Dyes and Pigments 84 (2010) 218–222

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

A novel method for the recovery of 4,4′-dinitrostilbene-2,2′disulfonic acid from the wastewater obtained from 4,4′-diaminostilbene-2,2′-disulfonic acid production

Wenchao Peng, Xiaobin Fan, Shulan Wang, Guoliang Zhang, Fengbao Zhang*

School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, People's Republic of China

ARTICLE INFO

Article history:
Received 6 May 2009
Received in revised form
25 August 2009
Accepted 6 September 2009
Available online 11 September 2009

Keywords:
Recycle
Oxidation
Wastewater
Reduction
Acidification
Precipitate

ABSTRACT

HPLC and electrospray ionization tandem mass spectrometry were used to show that ~30% of the DNS present in wastewater was reduced to 4-amino-4′-nitrostilbene-2,2′-disulfonic acid and 4,4′-diaminostilbene-2,2′-disulfonic acid during multiple-effect evaporation. A novel recovery method, which combines acidification and subsequent reduction, recovered of ~90% of the DNS that is lost during evaporation and, thereby, increased the yield of 4,4′-diaminostilbene-2,2′-disulfonic acid by 5%. In addition, many of the organic compounds present in the wastewater were removed.

1. Introduction

4,4′-diaminostilbene-2,2'disulfonic acid (DSD) is an important industrial intermediate widely used in production of direct dyes, fluorescent brighteners and mothproofing agents [1–5]. The preparation of DSD includes three steps [6] namely, sulfonation of *p*-nitrotoluene (PNT) to *p*-nitrotoluene-o-sulfonic acid (PNTSA) [7,8], oxidation of PNTSA to 4,4′-dinitrostilbene-2,2'disulfonic acid (DNS) [9], and reduction of DNS to DSD with iron powder [10]. 4-amino-4′-nitrostilbene -2,2′-disulfonic acid (ANSD) is another intermediate that can be further reduced to DSD, and is thus usually regarded as a minor byproduct of DSD. The mechanisms involved are illustrated in Fig. 1.

Normally, both sulfonation (Fig. 1a) and reduction (Fig. 1c) can be readily carried out with yields >98%, whereas the oxidation stage (Fig. 1b) is typically only ≤86% [1], which can (at least partly) be attributed to the excellent solubility of DNS in the wastewater. Whilst recycling based on multiple-effect evaporation is usually employed to recover DNS from the oxidation wastewater [11] (Fig. 2a), during this procedure, side reactions occur and a considerable amount of DNS (~30% of the amount in the oxidation wastewater) is lost, resulting in a decrease (5.5%) in the final yield of DSD.

This work concerns the study of the reactions of DNS that occur during the evaporation process using high-performance liquid chromatography (HPLC) equipped with photodiode array (PDA) and electrospray ionization tandem mass spectrometry (LC–ESI-MS/MS) [12–14]. As the lost DNS was reduced to ANSD and DSD, a novel method was developed to improve the yield of DSD (Fig. 2b) which combines an acidification process and subsequent filtration to recover the majority of the DNS, ANSD and DSD present in the evaporated wastewater, followed by reduction of the filter cake with iron to obtain pure DSD. The improved process not only increases the final yield of DSD by ~5% but also removes most of the organic matter.

2. Materials and methods

2.1. Materials

4,4′-dinitrostilbene-2,2'disulfonic acid (DNS), 4,4′-diaminostilbene-2,2′ disulfonic acid (DSD), and 4-amino-4′-nitrostilbene-2,2'disulfonic acid (ANSD) were provided by Huayu Chemical Company, Cangzhou, China, and were recrystallized from water to obtain purities of 99.5%. The powdered iron with relatively coarse grain size (mostly >40 mesh) was supplied by Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China. Other

* Corresponding author.
E-mail address: fbzhang@tju.edu.cn (F. Zhang).

0143-7208/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2009.09.005

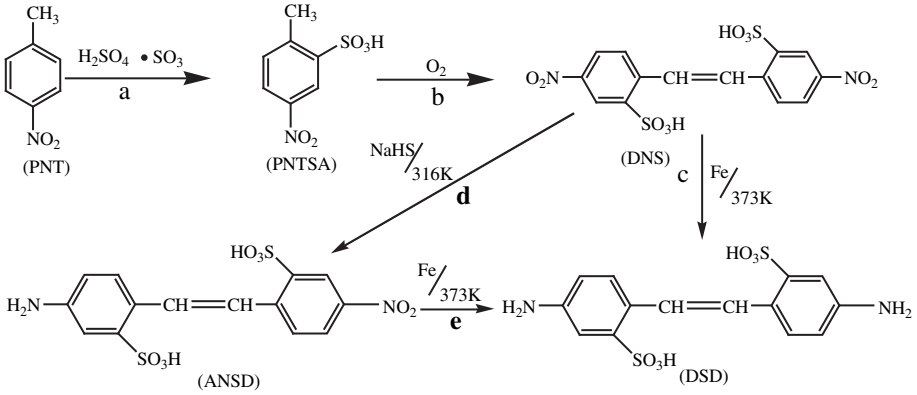

Fig. 1. The industrial process of DSD acid production. (a), sulfonation; (b), oxidation; (c), reduction of DNS to DSD; (d), reduction of DNS to ANSD; (e), reduction of ANSD to DSD.

chemical reagents and solvents (Merck) were either analytical or chromatography grade and were used without further purification.

2.2. Analysis

2.2.1. Sample preparation

Oxidation wastewater and evaporated wastewater (see Fig. 2) samples produced on various dates (five groups of samples) were collected from the Huayu Chemical Co. (Cangzhou, China) and stored at 4 °C. Before being injected into the HPLC, they were diluted and filtered through 0.22 μm membranes.

2.2.2. HPLC-PDA analysis

Analysis of the wastewater was performed with a Finnigan Surveyor HPLC integrated with quaternary gradient pumps, photodiode array detector, auto injector, degasser and system controller (all from Thermofisher Scientific, San Jose, CA, USA). A reversed-phase Hypersil ODS-2 C18 column (250 × 4.6 mm i.d., 5 μm particle size) (Thermo Scientific, US), with a guard column made of the same packing material, was used for separation. The mobile phase was acetonitrile–0.01 M ammonium acetate, and the elution profile was as follows: initially 100% 0.01 M ammonium acetate, then 8% acetonitrile after 8 min, 25% acetonitrile after 35 min, and 100% 0.01 M ammonium acetate after 40 min. The mobile phase was filtered through a 0.45 μm PTFE filter and degassed using ultrasound before passing through the column. The analysis was carried out at 0.8 mL min^{-1} flow rate at 25 °C. Xcalibur software was used for data acquisition and processing. The LC conditions described were suitable for ESI-MS because ammonium acetate did not impair the analysis by MS [12,14]. The analytes were identified by ESI-MS, and identification was confirmed by comparing their retention times with those of high purity standards.

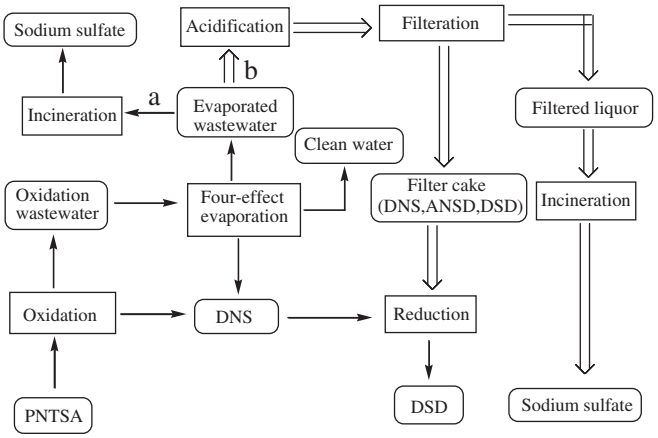

Fig. 2. The recycle method of the oxidation wastewater. (a), conventional method; (b), new method.

2.2.3. LC–ESI-MS analysis

LC–ESI-MS analysis was performed with a Finnigan Surveyor HPLC and autosampler coupled with an LCQ Advantage Max ion-trap mass spectrometer (Thermofisher Scientific, San Jose, CA, USA) equipped with electrospray (ESI) and atmospheric pressure chemical ionization (APCI) interfaces. The chromatographic separation was carried out using the conditions described in Section 2.2.2. Analysis was performed with an ESI interface in the negative-ion mode; the MS full scan range was 150–550 *m*/*z*. Spray voltage was 5.0 kV and the ion transfer capillary temperature was 300 °C. Nitrogen was used as

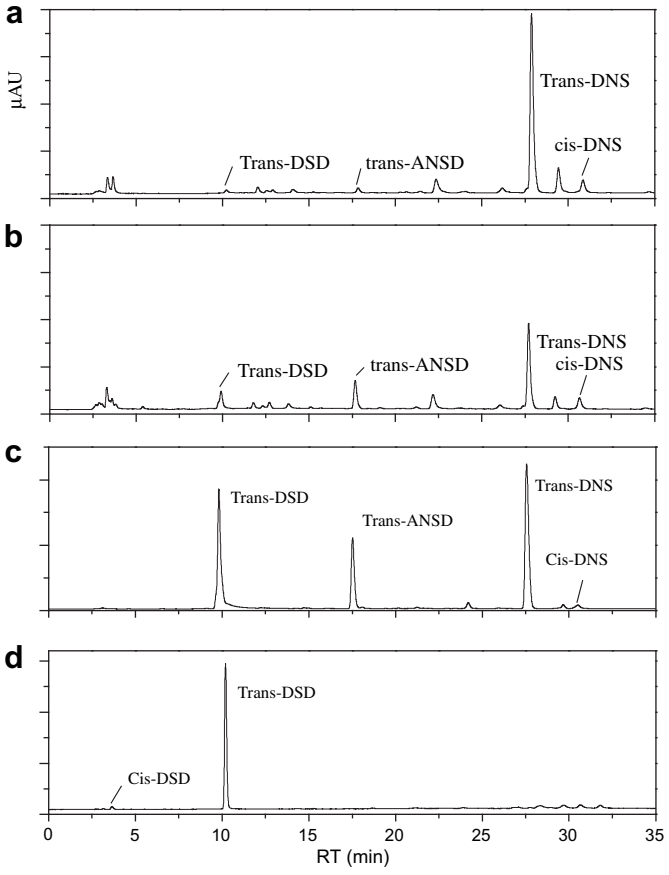

Fig. 3. HPLC chromatographs of (a), the wastewater before evaporation; (b), the wastewater after evaporation; (c), the filter cake before reduction; (d), the DSD acid product after the reduction.

sheath and auxiliary gases with flow rates set at 35 and 5 (arbitrary units defined by the software), respectively. The normalized collision energy for MS/MS experiments was 35% of the maximum settings. The precursor ion isolation width was 1.5 u (arbitrary units). The relative activation Q was chosen as 0.25 (default value), and the intensity thresholds of the ions in MS^2 were 1×10^5.

2.3. pH selection

The pH of 100 mL of evaporated wastewater in a 250 mL beaker was adjusted to the desired value with sulfuric acid, and the solution was allowed to stand for 12 h to precipitate DNS, ANSD and DSD. After filtration, the filter cakes were dissolved in water and analyzed by HPLC. By using external standards the amounts of DNS, ANSD and DSD were calculated. These experiments were carried out at a range of pH values to determine the recoverable amount of these substances, with five replicates at each pH.

2.4. Recycling of the oxidation wastewater

100 mL evaporated wastewater was adjusted to pH2.3 with sulfuric acid to precipitate the DNS, ANSD and DSD. After filtering, the filter cake was reduced with iron powder (Fig. 1c and 1e) to form DSD which was washed with dilute sulfuric acid (pH ~ 1) to remove impurities. Repeated experiments (five replicates) showed that the final DSD product was obtained with purity >97%.

3. Results and discussion

3.1. External calibration

Owing to the different absorption wavelengths of the compounds involved, the LC method (at 310 nm) was used for the separation and quantitative determination [14]. External calibration was used for the quantification of DNS, ANSD and DSD in the wastewater and in the filter cake by HPLC. Given that the amounts of the cis isomers were small, they were ignored in the following computation. Calibration plots of peak area versus concentration were obtained for the three analytes by linear regression of five data points in the range 1–500 ng at 310 nm with correlation coefficients $r^2 > 0.999$. The linear regression equations for trans-DNS, trans-ANSD and trans-DSD were $Y = 3.2x - 8003.4$, $Y = 9.1x + 779.9$ and $Y = 1.5x - 912.2$, respectively, where x is concentration of the analyte (g L^{-1}) and Y is peak area.

3.2. Dominant component identification

HPLC and ESI-MS chromatograms of the wastewater before and after evaporation are shown in Figs. 3 and 4. Analysis of the five groups of samples showed that they all had the same composition except for small differences in relative proportions of the components: the chromatograms shown are representative. Fig. 4 shows that the m/z values of the analytes at 9.82, 17.52 and 27.56 min were 369, 399 and 429, respectively. Consequently, the molecular weights (M_r) for the three analytes were 370, 400 and 430 using the negative-ion mode, corresponding to DSD, ANSD and DNS, respectively [15]. This conclusion is supported by the fragment ions data given in Table 1. The identification of the analytes was confirmed by comparing their retention times with those of high purity reference samples of those compounds.

3.3. Side reaction identification

From the HPLC chromatograms of the wastewater before and after evaporation (Fig. 3a and b) and the external calibrations, it was found that about 30% of the DNS component was lost during evaporation.

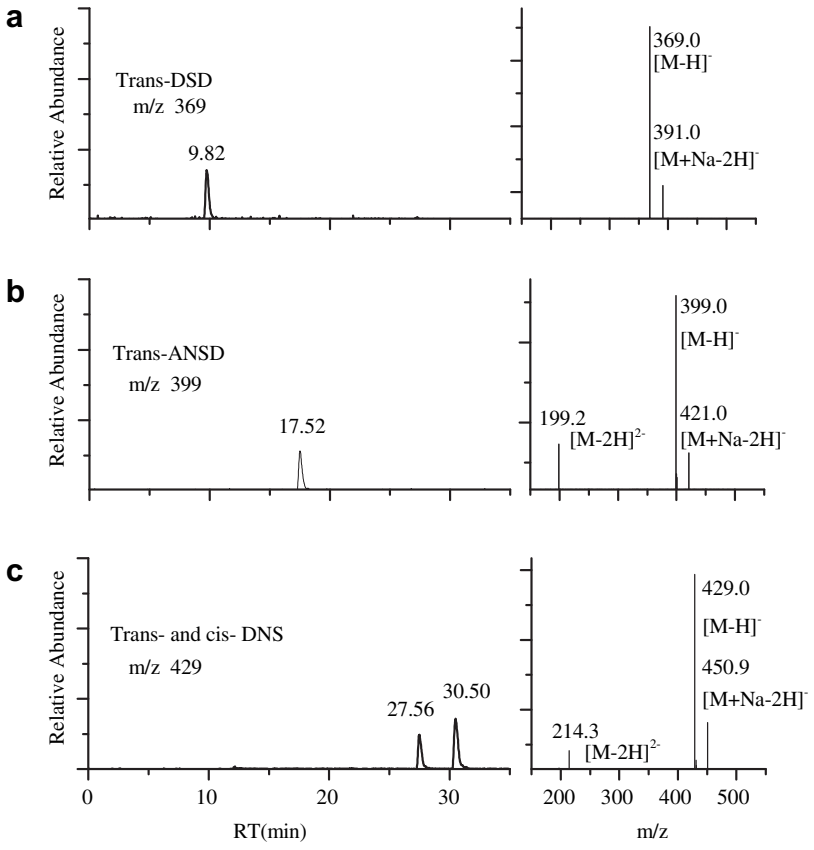

Fig. 4. Mass spectrum and m/z information of (a) trans-DSD, (b) trans-ANSD, (c) trans- and cis- DNS.

Table 1
MS/MS data of the main compounds in negative-ion mode.

Compound	Retention time	Molecular weight (g mol^{-1})	Collision voltage (V)	Precursor ion(m/z)[M-H]$^-$	Common fragment (m/z) SO_3^-	Other fragment ion [M-H-X]$^-$, X was given below the m/z value	
Trans-DSD	9.82	370	35	369	80	289 $-SO_3$	
Trans-ANSD	17.52	400	35	399	80	353 $-NO_2$	319 $-SO_3$
Trans-DNS	27.56	430	35	429	80	383 $-NO_2$	349 $-SO_3$
Cis-DNS	30.50	430	35	429	80	383 $-NO_2$	349 $-SO_3$

In addition, the amounts of ANSD and DSD increased, indicating they were formed during evaporation of the wastewater. These results suggested that a significant amount of DNS was reduced to DSD and ANSD during the evaporation process.

On the basis of that finding, we speculated that the loss of DNS could be minimized by recovering the ANSD and DSD products from the wastewater after evaporation. Moreover, since DNS, ANSD and DSD constitute the major proportion of the organic compounds dissolved in the wastewater (Fig. 3b), recovery of those compounds would also facilitate subsequent wastewater treatment [16–18].

3.4. pH selection

Since the solubilities of DNS, DSD and ANSD decrease rapidly with decreasing pH, they can be readily recovered from the wastewater by precipitation in acidic conditions. The experiments in Section 2.2 at eight pHs were performed to determine the optimum pH for maximum total amount of recovered DNS, DSD and ANSD. A representative HPLC chromatograph result of the filter cake (obtained at pH 2.3) is shown in Fig. 3c. Using the linear regression equations in Section 3.1, the amounts of DNS, ANSD and DSD were calculated, and the total amounts of these substances were thus obtained. These data for the 8 pH values were fitted by non-linear regression to obtain curves for the pH dependence of the amounts recovered (Fig. 5).

Fig. 5a shows the recovery of the DNS increasing with pH decrease from 4 to 2.2 then decreasing with further decrease of pH from 2.2 to 0.5. Similar trends were obtained for DSD and ANSD, with recovery maxima at different pHs. The pH values for optimum recovery of DNS, ANSD and DSD were found to be 2.2, 2.8 and 1.8, respectively. To avoid a complicated and costly procedure of sequentially decreasing the pH for each substance, one-step precipitation at an optimized pH was employed. Fig. 5b shows that the total amount of recovered DNS, DSD and ANSD was maximum at pH2.3 and hence this optimum pH was used for subsequent experiments, giving >90% recovery of DNS, DSD and ANSD.

3.5. Reduction

In view of the fact that both DNS and ANSD can be reduced to DSD, the filter cake containing DNS, ANSD and DSD could be reduced to DSD products [10,19]. The reactions involved are shown in Fig. 1c and e.

The HPLC results (Fig. 3c and d) show that DNS and ANSD disappear with significant increase of DSD after the reduction treatment, indicating successful reduction of DNS and ANSD. DSD with purity >97% was easily obtained by simply washing the DSD, obtained by reduction of the filter cake, with dilute sulfuric acid (pH ~ 1).

3.6. The novel recovery method

On the basis of the results discussed above, a novel recovery method (Fig. 2b) was developed to increase the yield of the DSD production. This new method can recover >90% of the DNS, ANSD and DSD dissolved in the evaporated wastewater by acidification, then reduction of the filter cakes with iron to convert DNS and ANSD to DSD. In industrial scale production, the amount of evaporated wastewater produced is about 4 $m^3\ T^{-1}$ of DSD production. By using the novel recovery process shown in Fig. 2b, an additional 50 kg DSD can be recovered so that the yield of DSD can be increased by 5%. That increase in DSD yield requires 2 kg sulfuric acid and 15 kg iron powder. Since the price of DSD is about 200 times and 10 times more than the costs of sulfuric acid and iron powder, respectively, the cost of DSD production can be reduced by about 5%. Moreover, because DNS, ANSD and DSD are the major organic components of the wastewater after evaporation, the

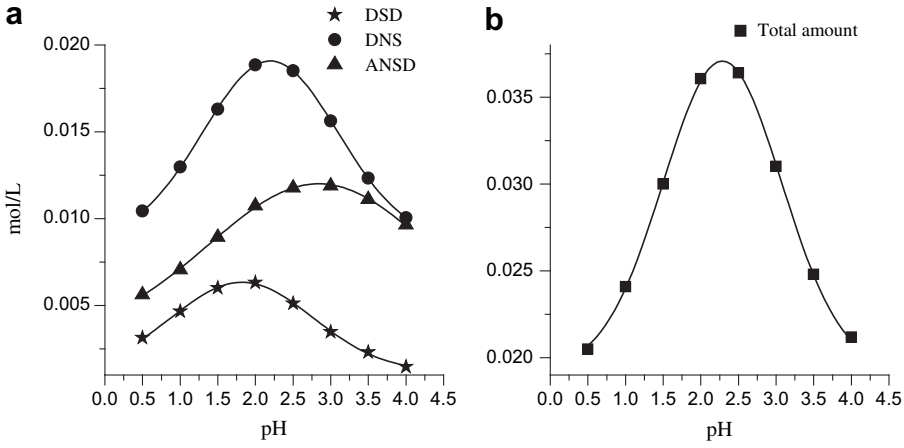

Fig. 5. The (a) amounts of DSD, ANSD and DNS recovered, (b) total amount recovered; at different pHs at 25 °C.

acidification/filtration used in this new recovery method removes most of these compounds and greatly facilitates further treatment of the wastewater.

We attempted another method for recovering the DNS lost in the evaporation process. The oxidation wastewater was first reduced to obtain DSD from ANSD and DNS, and the DSD was recovered by acidification. This method can recover more DSD because of the small solubility of DSD in acidic conditions (Fig. 5a). However, a red impurity (5-amino-2-formylbenzenesulfonic acid) was formed and was difficult to remove from the DSD product [20].

4. Conclusions

In the conventional recycling process much DNS is lost during multiple-effect evaporation of the oxidation wastewater, due to side reactions. By using HPLC-PDA and HPLC-ESI-MS, it was found that about 30% of the DNS in the wastewater is reduced to DSD and ANSD. A new method combining acidification and subsequent reduction with iron can recover more than 90% of the DNS lost during the evaporation process and give DSD with purity >97%. This treatment can increase the yield of DSD by 5%, and in addition remove most of the organic compounds in the wastewater [21], greatly facilitating further treatment of the oxidation wastewater.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No: 20776095) and the Program of Introducing Talents of Discipline to Universities (China, No: B06006).

References

[1] Liu Y, Zhang FB, Zhang GL. Kinetic study on the preparation of 4,4′-dinitrostilbene-2,2′-disulfonic acid (I) – kinetic study on the oxidation of 4,4′-dinitrobibenzyl-2,2′-disulfonic acid to prepare 4,4′-dinitrostilbene-2,2′-disulfonic acid. Dyes and Pigments 2003;56:181–7.
[2] Liu Y, Zhang FB, Zhang GL. Kinetic study on the preparation of 4,4′-dinitrostilbene-2,2′-disulfonic acid (II) – kinetic on the oxidation of p-nitrotoluene-o-sulfonic acid to 4,4′-dinitrobibenzyl-2,2′-disulfonic acid. Dyes and Pigments 2005;66:43–8.
[3] Modi BR, Naik NM, Naik DN, Desai KR. Synthesis of 4,4′-bis[(4-morpholino-6-arylureedo-s-traizin-2-yl)amino]stilbene-2,2-disulphonic acid derivatives and their use as fluorescent brig. Dyes and Pigments 1993;23:65–72.
[4] Rajagopal R, Seshadri S. Light-stabilised azo dyes containing a built-in ultraviolet absorber residue. Dyes and Pigments 1988;9:233–41.
[5] Rachel A, Lavedrine B, Aguer JP, Boule P. Photochemical study of 4,4′-dinitrostilbene-2,2′-disulfonate (DSD) degradation in water. Journal of Photochemistry and Photobiology A-Chemistry 2002;151:137–43.
[6] Li GZ, Zhang FB, Zhang GL, Han J. Recovery of Na2SO4 from remediation of wastewater and reuse for preparation of sodium 4-nitrotoluene-2-sulfonate (NTSNa). Desalination 2006;194:176–81.
[7] Green AG, Marsden F, Scholefield F. The colouring matters of stilbene group[J]. Journal of the Chemical Society 1904;85:1432–8.
[8] Mezei C.C., Georgescu N., Preparation process and plant for p-nitrotoluene-2-sulfonic acid.
[9] Skipka G., duerholz F., 4,4'-dinitrostilbene-2,2'-disulfonic acid salts.
[10] Lund B.R., Brown G.W., Bechamp Recuction of DNS to DAS using H_2SO_4 and trace of HOAc, 1987.
[11] Keith R.M., Karlapudi R., Richard M.S., 2004.
[12] Rao RN, Venkateswarlu N, Khalid S, Narsimba R, Sridhar S. Use of solid-phase extraction, reverse osmosis and vacuum distillation for recovery of aromatic sulfonic acids from aquatic environment followed by their determination using liquid chromatography-electrospray ionization tandem mass spectrometry. Journal of Chromatography A 2006;1113:20–31.
[13] Knepper TP. Mass spectrometric strategies for the analysis of polar industrial chemicals and their by-products in wastewater and surface water. Journal of Chromatography A 2002;974:111–21.
[14] Rao RN, Venkateswarlu N, Khalid S, Narsimha R. LC-PDA and LC-ESI-MS separation and determination of process-related substances arising from stilbene-type fluorescent whitening agents. Application to monitoring of their photodegradation products in industrial effluents and aqueous environmental systems. Journal of Separation Science 2005;28:443–52.
[15] Holcapek M, Volna K, Vanerkova D. Effects of functional groups on the fragmentation of dyes in electrospray and atmospheric pressure chemical ionization mass spectra. Dyes and Pigments 2007;75:156–65.
[16] Chai LM, Zhang FB, Zhang GL. Treatment of DSD acid wastewater using a weak basic resin. Desalination 2005;180:157–62.
[17] Zhu WP, Lang ZH, Wang L. Application of ferrous hydrogen peroxide for treatment of DSD-acid manufacturing process wastewater. Water Research 2001;35:2087–91.
[18] Yu G, Zhu WP, Yang ZH. Pretreatment and biodegradability enhancement of DSD acid manufacturing wastewater. Chemosphere 1998;37:487–94.
[19] Keum YS, Li QX. Reduction of nitroaromatic pesticides with zero-valent iron. Chemosphere 2004;54:255–63.
[20] Wong-Wah-Chung P, Mailhot G, Pilichowski JF, Bolte M. Competitive oxidative cleavage and epoxidation of 4,4′-diaminostilbene-2,2′-disulfonic acid by Fe(III) aqua complexes. New Journal of Chemistry 2004;28:451–6.
[21] Azbar N, Yonar T, Kestioglu K. Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent. Chemosphere 2004;55:35–43.