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Kinetics and mechanism study on the preparation of 4,4′-diaminostilbene-2,2′-disulfonic acid by reduction of 4,4′-dinitrostilbene-2,2′-disulfonic acid with zero-valent iron

Xiaobin Fan, Fengbao Zhang*, Guoliang Zhang, Guozhu Li

School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China

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Abstract

This research is aimed at improving the understanding of the reduction of 4,4′-dinitrostilbene-2,2′-disulfonic acid (DNS) by zero-valent iron for the manufacture of 4,4′-diaminostilbene-2,2′-disulfonic acid (DSD). The formation of 5-amino-2-formylbenzene sulfonic acid (ABAS) during the process indicates that oxidation with the cleavage of C=C double bond does occur besides the principle nitro-group reduction processes. The kinetics of the reduction of DNS and the formation of DSD are pseudo-first order. Typical k_{obs} and k'_{obs} for the reduction of DNS and formation of DSD are $0.10898 \pm 0.01841\ \text{min}^{-1}$ and $0.07167 \pm 0.00213\ \text{min}^{-1}$, respectively (with 20 g/L, 60–80 mesh and the BET surface area of $0.815\ \text{m}^2\ \text{g}^{-1}$ zero-valent iron, at 40 rpm mixing rate, 24 °C, neutral unbuffered conditions). Surface-area normalized rate constant (k_{SA}) for the reduction of DNS is $0.4012\ \text{L m}^2\ \text{h}^{-1}$. The effects of Fe^0 concentration, rate of mixing and temperature on the k_{SA} were investigated, and the results indicate that the rates of reaction were controlled by mass transfer.

Keywords: 4,4′-Dinitrostilbene-2,2′-disulfonic acid; Zero-valent iron; Kinetics; Reduction; 4,4′-Diaminostilbene-2,2′-disulfonic acid; 5-Amino-2-formylbenzene sulfonic acid; Mechanism

1. Introduction

4,4′-Diaminostilbene-2,2′-disulfonic acid (DSD) is an important industrial intermediate widely used in producing direct dyes, fluorescent brighteners and mothproof agents [1]. The reduction of 4,4′-dinitrostilbene-2,2′-disulfonic acid (DNS) is the final process in the synthesis of DSD. In this process, reduction methods in industrial scale include Bechamp method [2,3], the catalytic hydrogenation [4–8] and the electrochemical method [9–16]. Bechamp method (reduction of DNS by Fe^0) is of most interest, not only for its outstanding performance, but also because it is the most inexpensive and widely used methods of DSD synthesis.

However, in the last decades, scarce study has reached the kinetics and mechanism of the reduction of DNS by Fe^0. Although Terc suggested that stirring and the size of Fe^0 particles play an important role in the synthesis of DSD and the consumption of iron approaches the theoretical stoichiometric ratio as the size of Fe^0 particles is lowered to about 0.1 mm. [17], the author failed to incorporate the influence of these factors into the kinetic model and provide mechanistic insight. Furthermore, since the by-products are significantly reducing the yield and quality of desired product, and are difficult to be separated, a complete investigation on the formation of by-products is of great importance.

Therefore, the objective of this work was to further develop the mechanistic understanding of DNS reduction by zero-valent iron to develop strategies for the manufacture of DSD.

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* Corresponding author. Tel./fax: +86 22 27408778.
E-mail address: fbzhang@tju.edu.cn (F. Zhang).

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2. Experimental

2.1. Materials

4,4′-Dinitrostilbene-2,2′-disulfonic acid (DNS) was supplied by Huayu Chemicals Co. (China) and recrystallized from water to get a purity of 99.5%. 5-Amino-2-formylbenzene sulfonic acid (ABAS) was supplied by Bayer Chemicals Ltd with a purity of 90.4%. The powdered iron used in this study was commercially available (60–80 mesh, BET surface area of 0.815 $m^2\,g^{-1}$). Other chemical reagents and solvents were either analytic or chromatography grade and used without further purification.

2.2. Reduction kinetics

Typical kinetics of DNS reduction were investigated in batch experiments using untreated Fe^0. Serum vials (30 mL) containing desired amount of iron were filled with 15.0 mL of deionized unbuffered water, leaving 15.0 mL of headspace, and crimp-sealed with Teflon-lined septa. After 2 h to equilibrate on an end-over-end rotary shaker at 40 rpm at desired temperatures, the reaction was initiated by the addition of DNS with needle injection to get the equivalent concentration of 2.0×10^{-4} M. The reaction course was monitored by diluting the sample of 100 μL from the headspace and analyzing by reverse-phase high performance liquid chromatography (HPLC).

2.3. Analytical methods

Compounds were analyzed by reverse-phase high performance liquid chromatography (Hitachi) equipped with a quaternary gradient pump (L-2130) and a variable wavelength absorbance detector (L-2400). Sample was separated at room temperature on Spherisorb ODS-2 (5 μm pore size) C18-column with the size of either 200 mm × 4.6 mm or 250 mm × 4.6 mm (for product distribution and monitor of the reaction progress, respectively). A mixture of water, methanol, and either 1.7 g/L tetrabutylammonium bromide or 0.6 g/L tetramethylammonium bromide (for product distribution and monitor of the reaction progress, respectively) was used as eluent. Compounds were identified by comparing the retention times with available pure standards.

3. Results and discussion

3.1. Product distribution and mechanisms

The reduction of DNS by Fe^0 provides a complex product distribution (Fig. 1). The principal reaction product of DNS reduction by Fe^0 was demonstrated by HPLC to be DSD (Fig. 1). Reduction of DNS is achieved by a series of two-electron additions with the intermediate of nitroso and hydroxylamino compounds. At the same time, Fe^{2+}, finally leading to Fe_3O_4, are formed with Fe^0 as the ultimate electron donor [18]. Electron transfer from Fe^0 to the aqueous DNS may occur directly from the metal or indirectly through the oxide film [19].

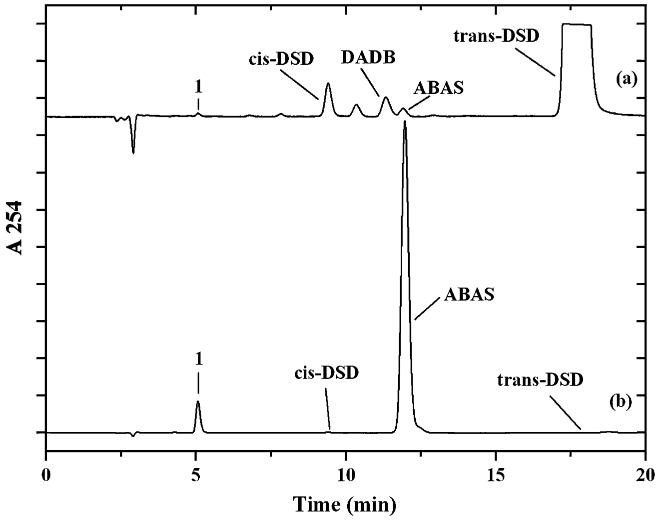
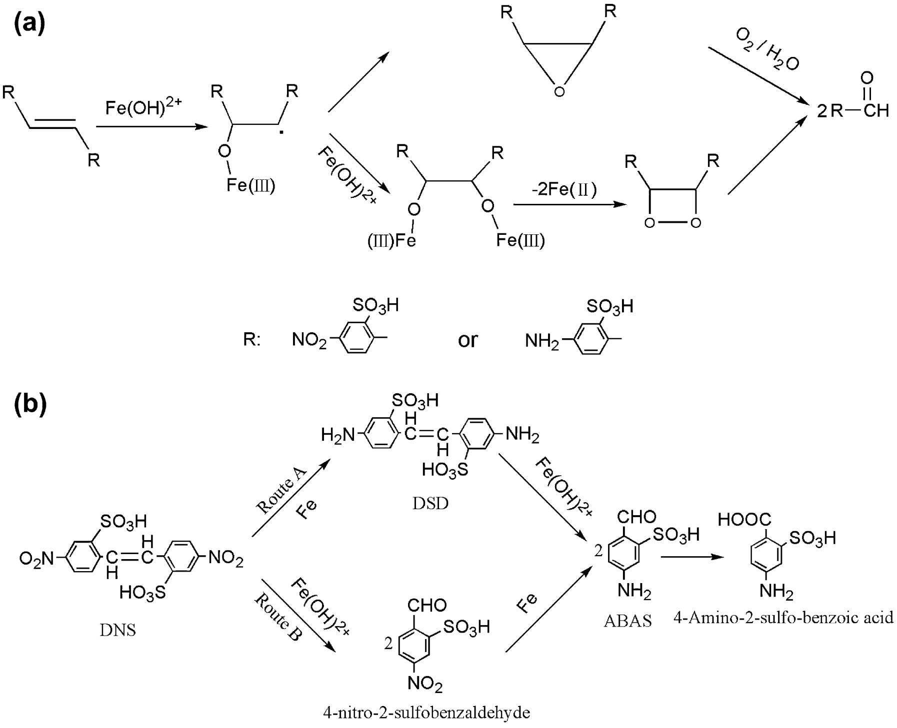


Fig. 1. HPLC chromatograms of ABAS (b) and DSD with its by-products (a). Samples were separated at room temperature on 200 mm × 4.6 mm Spherisorb ODS-2 (5 μm pore size) C18-column. A mixture of water, methanol, and 1.7 g/L tetrabutylammonium bromide was used as eluent.

cis-DSD and 4,4′-diamino-2,2′-bibenzyldisulfonic acid (DADB) are another two commonly cited products of DNS reduction. The former is due to a rapid photoisomerisation of *trans*-DSD in aqueous solution exposure to light or heat [20]. The latter one evidently resulted from the selective reduction of the C=C double bond [21]. Potential products not shown in Fig. 1 may include 4-amino-4′-nitrostilbene-2,2′-disulfonic acid, resulted from incomplete reduction of DNS, the intermediate of nitroso and hydroxylamino compounds [18].

Surprisingly, 5-amino-2-formylbenzene sulfonic acid (ABAS) was detected by comparing the retention time with an authentic standard (Fig. 1(b)). The reduction of DNS was performed in dark with pure DNS (without 4-nitro-2-sulfobenzaldehyde (NBS), checked by HPLC by comparing the retention times with an available pure standard), thus ruling out the possibility that ABAS may come from the degradation of DSD under solar light [22] or the reduction of 4-nitro-2-sulfobenzonic acid (NBS). The result indicates that the DNS/Fe^0 aqueous system was initiating an oxidation with the cleavage of C=C double bond besides the reduction process. Since previous studies have demonstrated that hydroxyl radicals and ferric species were involved in the reduction by Fe^0 in aqueous system [23], two possible pathways in the formation of ABAS were proposed by sharing the similar mechanism of DSD degradation by $Fe(OH)^{2+}$ [24] (Scheme 1(a)). The first pathway (route A in Scheme 1(b)) is due to the $Fe(OH)^{2+}$-induced degradation of DSD present as a result of DNS reduction. An alternate pathway to ABAS (route B in Scheme 1(b)) could occur if the NBS which resulted from the $Fe(OH)^{2+}$-induced double bond cleavage of DNS is further reduced by Fe^0 to form the aniline (ABAS). It should be noted that the by-product of **1** (Fig. 1) is supposed as



Scheme 1.

4-amino-2-sulfo-benzoic acid resulted from further oxidation of ABAS but there was lack of authentic standard.

3.2. Kinetics

Due to the instantaneous reduction of DNS by Fe^0 at manufacturing conditions, kinetic study was skillfully arranged by decreasing the reaction rate at mild temperature with low mixing rate. Typical reduction of DNS by Fe^0 is illustrated in Fig. 2. The total mass calculated by summing aqueous concentrations of DNS and DSD declines quickly and then rise gradually within 40 min. Since the final product comprised more than 94% of DSD, the deviation from the mass balance indicates that intermediate does exist in the reduction process. An unknown compound X with the retention time of 3.23 ± 0.02 min (in the HPLC condition for the monitor of the reaction progress) is proposed to be the nitroso or hydroxylamine compounds. Insertion chart (a) in Fig. 2 shows the plot of the area of X in HPLC and time. However, standards for nitroso and hydroxylamine compounds of DNS were not available, so this hypothesis is not confirmed.

It should be noted that another reason may also count for the deviation of mass balance. The tendency for DSD to remain adsorbed to the surface of either Fe^0 or to iron oxyhydroxide particles (formed on hydrolysis of ferric species present as a result of Fe^{2+} oxidation) would be expected to lower the measurable concentration of DSD in solution [25,26]. Nevertheless, the kinetics of the DSD formation should not be disturbed since our preliminary experiment had shown the loss of DSD from adsorption comprised less than 5% of the total DSD mass within 40 min. As a result, the kinetic models for disappearance and appearance of DNS and DSD, respectively, were established and rate constants were determined.

Insertion chart (b) in Fig. 2 illustrates the typical kinetics of DNS reduction by Fe^0. The disappearance of DNS and appearance of DSD fit the first-order kinetic models:

$$C = C_0\, e^{-k_{\mathrm{obs}}t} \quad (1)$$

$$C = C_0\left(1 - e^{-k'_{\mathrm{obs}}t}\right) \quad (2)$$

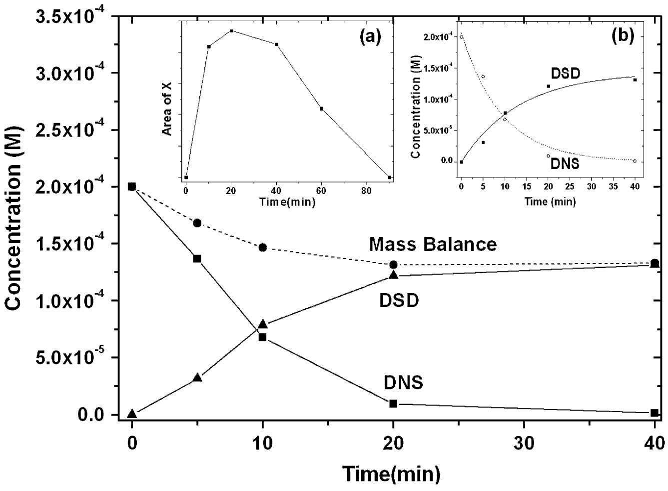


Fig. 2. Typical kinetics of DNS reduction by Fe^0 in the absence of light. The equivalent initial concentration of DNS = 2×10^{-4} M, $[Fe^0]$ = 20 g/L, mixed by rotation at 40 rpm, and T = 24 °C. The observed rate constants k_{obs} of the disappearance and formation of DNS and DSD were obtained by nonlinear fit with the pseudo-first-order model.

where C is the concentration of DNS or DSD at time t, C_0 is the initial concentration of DNS or final concentration of DSD, respectively, k_{obs} and k'_{obs} are the pseudo-first-order rate constants for disappearance of DNS and appearance of DSD, respectively. Nonlinear regressions using Eqs. (1) and (2) give $k_{obs} = 0.10898 \pm 0.01841$ and $k'_{obs} = 0.07167 \pm 0.00213$. It should be noted that when compared with the study by Agrawal and Tratnyek [18], similar k_{obs} and k'_{obs} were got in this study. The similarity may be due to the approximately 10-fold difference between the initial concentrations, which may lead to the decrease of k_{obs} resulted from the increasing saturation of reactive sites [25]. It may also be explained by the acceleration of the intermediate reaction at relatively high temperature.

Since studies on other nitro aromatic compounds (NACs) suggested that the rate of NAC reduction by iron metal was not only first order in NAC concentration but also that it also appeared to be first order with respect to the amount of iron available [18,27,28]. Therefore, k_{obs} can be expanded to $k_{SA}a_s\rho_m$. Where k_{SA} is the surface-area normalized rate constant ($\text{L h}^{-1}\text{ m}^{-2}$), a_s is the specific surface area of Fe^0 ($\text{m}^2\text{ g}^{-1}$), and ρ_m is the mass. The surface-area normalized rate constants for disappearance of DNS is $0.4012\ \text{L m}^2\text{ h}^{-1}$. It is in line with the range of previous studies on other NACs [18,27,28]. However, it should be noted that the value got in this study is slightly lower than that from Agrawal and Tratnyek [18], perhaps due to the untreated Fe^0 used in the studies and neutral unbuffered system.

3.3. Factors effecting k_{obs}

3.3.1. Effect of the weight of Fe^0

Although a_s which is used to calculate k_{SA} may be changed during the reduction due to the precipitation of iron oxides [18,29,30] and oxyhydroxides or adsorption of anilines to Fe^0 [20,29], deviation can be neglected within short time, and k_{SA} should be independent of the mass and specific surface area of the Fe^0. The effect of Fe^0 concentration on k_{obs} at constant mixing rate and reaction temperature was investigated. Linear relationship was observed over the range of Fe^0 weight studied (0.3 g, 0.4 g, 0.5 g, 0.6 g and 0.7 g) from Fig. 3, which is in line with the previously studies [18,27,28]. However, k_{obs} and k'_{obs} increased monotonically but nonlinearly with Fe^0 weight with the full scale from 0 g to 0.7 g (insertion chart in Fig. 3), especially for the formation of DSD, which presumably is due to the nonlinear relationship between the weight of Fe^0 and true reactive site on the surface of Fe^0 and reactive site saturation [31].

3.3.2. Effect of mixing rate

The influences of the mixing rate on k_{obs} for the disappearance of DNS and appearance of DSD were investigated in this study, and the result shows that k_{obs} clearly increases with the mixing rate (at constant initial Fe^0 concentration and temperature). The trend is linear with the square root of rpm (Fig. 4). Since numerous empirical determinations had demonstrated that velocity is proportional to the square of the mass-transfer coefficient for diffusion across a stagnant boundary layer [32], the result suggests that reactions involved were controlled by mass transfer.

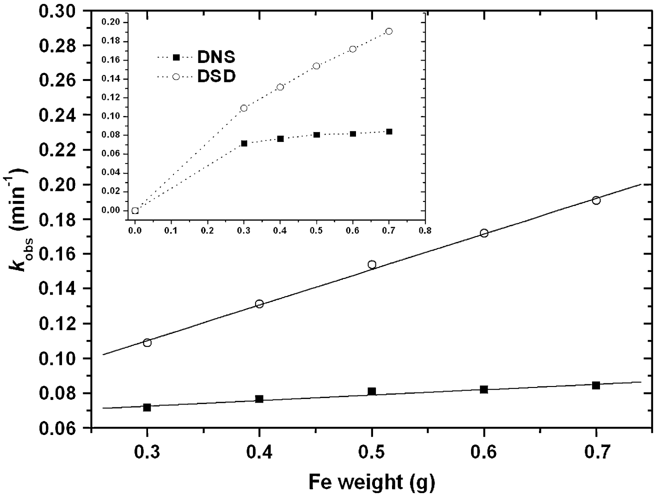


Fig. 3. Reduction of DNS by Fe^0 is performed in the absence of light. The equivalent initial concentration of DNS = 2×10^{-4} M, $[Fe^0] = 20$ g/L, and $T = 24$ °C.

3.3.3. Effect of temperature

The effect of temperature on k_{SA} was investigated in this work, and the result from Fig. 5 shows an evident increase of k_{obs} with the increase of temperature. This can be explained by the combination of the positive influence of temperature on the chemical reaction rate constant and the diffusion coefficient. Nonlinear fitting using the Arrhenius equation yields the observed activation energy (E_a) of 284 459.4 and 256 757.1 (J mol^{-1}) for disappearance of DNS and formation of DSD, respectively. However, due to the quick completeness of the reaction with the temperature above 30 °C, limited range of temperature (22 °C, 24 °C and 26 °C) was

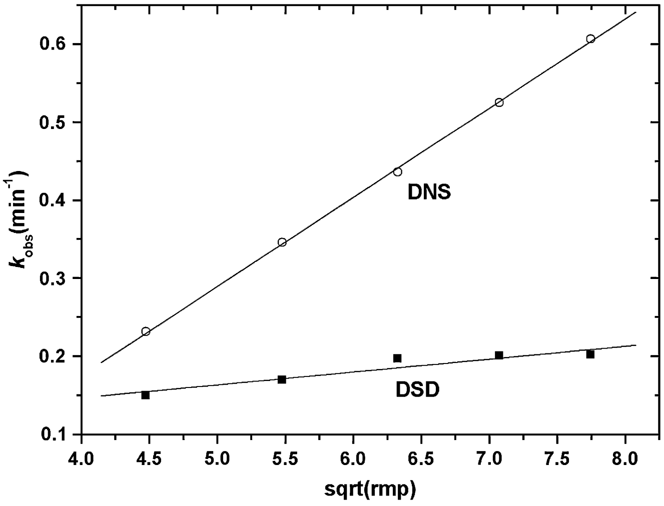


Fig. 4. Reduction of DNS by Fe^0 is performed in the absence of light. The equivalent initial concentration of DNS = 2×10^{-4} M, mixing by rotation at 40 rpm, and $T = 24$ °C.

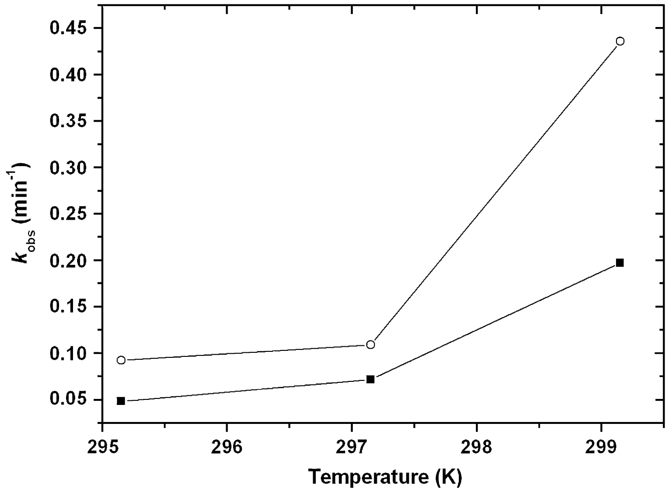


Fig. 5. Reduction of DNS by Fe^0 is performed in the absence of light. The equivalent initial concentration of DNS = 2×10^{-4} M, [Fe^0] = 20 g/L, and mixing by rotation at 40 rpm.

investigated, and lack of the power of statistics. It should be noted that for the surface reaction limitation and mass-transfer kinetics, the true chemical activation energy is not available.

4. Conclusion

The reduction of DNS by zero-valent iron metal in neutral unbuffered aqueous batch systems was studied. The reaction provided a complex product distribution. Besides the principal nitro-group reduction by Fe^0, oxidation with the cleavage of C═C double bond yielded 5-amino-2-formylbenzene sulfonic acid (ABAS). Kinetic study indicated that the reduction of DNS and the formation of DSD were pseudo-first order. The study on the effects of Fe^0 concentration on k_{obs} and k'_{obs} indicated that the kinetic models with the reduction rate constants (k_{SA}) normalized to the concentration of iron surface area fitted the disappearance of DNS but deviated from the formation of DSD. Linear relationship between the square root of rpm and k_{obs} for DNS and DSD indicated the mass transfer fall behind the chemical reaction rates. Increase of k_{obs} with the increasing temperatures could be explained by the acceleration of the chemical reaction and improvement in mass-transfer processes.

It should be noted that pH will influence the by-products formation and optimized condition with pH of 5–6 is always necessary for the manufacture of DSD with high quality [2,3]. However, this study reveals that the rate of reduction is mainly controlled by mass transfer. Anyone should expect that improvement in mass transfer (sufficient amount of Fe^0 with high mixing rate) will accelerate the reduction of DNS and formation of DSD, especially at high temperature.

Acknowledgement

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References

[1] Liu Ying, Zhang Fengbao, Zhang Guoliang. Dyes Pigments 2003;56:181.
[2] Windholz M. The Merck Index. 10th ed. p. 8.
[3] Lund BR, Brown GW. EP 221 021; 1987.
[4] Bizhanov FB, Dosumova BT. Izv Nats Akad Nauk Resp Kaz Ser Khim 1991;1:30.
[5] Kazmierczak A, Paryjczak T. Zesz Nauk Politech Lodz Chem 1991;616:249.
[6] Engelhardt T, Sauter H, Koppold J. DE 3916360; 1989.
[7] Balczewska H, Paryjczak T. Zesz Nauk Politech Lodz Chem 1987;41:253.
[8] Wolf F, Fischer H. J Prakt Chem 1975;317:103.
[9] Noel M, Anantharaman EN, Udupa HVK. J Appl Electrochem 1982;12:291.
[10] Bandlish BK, Casciani RV. DE 4110617; 1990.
[11] Udupa HVK. Indian Chem Eng 1988;30:53.
[12] Noel M, Anantharman EN, Udupa HVK. Indian J Technol 1981;19:100.
[13] Anantharaman EN, Subramanian GS, Udupa HVK. Trans SAEST 1969;4:38.
[14] Danciu V, Martre AM, Pouillen E, Mousset G. Electrochim Acta 1992;37:1993.
[15] Danciu V, Martre AM, Pouillen E, Mousset G. Electrochem Acta 1992;37:2001.
[16] Martre AM, Danciu V, Mousset G. Can J Chem 1993;71:1136.
[17] Terc. Chemicky Prumysl 1980;30:417.
[18] Agrawal Abinash, Tratnyek Paul G. Environ Sci Technol 1996;30:153.
[19] Balko BA, Tratnyek PG. J Phys Chem B 1998;102:1459.
[20] Husain Sajid, Narsimha R, Alvi SN. J Chromatogr 1992;596:127.
[21] Farris RE. Encyclopedia of chemical technology, vol. 21; 1983, p. 729.
[22] Wong-Wah-Chung P, Mailhot G, Bolte M. J Photochem Photobiol A Chem 2001;138:275.
[23] Hee Joo Sung, Feitz Andrew J, David Waite T. Environ Sci Technol 2004;38:2242.
[24] Wong-Wah-Chung P, Mailhot G, Pilichowski Jean-Francois. New J Chem 2004;28:451.
[25] Devlin JF, Klausen J, Schwarzenbach RP. Environ Sci Technol 1998;32:1941.
[26] Banerjee G, Malhotra SN. Corrosion 1992;48:10.
[27] Hundal LS, Singh J, Bier EL, Shea PJ, Comfort SD, Powers WL. Environ Pollut 1997;97:55.
[28] Burris DR, Hatfield K, Wolfe NL. J Environ Eng ASCE 1996;122:685.
[29] Scherer MM, Johnson KM, Westall JC, Tratnyek PG. Environ Sci Technol 2001;35:2804.
[30] Odziemkowski MS, Schumacher TT, Gillham RW, Reardon EJ. Corros Sci 1998;40:371.
[31] Daniel Gaspar J, Scott Lea A, Engelhard Mark H, Baer Donald R. Langmuir 2002;18:7688.
[32] Sherwood TK, Pigford RL, Wilke CR. Mass transfer. New York: McGraw Hill; 1975.