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The photocatalytic degradation of amino and nitro substituted stilbenesulfonic acids by TiO_2/UV and Fe^{2+}/H_2O_2/UV under aqueous conditions[☆]

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Abstract

The photodegradation products of 4,4′-dinitrostilbene-2,2′-disulfonic acid (DNSDA), 4-amino-4′-nitrostilbene-2,2′-disulfonic acid (ANSDA) and 4,4′-diaminostilbene-2,2′-disulfonic acid (DASDA) imparted by UV, TiO_2/UV and Fe^{2+}/H_2O_2/UV were characterized by IC, HPLC and LC-ESI-MS/MS. Direct photolysis with UV light allowed the transformation of *trans*-isomers to the corresponding *cis*-isomers followed by degradation to aromatic aldehydes and carboxylic acids. Whilst both TiO_2/UV and Fe^{2+}/H_2O_2/UV processes mineralized the model compounds, Fe^{2+}/H_2O_2/UV process was more rapid than TiO_2/UV.

Keywords: Stilbenesulfonic acids; Fluorescent whitening agents; Photocatalysis; TiO_2/UV; Fe^{2+}/H_2O_2/UV; Photodegradation

1. Introduction

The contamination of aquatic bodies by fluorescent whitening agents (FWAs) is one of the greatest environmental problems of recent times [1]. Several tons of these materials are discharged into the aquatic environment either directly or through the sewage treatment plants. Because of their low *n*-octanol−water partition coefficients [2] and high mobility within the aquatic system, FWAs are regularly found in natural waters. These are not easily degradable by the general treatment procedures and recalcitrance to environmental breakdown. In the production of not only fluorescent whitening agents but also optical brighteners and synthetic dyes, a variety of aromatic sulfonates are used as raw materials and intermediates in large quantities [3]. Thus, it is quite important to develop efficient treatment procedures for removal of aromatic sulfonates not only from industrial effluents but also from aquatic environment.

Conventional techniques like coagulation, adsorption on activated carbon, reverse osmosis and ultra filtration are non-destructive. These methods involve not only post-treatment of the adsorbents but also disposal of solid waste, which are quite expensive [4]. The advanced oxidation processes (AOPs) such as TiO_2/UV, O_3/UV, O_3/H_2O_2/UV, UV/H_2O_2, Fe^{2+}/H_2O_2 and Fe^{2+}/H_2O_2/UV are quite attractive in such cases [5−13]. Processes involving O_3/UV, O_3/H_2O_2/UV and H_2O_2/UV [10,11] require high-energy radiation and expensive equipment. The most frequently used Fe^{2+}/H_2O_2 process needs technically simple equipment and does not load the system with harmful or toxic substances [12,13]. Several workers have used solar radiation with TiO_2/UV and Fe^{2+}/H_2O_2/UV to minimize the treatment costs [14,15].

In the present work, photocatalytic degradation of stilbenesulfonates viz., 4,4′-dinitrostilbene-2,2′-disulfonic acid (DNSDA), 4-amino-4′-nitrostilbene-2,2′-disulfonic acid (ANSDA) and

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4,4′-diaminostilbene-2,2′-disulfonic acid (DASDA), was studied. The effectiveness of TiO_2/UV and Fe^{2+}/H_2O_2/UV processes at different conditions of treatment was evaluated. The effects of amino and nitro substituents on degradation were also studied.

2. Materials and methods

2.1. Chemicals

The chemicals used were of highest purity (>99%). 4, 4′-Dinitrostilbene-2,2′-disulfonic acid (DNSDA), 4,4′-diaminostilbene-2,2′-disulfonic acid (DASDA), 4-amino-4′-nitrostilbene-2,2′-disulfonic acid (ANSDA) were a kind gift from M/s. Vasant Chemicals Pvt. Ltd (Hyderabad, India). P25 titanium dioxide (ca. 80% anatase, 20% rutile; BET area ca. 50 m^2/g^1) was obtained from Degussa Co (Germany). Ferrous sulphate heptahydrate, hydrogen peroxide and sodium carbonate (S.D. Fine Chemicals, Mumbai, India) and Tris (hydroxymethyl) aminomethane (Ranbaxy Fine Chemicals Ltd, S.A.S. Nagar, India) were used.

2.2. Photoreactor

A laboratory-scale annular photoreactor consisting of a vertical Pyrex tube (520 mm height, 50 mm i.d. and volume 700 mL) with water-cooling jacket was used. The Pyrex glass tube consisting of a UV lamp (emission between 300–450 nm, power consumption of 15 W) (model TLD 15W/05, Philips, Holland) was immersed into the reactor. The suspension of TiO_2 was maintained by magnetic stirring and bubbling the air from the top of the reactor.

3. Experimental procedures

3.1. Direct photolysis with UV light

Aqueous solutions (0.1 mM) of DNSDA, ANSDA and DASDA were prepared separately at pH 2.5, 5.0 and 8.0 by dissolving the *trans*-isomers of the respective compounds and irradiated with UV light.

3.2. TiO_2/UV

Unless specified, aqueous TiO_2 dispersions were prepared by adding 2 g/L of TiO_2 to solutions containing 0.1 mM of DNSDA or ANSDA or DASDA separately and irradiated with UV light.

3.3. Fe^{2+}/H_2O_2/UV

Aqueous solutions were prepared by adding 13.6 mg/L $FeSO_4 \cdot 7H_2O$ (0.05 mM) and 1.6 mL/L of 30% (w/v) hydrogen peroxide (15 mM) to solution containing 0.1 mM of DNSDA or ANSDA or DASDA separately and irradiated with UV light.

In all the three cases, aliquots were collected at definite intervals of time, filtered through a 0.2 μm nylon membrane and analyzed by HPLC and TOC.

3.4. Analytical methods

3.4.1. High performance liquid chromatography (HPLC)

HPLC composed of two LC-10AT vp pumps, an SPD-M10A vp photodiode array detector, an SIL-10AD vp auto injector, a DGU-12A degasser and an SCL-10A vp system controller (all from Shimadzu, Kyoto, Japan) was used. A reversed-phase Inertsil ODS-3V C_{18} column (250 × 4.6 mm i.d., 5 μm particle size) (GL Sciences Ltd, Tokyo, Japan) was used for separation. The mobile phase, consisting of acetonitrile–0.01 M ammonium acetate, was initially programmed to elute 100% of 0.01 M ammonium acetate for 5 min, followed by a linear gradient of 10% acetonitrile for 20 min, 30% for 35 min, back to 100% ammonium acetate within 40 min and maintained the same up to 50 min. The analysis was carried out at room temperature at a flow rate of 1.0 mL/min. The chromatograms were recorded with PDA detector at 335 nm. The chromatographic and integrated data were recorded using an HP-Vectra (Hewlett Packard, Waldbronn, Germany) computer system.

3.4.2. LC-ESI-MS/MS

LC-ESI-MS/MS analyses were performed with an HP Series 1100 liquid chromatograph (Hewlett Packard, Palo Alto, CA, USA) and a Quattro LC triple-quadrupole mass spectrometer (Micromass, Manchester, UK) equipped with electrospray (ESI) and atmospheric pressure chemical ionization (APCI) interfaces. Nitrogen was used as a nebulizer and dissolvation gas. The operating parameters were: nebulizer gas flow, 0.9 L/min; disolvation gas flow, 10.0 L/min; nebulizer pressure, 50 psi; capillary voltage, 2.9 kV; cone voltage, 25 V; ion energy, 2.0 V; source block temperature, 100 °C; and disolvation temperature, 100 °C. The mass spectra were recorded in negative ion mode over the mass range of *m/z* 50 to 500 with 0.21 scans/s. Argon was used as a collision gas, and the pressure in the collision cell was maintained at 3.5×10^{-4} mbar. Collision voltages for MS/MS were 20 V for benezenesulfonic acids and 40 V for stilbenesulfonic acids.

3.4.3. Ion chromatography (IC)

The concentration of SO_4^{2-}, NO_3^- and NH_4^+ was measured using Dionex ion chromatograph (model-DX-500). IonPac AS 14A anion exchange column with 8.0 mM of Na_2CO_3 and 1.0 mM of $NaHCO_3$ as a mobile phase was used for determination of SO_4^{2-} and NO_3^-. IonPac CS 14 column with 9.0 mM methanesulfonic acid as a mobile phase was used for determination of NH_4^+. The analyses were carried out at 1.0 mL/min flow rate at room temperature.

3.4.4. Total organic carbon (TOC)

Total organic carbon was measured using an elementar TOC analyzer (Elementar, Germany) by combustion-infrared method. Na_2CO_3 equivalent to 500 mg/L of TIC (4412.2 mg Na_2CO_3 dissolved in 1 L water) and Tris (hydroxymethyl) aminomethane equivalent to 500 mg/L of TOC (1260.7 mg dissolved in 1 L water) solutions were used as standards for calibration. Samples homogenized were injected (1 mL) into a heated reaction chamber packed with cobalt oxide catalyst. Water was vaporized, total carbon (TC) and total inorganic carbon (TIC) were measured by a nondispersive infrared analyzer. Total organic carbon (TOC) was calculated as TOC = TC − TIC.

4. Results and discussion

The photodegradation of DNSDA, ANSDA and DASDA in aqueous solution and in the presence of direct UV light followed by TiO_2/UV and Fe^{2+}/H_2O_2/UV processes was studied.

4.1. Direct photolysis by UV light

The solutions of 0.1 mM *trans*-DNSDA, ANSDA and DASDA were exposed to UV light at pH 2.5, 5.0 and 8.0 for 48 h. Initially all the compounds were converted into their corresponding *cis*-isomers. Later the corresponding aldehydes and carboxylic acids were formed. At pH 2.5, it took 2 h for DASDA to convert into aldehydes and carboxylic acids whereas 6 h and 48 h for ANSDA and DNSDA, respectively. At pH 5.0 and 8.0 both DNSDA and DASDA were readily converted into their *cis*-isomers and the equilibrium was reached within 1 h. Later the compounds were slowly converted into aldehydes and carboxylic acids. The *cis*-isomer was predominant at the end of 48 h. At pH 5.0 and 8.0, 86% and 71% of DASDA and 83% and 68% of DNSDA were converted into aldehydes and carboxylic acids, respectively. But the conversion of *trans*-ANSDA to *cis*-ANSDA was very slow compared to DNSDA and DASDA. Most of the *trans*-ANSDA was not degraded even after 48 h of irradiation. Around 15% of it was converted into *cis*-ANSDA, aldehydes and carboxylic acids. This could be due to its thick orange color, which might prevent the penetration of UV light into the solution. From the HPLC chromatograms (Fig. 1), it could be seen that the degradation products were stable (the reduction in TOC was negligible) till 48 h. The compounds were not completely mineralized. The intermediates formed and their mass spectral data are given in Table 1.

4.2. Photocatalytic degradation by TiO_2/UV

4.2.1. Effect of concentration of TiO_2

Preliminary experiments to optimize the concentration of TiO_2 required to degrade stilbenesulfonic acids were conducted. The removal of TOC from 0.1 mM DNSDA was studied by irradiating the solutions containing TiO_2 from 0.5 g/L to 5.0 g/L. These were the optimal concentrations of TiO_2 Degussa P25 depending on the nature of the compound and geometry of the photoreactor as reported elsewhere [6–8]. The removal of TOC was increased by increasing the concentration of TiO_2 up to 2 g/L. TOC (35%) was removed at a concentration of 2 g/L TiO_2 within 2 h. Thereafter there was no change up to 3 g/L. Later it was decreased as the concentration of TiO_2 increased from 3 g/L to 5 g/L. This could be due to the aggregation of TiO_2 particles at high concentrations, resulting in a decrease in the surface active sites. Several authors [7,8] had explained this phenomenon in terms of scattering effect due to which the reduction in penetration of light occurs at high concentration of suspended catalyst. Thus, 2 g/L of TiO_2 was found to be the optimum concentration for further experiments.

4.2.2. Effect of pH

The TiO_2 surface carries a net positive charge at low pH and facilitates the adsorption of negatively charged sulfonic acids and promotes rapid photocatalytic degradation. The removal of TOC at pH 2.0, 4.0, 6.0 and 8.0 was studied for 6 h. It was maximum at pH 4.0 for all the test compounds. A maximum of 65%, 72% and 81% of TOC was removed in case of DASDA, ANSDA and DNSDA, respectively. As the pH was raised, the removal rates were decreased to 56% for DASDA, 62% for ANSDA and 74% for DNSDA at pH 6.0 and 33% for DASDA, 44% for ANSDA and 56% for DNSDA at pH 8.0. These results indicate that the removal of all the test compounds was more at pH 4.0. Slightly less removal of TOC was observed at pH 2.0 compared to pH 4.0. This could be due to the agglomeration of TiO_2 particles at highly acidic pH, which reduces the surface area of the catalyst [16]. These findings correlate with the earlier results of Saner et al. [7] who reported that the acidic pH was more suitable for the negatively charged dyes. It could be more likely because TiO_2 surface contains positive charge at low pH values (pH_{zpc} 6.8) [5].

4.2.3. Effect of the initial concentration of sulfonic acids

Fig. 2 shows the effect of the initial concentrations of the test compounds on their degradation keeping the concentration of TiO_2 constant at 2 g/L. It could be seen from Fig. 2 that the test compounds disappeared very fast at lower concentrations and as the concentration increased the rates of decomposition were decreased. The disappearance of test compounds followed the first order kinetics after dark adsorption. About 87% of 0.1 mM DASDA, 75% of ANSDA and 66% of DNSDA disappeared within 2 h. The rates of disappearance decrease in the order: DASDA, ANSDA and DNSDA. The estimated rate constants (k) at 0.1 mM concentration were 0.015/min, 0.010/min and 0.007/min for DASDA, ANSDA and DNSDA, respectively. These rates decreased as the initial concentration of the test compounds was increased. It was found that 93%, 82% and 75% of DASDA, ANSDA and DNSDA were disappeared when the initial concentration was 0.05 mM, whereas 64%, 56% and 49% when it was 0.2 mM. As the available sites on TiO_2 surface for sulfonic acid molecules were fixed, the relative percent of disappearance was decreased at higher concentration of sulfonic acids.

There is an ongoing debate whether the photocatalytic oxidation occurs on the surface of TiO_2 or in the solution. The rate of disappearance of the test compounds followed the order: DASDA > ANSDA > DNSDA which is in reverse to adsorption of tested compounds. If the disappearance depends only on adsorption on TiO_2 surface it should have followed the order as in adsorption, but the trend was reverse. These observations indicate that the disappearance of the test compounds could be a mixed phenomenon on the surface of TiO_2

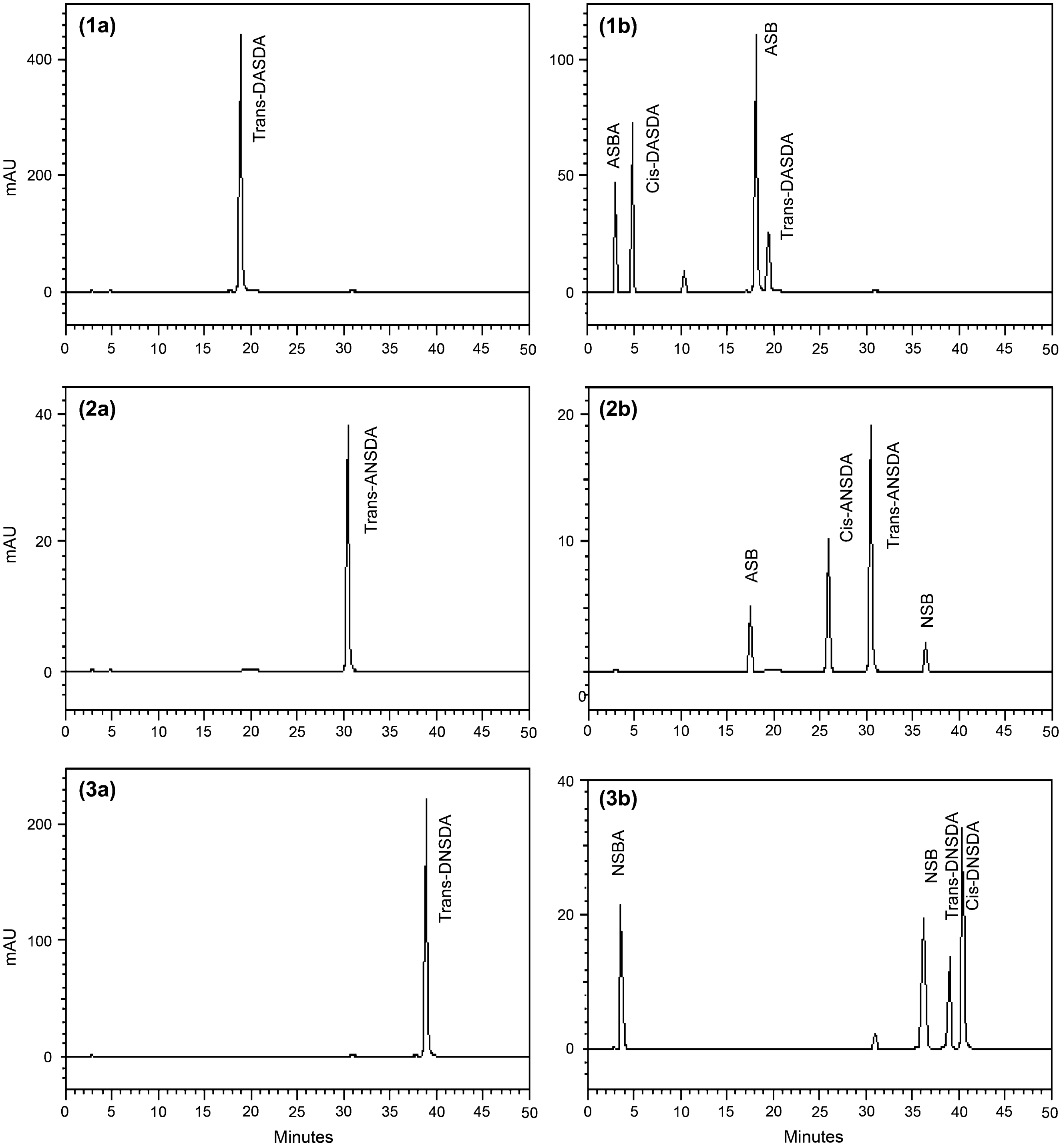

Fig. 1. HPLC chromatograms of 0.1 mM (1) DASDA, (2) ANSDA and (3) DNSDA (a) before irradiation with UV light and (b) after 48 h of irradiation at pH 5.0.

and also in solution. The results obtained by the direct photolysis also support this hypothesis.

4.3. Photocatalytic degradation by $Fe^{2+}/H_2O_2/UV$

4.3.1. Effect of the concentration of Fe^{2+} ion

The concentration of Fe^{2+} is one of the critical parameters in Fenton and the photo-Fenton processes. In the present study, various concentrations of Fe^{2+} (0.05 mM, 0.08 mM, 0.1 mM, 0.12 mM and 0.15 mM) were evaluated at 10 mM H_2O_2 and pH 3.0. It was observed that the removal of TOC was increased with an increase in Fe^{2+} concentration. Within 60 min, 62–87% of TOC was removed at 0.05 mM of Fe^{2+} whereas 100% at 0.15 mM of Fe^{2+}. Even though TOC removal was high at higher concentration, 0.05 mM of Fe^{2+} was used to avoid the formation of sludge.

Table 1
LC-ESI-MS data of the products/intermediates formed on photo-oxidation of DNSDA, ANSDA and DASDA

Compound	Product/intermediate	Molecular and fragment ions with assignment
DNSDA	*cis*-DNSDA	429 $[M-H]^-$, 383 $[M-H-NO_2]^-$, 349 $[M-H-SO_3]^-$, 303 $[M-H-NO_2-SO_3]^-$, 285 $[M-H-SO_3-SO_2]^-$, 80 $[SO_3^{\bullet -}]$
	4-Nitro-2-sulfobenzaldehyde	230 $[M-H]^-$, 202 $[M-H-CO]^-$, 184 $[M-H-NO_2]^-$, 156 $[M-H-CO-NO_2]^-$, 80 $[SO_3^{\bullet -}]$
	4-Nitro-2-sulfobenzoic acid	246 $[M-H]^-$, 202 $[M-H-CO_2]^-$, 80 $[SO_3^{\bullet -}]$
ANSDA	*cis*-ANSDA	399 $[M-H]^-$, 353 $[M-H-NO_2]^-$, 319 $[M-H-SO_3]^-$, 273 $[M-H-NO_2-SO_3]^-$, 255 $[M-H-SO_3-SO_2]^-$, 80 $[SO_3^{\bullet -}]$
	4-Nitro-2-sulfobenzaldehyde	230 $[M-H]^-$, 202 $[M-H-CO]^-$, 184 $[M-H-NO_2]^-$, 156 $[M-H-CO-NO_2]^-$, 80 $[SO_3^{\bullet -}]$
	4-Nitro-2-sulfobenzoic acid	246 $[M-H]^-$, 202 $[M-H-CO_2]$, 80 $[SO_3^{\bullet -}]$
	4-Amino-2-sulfobenzaldehyde	200 $[M-H]^-$, 172 $[M-H-CO]^-$, 136 $[M-H-SO_2]^-$, 108 $[M-H-CO-SO_2]^-$, 80 $[SO_3^{\bullet -}]$
	4-Amino-2-sulfobenzoic acid	216 $[M-H]^-$, 172 $[M-H-CO_2]$, 80 $[SO_3^{\bullet -}]$
DASDA	*cis*-DASDA	369 $[M-H]^-$, 289 $[M-H-SO_3]^-$, 225 $[M-H-SO_3-SO_2]^-$, 80 $[SO_3^{\bullet -}]$
	4-Amino-2-sulfobenzaldehyde	200 $[M-H]^-$, 172 $[M-H-CO]^-$, 136 $[M-H-SO_2]^-$, 108 $[M-H-CO-SO_2]^-$, 80 $[SO_3^{\bullet -}]$
	4-Amino-2-sulfobenzoic acid	216 $[M-H]^-$, 172 $[M-H-CO_2]$, 80 $[SO_3^{\bullet -}]$

4.3.2. Effect of pH

The effect of pH (2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0) of the medium on degradation was studied. The removal of TOC was maximum at pH 3.0 and 4.0 whereas there was no change in TOC at pH 8.0. Within the irradiation period of 60 min, TOC removal was 89%, 72% and 64% for DASDA, ANSDA and DNSDA at pH 3.0 and 4.0 at the initial concentration of 0.1 mM, whereas 42%, 34% and 22% at pH 2.0, 81%, 63% and 54% at pH 5.0, 72%, 54% and 42% at pH 6.0, 32%, 16% and 11% at pH 7.0 were removed. These results indicate that the solution pH between 3.0 and 4.0 was favorable for removal of all the test compounds. Previous studies on Fe^{2+}/H_2O_2/UV process [13] also reported that the optimal pH for a Fenton reaction was 3.0.

4.3.3. Effect of concentration of H_2O_2

Effect of concentration of H_2O_2 at the levels of 2–25 mM/L was studied. On increasing the concentration of H_2O_2, the removal of TOC was increased. When the concentration of H_2O_2 increased from 2 mM to 8 mM, the removal of TOC increased. This could be explained by the effect of the hydroxyl radicals produced additionally. Thereafter it was steady up to 15 mM, later a reverse trend was followed. Thus the H_2O_2 concentration was optimized between 8 mM and 15 mM for removal of 0.1 mM of the test compounds from water.

4.3.4. Effect of the initial concentration of sulfonic acids

The disappearance of the test compounds followed first order kinetics after dark reaction. The rate constants (k) were 0.076/min, 0.036/min and 0.022/min for 0.1 mM DASDA, ANSDA and DNSDA, respectively. Fig. 3 shows the effect of initial concentrations of test compounds on their degradation. It could be seen that the rate constants were decreased with an increase in the initial concentration. About 92% of DASDA, 70% of ANSDA and 51% of DNSDA were disappeared within 20 min at the initial concentration of 0.1 mM. It could be clearly seen from Fig. 4 that the rates of disappearance decrease in the order: DASDA > ANSDA > DNSDA. Within 20 min 98% of DASDA 86% of ANSDA and 64% of DNSDA were disappeared when the initial concentration was 0.05 mM, whereas 65%, 46% and 39% were disappeared when it was 0.2 mM. When the initial concentration of sulfonic acid was increased, the concentration of hydroxyl radicals remained constant for all molecules and hence the removal rates were decreased. Once the concentration of sulfonic acid was increased, it absorbs more of the UV light. Hence the light will not reach the surface of the photocatalyst, thus the efficiency of photodegradation decreased [10]. The rate constants in Fe^{2+}/H_2O_2/UV process were nearly five times greater than those of TiO_2/UV process indicating that the rates of reaction of sulfonic acids with hydroxyl radicals produced in Fe^{2+}/H_2O_2/UV process were more compared to the adsorption on the surface of TiO_2.

4.3.5. Effect of substituent groups on degradation

The disappearance of test compounds and the removal of TOC by TiO_2/UV process at optimized conditions is shown in Fig. 4. It could be clearly seen from Fig. 4 that the rates of removal of TOC followed the order: DNSDA > ANSDA > DASDA which was similar to the adsorption on TiO_2 surface, whereas the disappearance of test compounds followed DASDA > ANSDA > DNSDA. These observations indicate that the disappearance of the test compounds occurred both on the surface of TiO_2 and in solution. At optimized conditions DASDA was disappeared completely within 3 h, whereas it took 5 h for ANSDA and 6 h for DNSDA. This was directly related to the substituents on the aromatic rings. In case of DASDA, the amino-groups on both the benzene rings of the stilbene moiety, activate the molecule to readily react with the hydroxyl radicals. It also adsorbs on the surface of TiO_2 thus disappears from the solution quickly. Whereas in case of DNSDA, the nitro groups deactivate the ring and react slowly with the hydroxyl radicals. The adsorption onto TiO_2 surface was mainly responsible for disappearance, hence relatively slower disappearance was observed. The removal of TOC followed the same order as it was in adsorption on TiO_2 surface. It could be clearly seen from Fig. 4 that for the removal of 90% TOC form the solution of DASDA it took 16 h, whereas

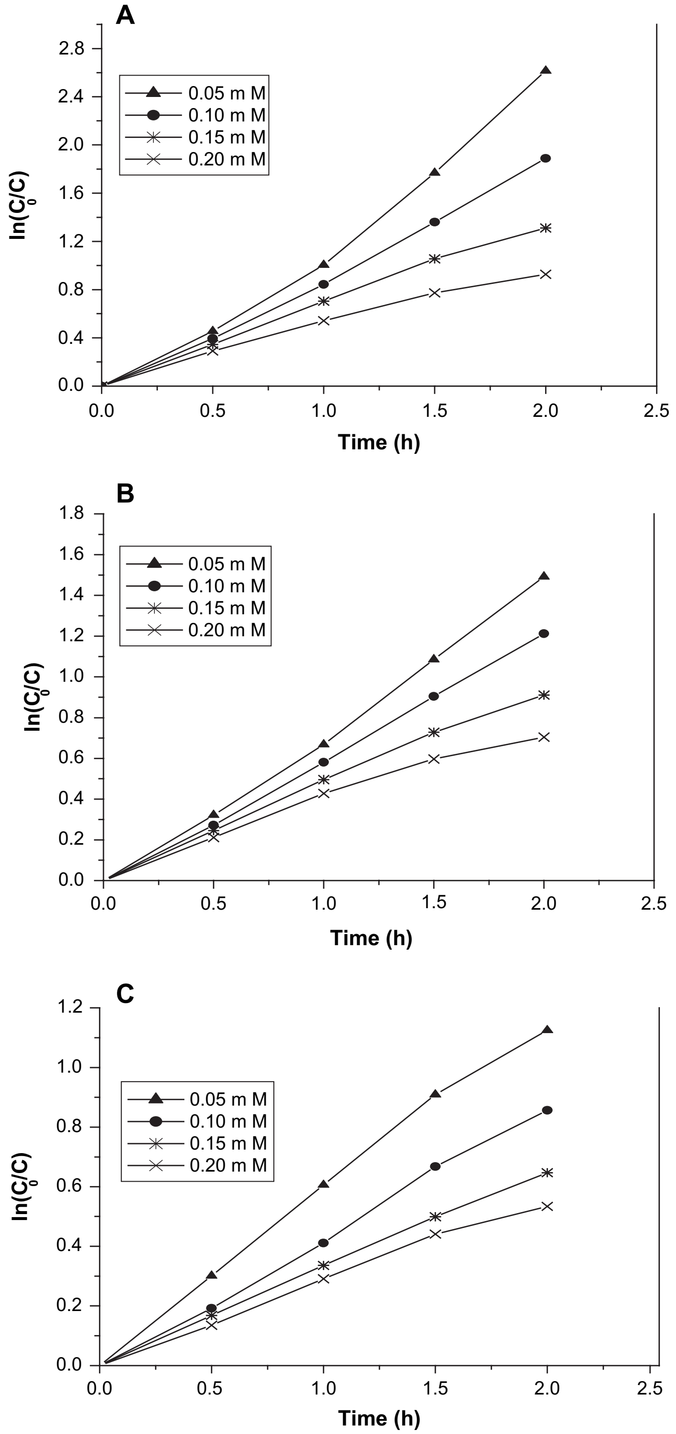

Fig. 2. Effect of initial concentration of (A) DASDA, (B) ANSDA and (C) DNSDA on the disappearance of test compounds by TiO_2/UV. (Concentration of TiO_2 2 g/L, pH 4.0 and irradiation time 2 h.)

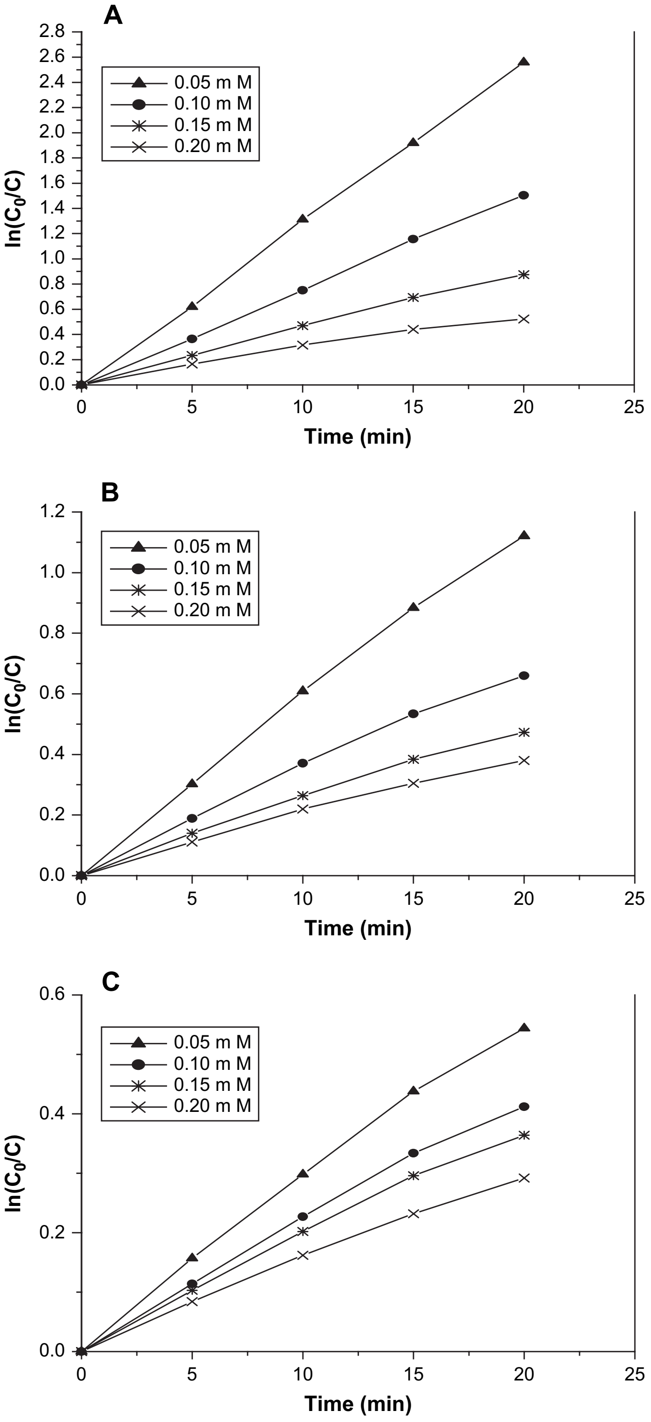

Fig. 3. Effect of initial concentration of (A) DASDA, (B) ANSDA and (C) DNSDA on the disappearance of the test compound by Fe^{2+}/H_2O_2/UV. (Concentration of Fe^{2+} 0.05 mM, concentration of H_2O_2 15 mM, pH 4.0, and irradiation time 20 min.)

12 h and 10 h for ANSDA and DNSDA, respectively. The reason for the faster removal of TOC from the aqueous solution of DNSDA could be due to (i) high degree of adsorption of the degraded products on surface of TiO_2 and (ii) faster reaction between degraded products and hydroxyl radicals.

Both the disappearance of the test compounds and the removal of TOC by Fe^{2+}/H_2O_2/UV process followed the same order as DASDA > ANSDA > DNSDA. At optimized conditions DASDA was disappeared completely within 15 min, whereas it took 45 min for ANSDA and 90 min for DNSDA. TOC (90%) was removed from the solution of DASDA in 90 min whereas it took 150 min for ANSDA and 180 min for DNSDA. In Fe^{2+}/H_2O_2/UV, the degradation of the test compounds was mainly due to the hydroxyl radicals.

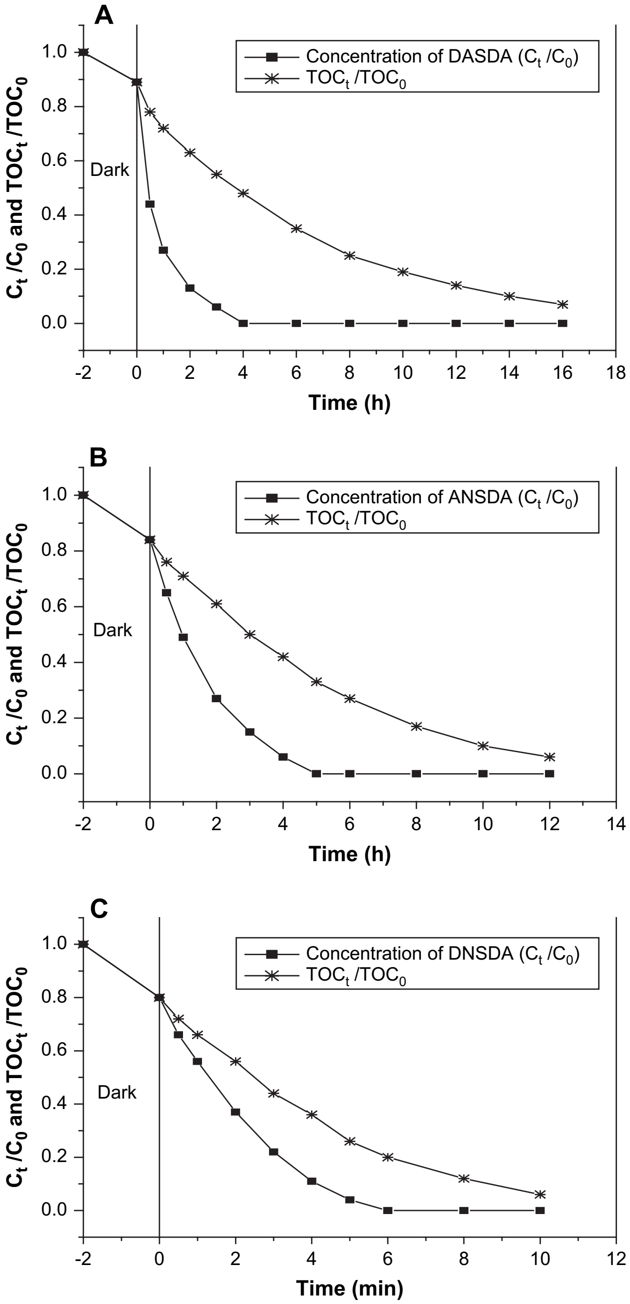

Fig. 4. Disappearance of test compounds and removal of TOC at the optimized conditions by TiO_2/UV. (A) DASDA, (B) ANSDA and (C) DNSDA. (Concentration of TiO_2 2 g/L, concentration of sulfonic acid 0.1 mM and pH 4.0.)

DASDA with two amino groups was removed quickly as the addition of H_2O_2 to the medium followed by ANSDA with one amino- and one nitro-group and DNSDA with two nitro groups. This could be due to the electron releasing effect of the amino groups, which facilitate the faster attack of the hydroxyl radicals on the carbon–carbon double bond of the stilbene moiety of DASDA whereas the nitro group deactivates the attack of hydroxyl radical in DNSDA. These results explain how DASDA was disappeared quickly even though its adsorption on TiO_2 was less compared to ANSDA and DNSDA.

4.4. Determination of nitrogen and sulfur containing species

Earlier studies on photocatalytic degradation of nitrogen and sulfur containing aromatics demonstrated that both the electrons and hydroxyl radicals react with nitrogen and sulfur containing groups [9,10]. The relative abundance of the end products (SO_4^{2-}, NH_4^+ and NO_3^-) of mineralization largely depends on the initial oxidation states of sulfur and nitrogen, substrate structure and on the mode of adsorption onto the surface of photocatalyst. Similar ions were formed by TiO_2/UV and Fe^{2+}/H_2O_2/UV processes. SO_4^{2-} was formed because of SO_3 groups in all the compounds. The formation of NO_3^- and NH_4^+ was mainly due to the presence of nitro and amino substituents. NO_3^- was observed in the mineralized products of DNSDA, while NH_4^+ from DASDA. Both NO_3^- and NH_4^+ were observed in mineralized products of ANSDA as it contained both nitro and amino groups. In addition to the decrease in TOC, the formation of inorganic ions shows evidence for mineralization of test compounds. The maximum amounts of SO_4^{2-} and NO_3^- were formed after irradiation for 90 min, 150 min and 180 min from DASDA, ANSDA and DNSDA by Fe^{2+}/H_2O_2/UV whereas it took 16 h, 12 h and 10 h by TiO_2/UV process. The concentration of NH_4^+ was increased initially, but after long irradiation, it was found to decrease. This could be due to the conversion of NH_4^+ into NO_3^- or N_2.

4.5. Degradation pathways

The photodegraded products were analyzed by LC-ESI-MS/MS. Table 1 gives the mass spectral fragments of the products obtained by direct photolysis. The *trans*-isomers were initially converted into their corresponding *cis*-isomers followed by the formation of aldehydes and carboxylic acids due to the cleavage of carbon–carbon double bond of stilbene moiety. The pathways of degradation are shown in Fig. 5. The major components of the degradants produced by both TiO_2/UV and Fe^{2+}/H_2O_2/UV processes were found to be similar at the initial reaction times and further disappearance of these compounds were observed. The formation of phenolic compounds by the attack of hydroxyl radical on the aromatic moiety could not be excluded. But the compounds under study had high absorption of light, which led to the conversion of *trans*-isomer to *cis*-isomer. Further carbon–carbon double bond of the stilbene moiety, which is in conjugation with the aromatic double bonds, stabilizes the radical formed by the attack of hydroxyl radical forming aldehydes and carboxylic acids more rapidly. This was more facile compared to the substitution of sulfonic acids to phenols. The detection of minor degradants was difficult due to their instability.

5. Conclusions

Three different oxidation processes viz., (i) direct photolysis, (ii) TiO_2/UV and (iii) Fe^{2+}/H_2O_2/UV (photo-Fenton) for treatment of stilbenesulfonic acids in aqueous environment were investigated. The sulfonic acids were initially converted

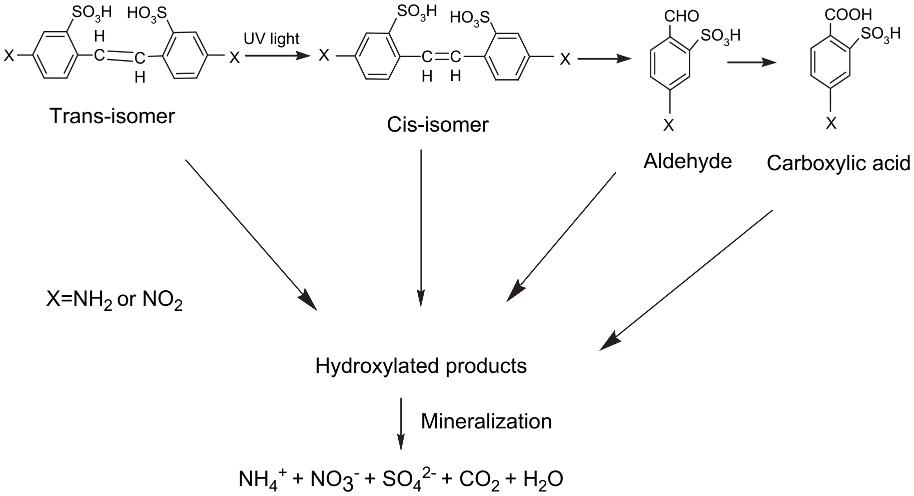

Fig. 5. Photodegradation pathways of stilbenesulfonic acids.

to the corresponding *cis*-isomers followed by the degradation into aldehydes and carboxylic acids under direct photolysis with UV light. The reduction in TOC was found to be negligible after 48 h of irradiation. $Fe^{2+}/H_2O_2/UV$ process was more effective in the removal of tested stilbenesulfonic acids. In both TiO_2/UV and $Fe^{2+}/H_2O_2/UV$ processes the disappearance of test compounds followed the first order kinetics. The order of removal of TOC in TiO_2/UV process followed: DNSDA > ANSDA > DASDA whereas in $Fe^{2+}/H_2O_2/UV$ process it was DASDA > ANSDA > DNSDA. The time required for 90% TOC removal was 10 h, 12 h and 16 h in TiO_2/UV process whereas it was 180 min, 150 min and 90 min in $Fe^{2+}/H_2O_2/UV$ process for DNSDA, ANSDA and DASDA, respectively. Effect of substituents on their disappearance was also studied. DASDA, containing two amino groups, disappeared very quickly by both the techniques followed by ANSDA with one amino- and one nitro-group and DNSDA with two nitro groups.

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