the nature of the dye-fibre bond, the light stability of the released hydrolysed dye molecules, and the performance of the salts [3]. It has been found that reactive dyes exhibit lowest stability when they are exposed simultaneously to light, perspiration and oxygen in a wet environment [4]. Histidine in perspiration has remarkable influence on the fading of azo dyes on cellulose under light [5]. Water soluble anionic azo dyes have been widely used for the coloration of textiles, and investigation of photocatalytic decoloration of these dyes by employing a selected reduction based on bisulfite-mediated borohydride has revealed high toxicity of the degradation products [6]. As the toxicitiy of benzidine-based azo dye is higher than that of azo dye, there is a clear need to develop a treatment process which not only decolorizes the dyes, but also removes the toxic mutagenic components from degradation [7].

In terms of the determination of aromatic amine products, it was confirmed by GC–MS and LC–MS techniques that the reduction of azo dyes via both sodium dithionite and enzyme released similar amines [8]. The high-performance liquid chromatography (HPLC) has been employed to determine the aromatic amines produced from the reduction of azo colorants in toys [9]. HPLC and Capillary zone electrophoresis (CZE) method have been used to separate and detect certain carcinogenic amines liberated from azo dyes following sodium dithionite treatment [10,11].

It is of note that the above discussed studies are mainly focused on two aspects, including the investigation on the impact of perspiration on photo-related fading of azo dyes, and the analytical methodology of aromatic amines released from azo dyes. However, the former did not involve the research of degradation production; while the latter was about the determination of aromatic amines

* Corresponding author. College of Chemical Engineering, Wuhan Textile University, Wuhan 430073, China.
E-mail address: echohyli@163.com (H. Li).

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Table 1
Components of AATCC standard artificial perspiration.

component	concentration(g/L)
L-Histidine hydrochloride	0.25
Lactic acid (85%)	1.0
Disodium hydrogen phosphate	5.0
Sodium chloride	10.0

released from degradation of azo dyes via reacting with chemical reductant (such as sodium hydrosulfite) which was different from that of the photo-perspiration system. Therefore, it is necessary to study the photochemical reaction of azo dyes in perspiration and determine the aromatic amines products formed from the reaction process.

Hollow fiber membrane liquid phase micro-extraction (HF-LLLME), which possesses the advantages of liquid–liquid extraction (LLE) and solid phase micro-extraction (SPME), has been widely used for the separation and enrichment of aromatic amines in the complex matrix [12–15]. Capillary electrophoresis (CE) has been witnessed as one of the most rapidly developed analytical techniques in the past few years due to its attractive features, such as high separation efficiency, reduced analysis time and relatively simple operation [16–18]. The technique of CE coupled with HF-LLLME is advantageous in analyte enrichment, determination efficiency and consuming less organic solvents (μL).

2. Materials and methods

2.1. Chemicals

All chemicals are of analytical grade unless otherwise indicated. Aniline, o-toluidine, 4-chloroaniline and 4-nitroaniline were purchased from Aladdin Reagents (Shanghai, China). Tris–hydroxy methyl aminomethane (Tris), L-histidine, lactic acid, sodium hydroxide, sodium dihydrogen phosphate, sodium chloride, hydrochloric acid were from China National Medicines Corporation Ltd (Shanghai, China). Commercial dye C.I. Reactive Red 2 and C.I. Acid Red 35 was purchased from Guangzhou Rongqing Chemical Products Co., Ltd. (Guangzhou, China).

2.2. Photochemical reactor

A laboratory-scale reactor consisting of a vertical Pyrex tube (310 mm height, 72 mm i.d. and volume 1200 mL) with water-cooling jacket was used. Some part of UV lamp (254 nm, 15 W, Shanghai Yayuan Lighting Appliance Co., Ltd, China) was immersed into the sample solution. The reaction mixture was maintained with magnetic stirring.

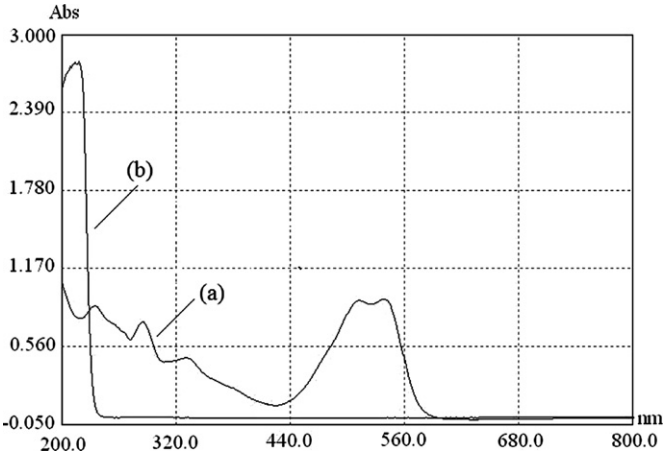


Fig. 1. Absorption spectra of C.I. Reactive Red 2 (a) and AATCC perspiration (b).

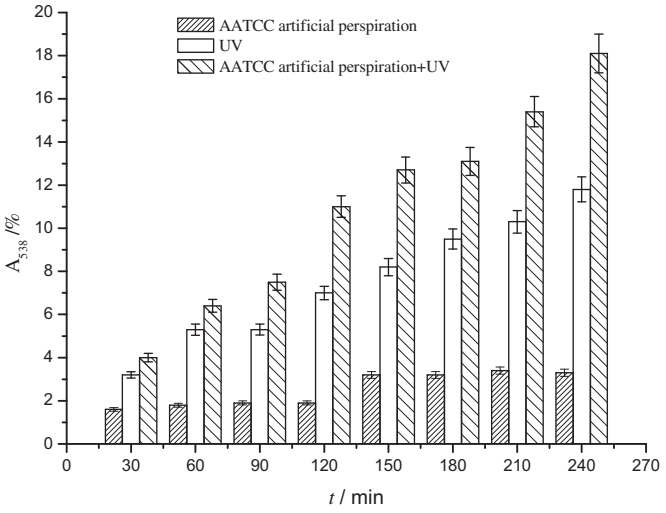


Fig. 2. The decoloration rate of C.I. Reactive Red 2 under different conditions.

2.3. Experimental procedures

2.3.1. The effects of perspiration

The American Association of Textile Chemists and Colorists (AATCC) standard was used as artificial perspiration and its components are shown in Table 1. The simulated dyes-perspiration system was prepared by dissolving part of the AATCC artificial perspiration components or AATCC artificial perspiration into 1.0 L C.I. Reactive Red 2 solution with a concentration of 50 mg/L. All experiments were carried out using 15W UV lamp in the reactor, and samples were taken for analysis at different time intervals.

2.3.2. The effects of pH

1.0 L C.I. Reactive Red 2 solution (50 mg/L) containing AATCC standard artificial perspiration was placed in a quartz reaction vessel and the photo-reaction was carried out with magnetic

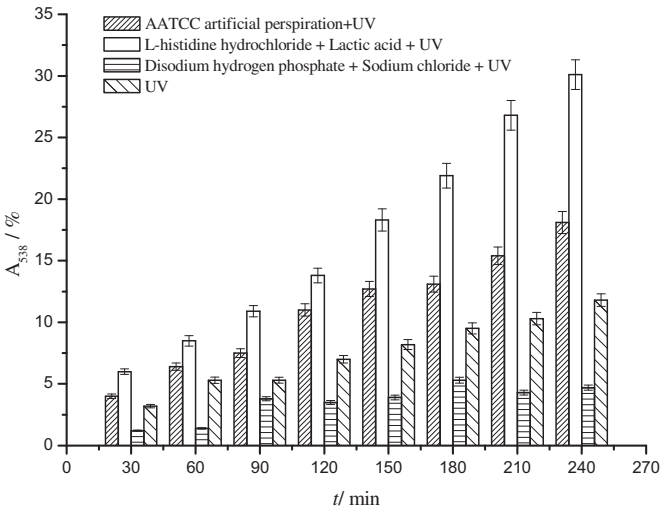


Fig. 3. Effects of the different components of AATCC standard perspiration on decoloration of C.I. Reactive Red 2.

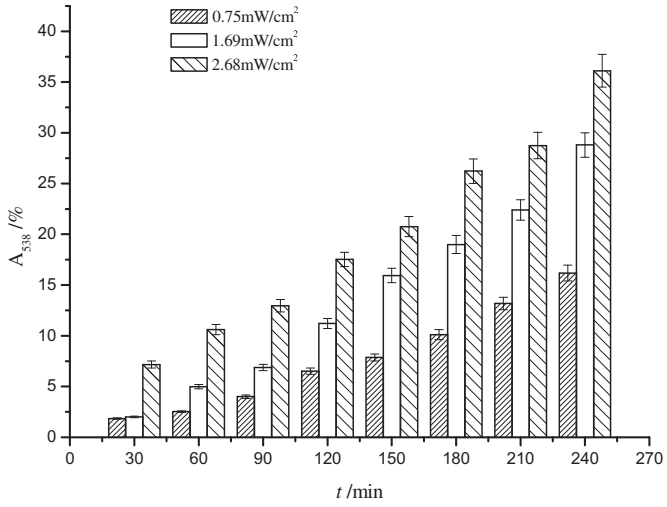


Fig. 4. Effects of light intensity on decoloration of C.I. Reactive Red 2.

stirring. The pH of simulated reaction solution was adjusted by using alkaline (NaOH) or hydrochloric acid (HCl).

2.3.3. The effects of light intensity

1.0 LC.I. Reactive Red 2 solution (50 mg/L) containing AATCC standard artificial perspiration was placed in a quartz reaction vessel and the photo-reaction was carried out with magnetic stirring under different light intensity by using varied number of 15W UV lamps.

2.4. Analysis methods

2.4.1. UV–vis

The UV–vis absorption was recorded with CARY 50 Scan UV–Vis Spectrophotometer (Varian, America) for the wavelength 200 ~ 800 nm. The decoloration percentage of C.I. Reactive Red 2 (A_{538}%) was calculated as below:

$$A_{538}\% = \frac{A_{0,538} - A_{t,538}}{A_{0,538}} \times 100\% \quad (1)$$

Here, $A_{0,\ 538}$ was the absorbance of the initial C.I. Reactive Red 2 solution and $A_{t,\ 538}$ was the absorbance of the C.I. Reactive Red 2 solution measured at different reaction time intervals.

2.4.2. HF-LLLME

The donor phase contained NaOH-NaCl solution at pH 9 with the concentration of NaCl of 200 g/L, while n-octanol was used as organic phase. Hydrochloric acid was used as receving phase with pH at 1, and the extraction time was set up as 60 min. All HF-LLLME experiments were performed using polypropylene hollow fibre membranes (600 μm I.D., 200 μm thickness and 0.2 μm pore size) from Tianjin MOTIMO Membrane Technology Ltd. (China). After extraction, the acceptor solution was analyzed by CE.

Table 2
Kinetic data of photochemical reactions measured for the ATTCC perspiration systems.

light intensity	k	R^2
0.75 mW/cm^2	0.0354	0.9904
1.69 mW/cm^2	0.0713	0.9915
2.86 mW/cm^2	0.1023	0.9894

2.4.3. CE

Capillary chromatography (CE) analysis was carried out on a Beckman Coulter P/ACE™ MDQ, which was equipped with a diode array detector. The condition for CE analysis was set up as: Detection wavelength 194 nm, separation voltage 25 KV, injection pressure 2 psi, injection period 5s. Before each injection, the capillary was sequentially flushed for 2 min under 2 psi pressure with 0.1 mol/L sodium hydroxide, distilled water, and buffer solution, respectively. 30 mmol/L Tris was used as electrophoresis buffer and the pH was adjusted to 3 by using phosphoric acid.

2.4.4. GC-MS

Gas chromatography/mass spectrometry (GC-MS) analysis was carried out using an Agilent HP5973 system. Textiles-Test method for banned azo colourant GC-MS method (The national standards of P R C GB/T 17592.1–1998) was employed in analyzing the aromatic amines produced from the photochemical degradation of azo dye mixed with artificial perspiration.

3. Results and discussion

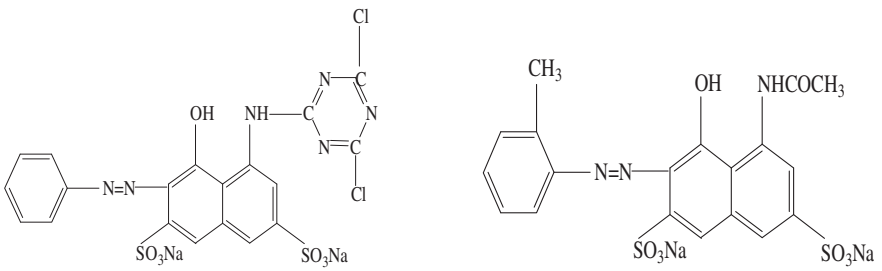
3.1. UV–vis spectrum of C.I. Reactive Red 2 and AATCC artificial perspiration

Fig.1 shows that there is no absorption of AATCC artificial perspiration in the visible light region, indicating that AATCC artificial perspiration has no interference on the measurement of A_{538} for C.I. Reactive Red 2.

3.2. The effect of artificial perspiration

Simulated reaction solution was prepared according to 2.3.1. The decoloration percentage of C.I. Reactive Red 2 in ATTCC artificial perspiration is shown in Fig. 2.

Fig. 2 shows that perspiration has minor effect on the removal of azo dyes. The decoloration rate was 3.3% at reaction time of



C.I. Reactive Red 2 C.I. Acid Red 35

Fig. 5. Molecular structure of azo dyes.

Table 3
The results of standard aromatic amines detection.

Aromatic amilines	Linear range (μg/L)	Detection limit(μg/L)	Enrichment factor	Correlation coefficient	RSD% ($n = 3$)
Aniline	10–100	4	680	0.9987	4.67
O–toluidine	10–100	2	1250	0.9964	6.84
4–chloroaniline	10–100	1	840	0.9982	5.03
4–nitroaniline	10–100	10	410	0.9927	10.81

240 min, and the reduction of azo dyes did not increase with the extension of reaction time. When irradiated by UV light alone, the decoloration rate was gradually enhanced with increase of irradiation time. But for the light-perspiration system, the decoloration rate improved remarkably with the increase of irradiation time. The decoloration rate of 18.9% was observed at 240min, and it was higher than the summation of decoloration rate for perspiration alone and irradiation alone. We may conclude that perspiration has significant impact on the photochemical decoloration of azo dyes.

3.3. The effect of the different components of artificial perspiration

In order to study the effect of different components of AATCC standard towards the decoloration of C.I. Reactive Red 2, the solution of mixture of L-histidine hydrochloride and Lactic acid, disodium hydrogen phosphate and sodium chloride, and AATCC standard perspiration were investigated, respectively. The results are depicted in Fig. 3.

As shown in Fig. 3, the decoloration rate of C.I. Reactive Red 2 is 30.1% in the presence of a mixture of lactic acid and L-histidine hydrochloride, which is higher than the decoloration rate 18.9% with AATCC standard perspiration. This suggests that the organic components of perspiration play major role on the removal of azo dyes. The decoloration rate of C.I. Reactive Red 2 was lower in the presence of a disodium hydrogen phosphate and sodium chloride than in UV alone. We also observed that the decoloration rate of C.I. Reactive Red 2 increased in the absence of disodium hydrogen phosphate and sodium chloride from the ATTCC standard perspiration. These confirmed that the inorganic salt in perspiration has inhibiting function.

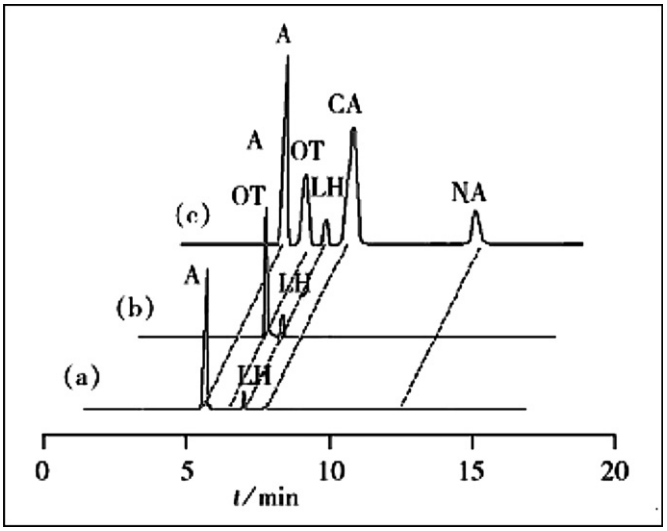


Fig. 6. CE of the synergetic degradation of azo dyes under photo-perspiration (a) degraded sample of C.I. Reactive Red 2 after HF- LLLME, (b) degraded sample of C.I. Acid Red 35 after HF- LLLME, (c) degraded sample of C.I. Reactive Red 2 with 10 μg/L of standard aromatic amines after HF- LLLME.

Table 4
The determination results of aromatic amines generated from azo dye.

sample	Added (μg/L)	Found (μg/L)	Recovery (%)
aniline	10	17.67–18.10	90.8–93.0
O–toluidine	10	16.8–17.10	93.4–97.1

3.4. The effect of pH

In order to evaluate the influence of pH, the decoloration of C.I.Reactive Red 2 was investigated under pH of 3.0, 5.0, 6.8 (initial value) and 9.0, respectively. Simulated reaction solution was prepared according to 2.3.2., and the results of decoloration rate of C.I. Reactive Red 2 in AATCC was 22.3%, 13.8%, 17.9% and 33.7% respectively.

The decoloration rate was enhanced with the increase of pH value in the range of 5.0–9.0. We assume that the basic conditions favor the formation of hydrazone form (=N-N-) from the azo form (-N=N-) under UV radiation, and hydrazone is more apt to be reduced thus promoting the reduction degradation of azo dyes.

3.5. The effect of light intensity

It has been reported that increase of light intensity promotes the oxidation or reduction degradation [6]. A similar result was found as shown in Fig. 4. Simulated reaction solution was prepared according to 2.3.3. The decoloration rate was enhanced with increasing light intensity at the same exposure time. As for a light intensity of 2.68 mW/cm^2, decoloration rate of 35% was reached for C.I. Reactive Red 2 at an irradiation period of 240 min.

Calculation based on the Lambert–Beer law indicated a linear relationship for the $-\ln C_t/C_0 \sim t$ of azo dye. The results in Table 2 show that the removal of C.I. Reactive Red 2 follows the first order kinetics and the apparent rate constant increases with enhanced light intensity.

3.6. Determination of aromatic amine formed from the photochemical reaction of azo dyes-perspiration system

It is normally difficult to directly analyze trace analyte from complex substances due to low concentration and interference. Therefore, HP-LLLME-CE was applied in the present work to analyze the aromatic amines generated from the degradation of azo dyes in the presence of perspiration.

3.6.1. Determination of aromatic amine standard samples

Aniline (A) , o-toluidine (OT) , 4-chloroaniline (CA) and 4-nitroaniline (NA) were representative carcinogenic aromatic amines generated from the degradation of azo dyes in the presence of perspiration. Standard solutions of the four kinds of aromatic amines with concentration of 4 , 10 , 15 and 20 μg/L were prepared by dilution of aromatic amines mixed stock solution (100 mg/L) with AATCC standard. HF-LLLME-CE was employed to analyse the aromatic amines. The detection linear range, detection limit, enrichment factor, correlation coefficient and RSD% ($n = 3$) are summarized in the Table 3.

3.6.2. Determination of aromatic amines generated from azo dyes

Light-induced reductive degradation of azo dyes in perspiration matrix has been reported [5] and the azo bond (-N=N-) is reduced first, followed by the destruction of the large conjugated system within the molecule, resulting the degradation/decoloration and formation of aromatic amines. Aniline would be formed rationalized on the molecular structure of C.I. Reactive Red 2 and o-toluidine generated from C.I. Acid Red 35 Similarly. Molecular structure of azo dyes were showed Fig. 5.

C.I. Reactive Red 2 and C.I. Acid Red 35 simulated solutions were degraded separately under light at intensity 3.5 mW cm^{-2} for 240 min, and the sample were analyzed by HF-LLLME-CE as shown in Fig.6.

In comparison with Fig. 6(c)Fig.6(a) and Fig.6 (b) reveal that aromatic amines were detected with HF-LPME, and the absorption at 7.92min corresponded to L-histidine hydrochloride (LH) from AATCC standard, and the absorption at 5.01min in Fig.6 (a) came from aniline, and at 5.79 min in Fig.6 (b) came from o-toluidine. While Fig.6(c) demonstrates that all the four added aromatic amines have been detected upon application of HF-LLLME, The absorptions in Fig.6(c) were stronger than that in Fig.6(a) due to the addition of standard aniline. The recovery rate of added aromatic amines in the degradation samples of aromatic amines were measured as listed in Table 4 ($n = 3$). The results show that HF-LPME-CE technique is effective and useful in the enrichment, separation and detection of aromatic amines in a complex system.

The GC-MS methodology was employed according to 2.4.4. The determination results were consistent with CE methodology.

4. Conclusion

We have demonstrated the synergistic effect of perspiration towards the photo-induced degradation and decoloration of azo dyes. The photo-perspiration degradation of azo dyes are remarkably affected by the organic components of perspiration and light intensity. The employment of HF-LLLPME-CE could realize the determination of aromatic amines in perspiration matrix and determination of aniline and o-toluidine generated from the photo-induced degradation of aromatic amines under light-perspiration system.

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References

[1] Rauf MA, Ashraf SS. Radiation induced degradation of dyes-An overview. J Hazard Mater 2009;166:6–16.

[2] Oliveira DP, Carneiro PA, Rech CM, Zanoni MV, Claxton LD, Umbuzeiro GA. Mutagenic compounds generated from the chlorination of disperse azo-dyes and their presence in drinking water. Environ Sci Technol 2006;40:6682–9.

[3] Csepregi Z, Aranyosi P, Rusznák I, TÖke L, Víg A. The light stability of azo dyes and azo dyeings II. perspiration-light stability of dyeings with reactive and non-reactive derivatives, respectively, of two selected azochromophores. Dyes Pigm 1998;37:15–31.

[4] Zhuang DH, Zhang LY, Pan DW, He JX. Fading of reactive dyes on cellulose under light and perspiration. Coloration Technol 2007;123:80–5.

[5] Okada Yasuyo, Sugane Akimi, Watanabe Aki, Morita Zenzo. Effects of histidine on the fading of Cu-complex azo dyes on cellulose and a testing method for color fastness to light and perspiration. Dyes Pigm 1998;38:19–39.

[6] Dong YC, Dong WJ, Liu CY, Chen Y, Hua JK. Photocatalytic decoloration of water-soluble azo dyes by reduction based on bisulfite-mediated borohydride. Catal Today 2007;126:456–62.

[7] Bafana A, Chakrabarti T, Muthal P, Kanade G. Detoxification of benzidine-based azo dye by E. gallinarum: time-course study. Ecotoxicol Environ Saf 2009;72:960–4.

[8] Bhaskar M, Gnanamani A, Ganeshjeevan RJ, Chandrasekar R, Sadulla S, Radhakrishnan G. Analyses of carcinogenic aromatic amines released from harmful azo colorants by Streptomyces SP. SS07. J Chromat A 2003;1018:117–23.

[9] Garrigós MC, Reche F, Marín ML, Jiménez A. Determination of aromatic amines formed from azo colorants in toy products. J Chromat A 2002;976:309–17.

[10] Borroós S, Barberá G, Biada J, Agulló N. The use of capillary electrophoresis to study the formation of carcinogenic aryl amines in azo dyes. Dyes Pigm 1999;43:189–96.

[11] Ding JH, He HX, Lin HL, Zhang H, Qiu CF. Determination of cancerogenic aromatic amines from textiles using ionic liquid-based liquid phase micro-extraction coupled with high performance liquid chromatography. Chin J Anal Chem 2008;36:1662–6.

[12] Sarafraz-Yazdi A, Amiri A. Liquid-phase microextraction. Trends Anal Chem 2010;29:1–14.

[13] Yunli W, Bin H. Simultaneous determination of several phytohormones in natural coconut juice by hollow fiber-based liquid–liquid–liquid microextraction-high performance liquid chromatography. J Chromat A 2009;1216:7657–63.

[14] Deng Y, Wellons A, Bolla D, Krzyaniak M, Wylie H. Separation and identification of photodegradation products of benzoic acid by capillary zone electrophoresis. J Chromat A 2003;1013:191–201.

[15] Zhao RS, Lao WJ, Xu XB. Headspace liquid-phase microextraction of trihalomethanes in drinking water and their gas chromatographic determination. Talanta 2004;62:751–6.

[16]. Bossi A, Piletsky SA, Turner APF, Righetti PG. Repartition effect of aromatic polyaniline coatings on the separation of bioactive peptides in capillary electrophoresis. Electropho 2002;23:203–8.

[17] Ye SQ, Huang F. Separation of carcinogenic aromatic amines in the dyestuff plant waste water treatment. Desalination 2007;206:78–85.

[18] Sun H, Lau KM, Fung YS. A new capillary electrophoresis buffer for determining organic and inorganic anions in electroplating bath with surfactant additives. J Chromat A 2010;1217:244–3250.