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Photocatalytic degradation of nitrobenzenes with combustion synthesized nano-TiO_2

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Abstract

The photocatalytic degradation of nitrobenzene and substituted nitrobenzenes under UV exposure was investigated with combustion synthesized nano-TiO_2 and commercial TiO_2 catalyst, Degussa P-25. The experimental data indicated that the photodegradation kinetics was first order. The photocatalytic degradation rates were considerably higher when catalyzed with combustion synthesized TiO_2 compared to that of Degussa P-25. The degradation rate coefficients followed the order: 1-chloro,2,4-dinitrobenzene $\simeq$ 4-nitrophenol > 2-nitrophenol > 1-chloro,4-nitrobenzene > 3-nitrophenol > 2,4-dinitrophenol > 1-chloro,2-nitrobenzene > nitrobenzene > 1,3-dinitrobenzene. Plausible mechanisms and reasons for the observation of the above order are discussed.

Keywords: Photocatalytic degradation; Nano-TiO_2; Nitrobenzene; Nitrophenol; Chloronitrobenzene; Kinetic analysis; Combustion-synthesized catalyst; Degussa P-25

1. Introduction

Photocatalytic degradation is a promising technique for remediation of water because of the complete mineralization of organic pollutants to harmless inorganic compounds. For the past two decades, extensive research has been carried out both in the study of kinetics of photodegradation of various organic pollutants and in the development of catalysts of high photoactivity [1–9]. The efficiency of photocatalytic reactions depends on the ability of excitation of electrons of semiconductive photocatalysts from valence band to conduction band upon sufficient input of energy (photons) greater than its band gap energy [4,9]. This excitation leads to the generation of holes that react with adsorbed hydroxyl species or water molecules thereby producing reactive hydroxyl radicals. The highly reactive hydroxyl radicals [10] that are formed can mineralize organic compounds ultimately to CO_2 and H_2O. Among several photocatalysts like Si, WO_3, CdS, ZnS, SnO_2, TiO_2 and Fe_2O_3, TiO_2 is the most popular because of its attractive properties, including the ability to mineralize a wide variety of organic pollutant [5]. The anatase phase of TiO_2 is an effective photocatalyst while the rutile phase is considered to be catalytically less active [5]. The mode of preparation of TiO_2 influences the composition of anatase and rutile phases and, therefore, its photocatalytic activity.

Several investigators have devised techniques to enhance the photoactivity of TiO_2 by adopting diverse techniques to produce nano-sized anatase phase of titania such as inert gas condensation, sol–gel method and hydrothermal processing [11–13] or doping inorganic species like C, N, F or metals and other chelating groups [6,14].

A new technique for production of nano-sized 100% anatase phase titania using solution combustion technique has been reported [6–9]. Pure anatase phase is ensured by this technique because of short time exposure to very high temperature (800 °C). Combustion synthesized TiO_2 catalyst is reported to have highly homogenous particle size (8 ± 2 nm), high BET surface area (240 m^2/g), reduced band gap energy (2.18 and 2.65 eV) and high content of hydroxyl species compared to that of Degussa P-25. Thus, the combustion-synthesized catalyst was found to be more efficient than

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Degussa P-25 for the photocatalytic degradation of dyes and phenolic compounds [6–9].

Nitrobenzene and its derivatives like nitrophenols, chloronitrobenzenes, dinitrobenzene are prominent water pollutants due to its high solubility and stability. They are major intermediates in the production of various chemicals like dyes, drugs, pesticides, herbicides, fungicides, wood preservatives and explosives [15–18]. As per environmental protection agency (EPA), nitroaromatic compounds are highly toxic, skin and eyes irritants, affect central nervous system, cardio-vascular system (reduce oxygen carrying capacity of blood) and are suspected to be possible carcinogenic or mutagenic agents.

The reactivity of nitro-aromatic compounds can be significantly affected by the electronic nature of substitutents and by their positions in the aromatic rings. Though various research groups have investigated the photocatalytic degradation of nitrobenzene [19–21], nitrophenols [22–29] and chloronitrobenzene [20] using different catalysts, a consolidated or comprehensive study of effect of substitution in nitrobenzene has not yet been reported. Therefore, we have investigated the effect of hydroxy (strongly activating), chloro (weakly deactivating) and nitro (strongly deactivating group) on the photocatalytic degradation of nitrobenzene. The kinetics of photocatalytic degradation of nitrobenzene and substituted nitrobenzenes under UV exposure using combustion-synthesized nano-TiO_2 (CST) was investigated and compared against commercial Degussa P-25 catalyst.

2. Experimental

2.1. Materials

Nitrobenzene (Ranbaxy, India), 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 1-chloro,2-nitrobenzenes, 1-chloro,4-nitrobenzene, 1,3-dinitrobenzene, 2,4-dinitrophenol, 1-chloro,2,4-dinitrobenzene (all from Rolex, India), titanium isopropoxide (Lancaster Chemicals, UK), hydrogen peroxide (Sigma–Aldrich, USA) and nitric acid (S.D. Fine Chemicals, India), acetonitrile (HPLC grade, Merck, India) were used. Water was double distilled and filtered through a Millipore membrane filter prior to use.

2.2. Catalyst preparation and characterization

Combustion synthesis technique is a single step process without any downstream processing. Stiochiometric amounts of precursor titanyl nitrate (obtained by nitration of titanium hydroxide, which is obtained by hydrolysis of titanium isopropoxide) and fuel (glycine) are mixed in water and combusted in a muffle furnace preset at 350 °C. Combustion is of smoldering type without any flame, just a spark appears at a corner and spreads over the mass yielding highly porous nano-sized yellowish substance, pure anatase TiO_2. Phase transition to other phases like rutile or brookite is prevented in this process because the material is exposed to very high temperature only for a short duration. The catalyst was characterized by various techniques like XRD, TEM, BET, XPS, TG-DTA, IR and UV spectroscopy. Further details on catalyst preparation and characterization are provided elsewhere [6–8].

2.3. Photochemical reactor

The photochemical reactor used in the present study consisted of a jacketed quartz tube of 3.4 cm i.d., 4 cm o.d., and 21 cm length. A high-pressure mercury lamp of 125 W (Philips Lamps, India) was placed inside the quartz reactor after careful removal of outer casing of the lamp. The ballast and capacitor were connected in series to lamp to avoid any voltage fluctuations. The assembly of lamp and the quartz reactor was placed concentrically inside a Pyrex glass outer reactor, 5.7 cm i.d., and 16 cm height, filled with solution. The solution taken in the outer reactor was stirred continuously using a magnetic stirrer. Water was circulated in the annular space of jacketed reactor to ensure constant temperature. The whole system was confined in a dark enclosure to prevent any interruption due to stray light. Further details on the operation of the reactor and range of energy emission are given elsewhere [6]. The lamp predominantly emitted the wavelength 365 nm corresponding to the energy of 3.4 eV and photon flux is 5.8×10^{-6} mol of photons/s.

2.4. Degradation experiments

Predetermined amount of nitrobenzene/substituted nitrobenzene was dissolved in double distilled Millipore filtered water. The degradation experiments were carried out with different initial concentrations of the organic compounds with a constant catalyst loading of 1 kg/m^3. Experiments with combustion-synthesized catalyst and Degussa P-25 were done simultaneously in parallel systems to ensure similarity. All reactions were carried out for about 2–3 h till the concentration reduces to less than 10% of the initial concentration. Samples were collected at regular intervals for subsequent analysis. The samples were filtered through Millipore membrane filters and then centrifuged to remove the catalyst particles prior to the analysis.

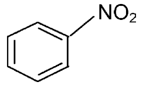
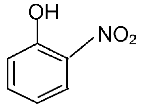
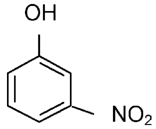
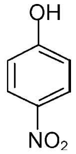
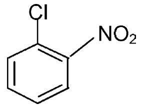
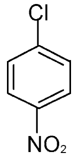
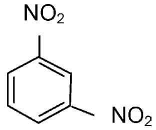
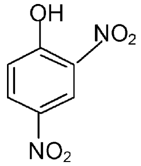
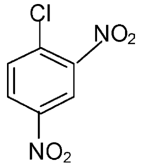
2.5. Sample analysis

The concentration of the organics in the samples was measured by UV-visible spectrophotometer (Shimadzu, UV-2100). The calibration based on Beer–Lambert law was done a priori for nitrobenzenes, nitrophenols, and chloronitrobenzenes at a wavelength of maximum absorptivity, λ_{max}, 268, 280, 272, 320, 260, 278, 240, 250, 248 nm for nitrobenzene, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 1-chloro,2-nitrobenzenes, 1-chloro,4-nitrobenzene, 1,3-dinitrobenzene,2,4-dinitrophenol, 1-chloro,2,4-dinitrobenzene, respectively.

HPLC system (Water Inc., USA) used for sample analysis consisted of an isocratic pump (Waters 501), a Rheodyne injector with a sample loop of 500 μl and a reverse phase C-18 column and an UV detector (GBC, Australia). The eluent stream of 80 vol.% water, 20 vol.% acetonitrile was pumped as a flow rate of 0.8 ml/min. The UV detector was operated at λ_{max} of the compound and the output was stored digitally using a data acquisition system.

Some experiments were repeated for reproducibility and the variation in the degradation rate coefficients was less than 5%.

Table 1
Molecular structures of the pollutants degraded

Compounds	Molecular structure
Nitrobenzene	
2-Nitrophenol	
3-Nitrophenol	
4-Nitrophenol	
1-Chloro,2-nitrobenzene	
1-Chloro,4-nitrobenzene	
1,3-Dinitrobenzene	
2,4-Dinitrophenol	
1-Chloro,2,4-dinitrobenzene	

3. Results and discussion

No appreciable degradation of nitrobenzenes was observed over TiO_2 either in absence of irradiation or in absence of catalyst. The structures of the nitrobenzenes degraded in this study are given in Table 1. As a catalyst loading of 1 kg/m^3 was found to be the optimum for degradation of various dyes and phenolic compounds [6–9], the same catalyst loading was used for the present study. All compounds were stirred in dark for 30 min prior to UV irradiation and no significant decrease in the concentration was observed. The initial concentration, therefore, was used for the kinetic analysis. The HPLC analysis of the samples showed distinct peaks for the parent compound and its intermediates. However, the ratio of the absorption of the intermediates to the absorption of the parent compounds at λ_{max} is small at initial times (<45 min). Therefore, the absorption of intermediates at λ_{max} can be neglected. Further, analysis of the samples using UV-visible spectrophotometer showed a continuous decrease in the UV-visible absorption at λ_{max}. Therefore, the simpler method of UV-visible absorption spectroscopy was used for tracking degradation.

Figs. 1–9 show the degradation profile for nitrobenzene, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 1-chloro,2-nitrobenzene, 1-chloro,4-nitrobenzene, 1,3-dinitrobenzene, 2,4-dinitrophenol and 1-chloro,2,4-dinitrobenzene, respectively for four different initial concentrations with both CST and Degussa P-25. In the figures, filled and open symbols denote degradation of organics catalyzed with Degussa P-25 and CST, respectively. In case of reactions catalyzed by Degussa P-25, the concentration reaches a saturation beyond which no appreciable degradation is observed. However, in case of reactions catalyzed by CST, the concentration drops below detection limits.

Most of the heterogeneous photocatalytic degradation reactions follow Langmuir–Hinshelwood (L–H) kinetics [6] $r_0 = k_{ov}K_0C_0/(1 + K_0C_0)$, where r_0 is the initial rate and C_0 is the initial concentration. The initial rates of the reaction were determined by extrapolating the tangent (based of the linear fit of the first 3–4 points, i.e. up to 30 min of degradation) of the concentration profile (Figs. 1–9) back to initial condition. For degradation of dyes catalyzed by CST, it was determined that *L–H parameter* for the equilibrium adsorption K_0 is negligible [7,8]. Further, the photodegradation of phenol and substituted phenols using CST followed a first order rate expression, $r_0 = k_0C_0$, where k_0 is the combined kinetic rate coefficient from direct hole, hydroxyl attack, and equilibrium adsorption constant [9]. In Fig. 10(a), the nearly linear variation of r_0 and C_0 confirms that nitrobenzene degradation catalyzed by CST also follows first order kinetics. In order to compare the efficiency of CST catalyst over Degussa P-25, a similar plot is shown for reactions with commercial catalyst in Fig. 10(b). The degradation rate coefficient, k_0, can be easily obtained from the slope of linearly regressed line in Fig. 10(a) and (b). The rate coefficients for all compounds are listed in Table 2 and follow the

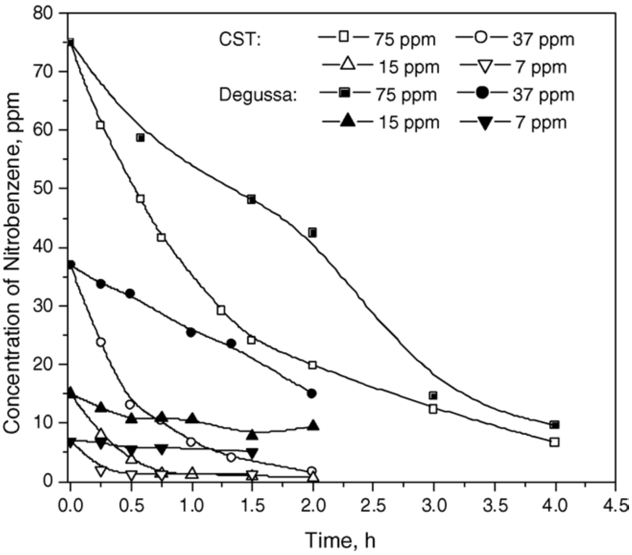


Fig. 1. Degradation profile for nitrobenzene under UV exposure in presence of combustion synthesized TiO_2 (CST) and Degussa P-25.

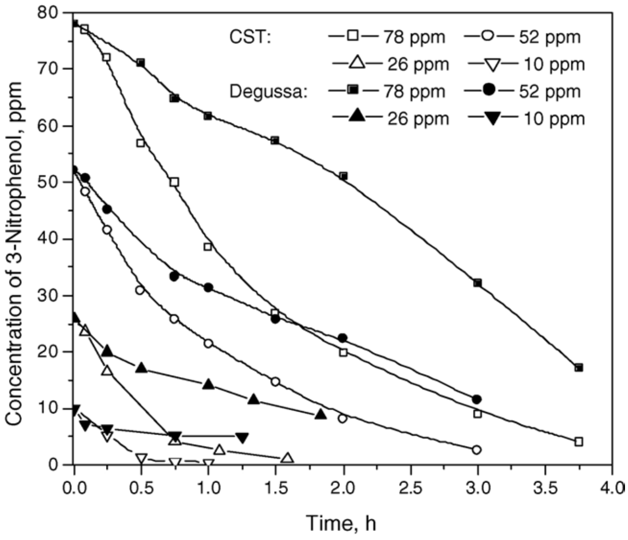


Fig. 3. Degradation profile for 3-nitrophenol under UV exposure in presence of combustion synthesized TiO_2 (CST) and Degussa P-25.

order: 1-chloro,2,4-dinitrophenol ≃ 4-nitrophenol > 2-nitrophenol > 1-chloro,4-nitrobenzene > 3-nitrophenol > 2,4-dinitrophenol > 1-chloro,2-nitrobenzene > nitrobenzene > 1,3-dinitrobenzene. It should be noted that the degradation rate coefficients of all reactions catalyzed by CST are higher than that of reactions catalyzed by Degussa P-25 (column 4 of Table 2). Possible reasons for the observation of the above order for the rate coefficients are discussed below.

Hydroxy substitution strongly activates the aromatic ring for attack of electrophilic hydroxyl radical, and, therefore, the reactivity of nitrophenols are higher than that of nitrobenzene. Degradation of nitrophenol by attachment of hydroxyl radical to the aromatic ring resulting in the formation of nitrocatechol or nitrohydroquinone is more prominent compared to the formation of dihydroxy compounds by replacement of nitro group [18,22–24]. As –OH group is ortho- or para-directing group and $–NO_2$ is a meta-directing group, both groups influence the site of attack of hydroxyl radical. In 4-nitrophenol and 2-nitrophenol, both groups direct the radical to ortho- and para-position, respectively. However, for 3-nitrophenol, the hydroxy group dominates over the influence of nitro group in directing the radical to attack the para-position [18]. Hence, 3-nitrophenol degrades the slowest among the three nitrophenols, which is in accordance with literature [18,24,25]. While some investigators have reported that the degradation of 4-nitrophenol and 2-nitrophenol are comparable [24,25], it was observed in this study that 4-nitrophenol degrades faster

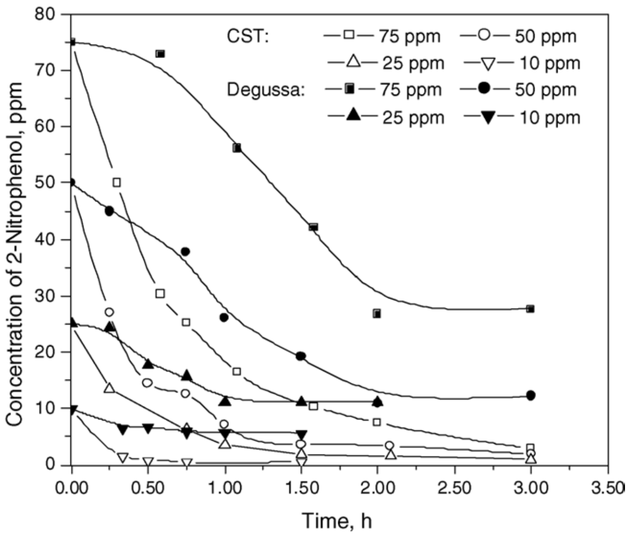


Fig. 2. Degradation profile for 2-nitrophenol under UV exposure in presence of combustion synthesized TiO_2 (CST) and Degussa P-25.

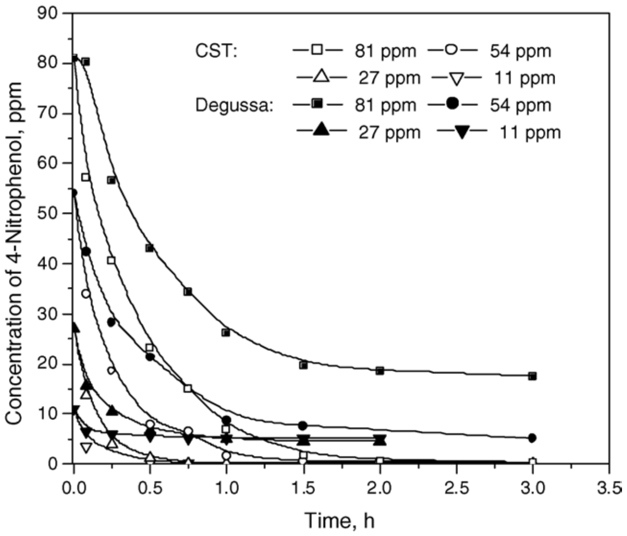


Fig. 4. Degradation profile for 4-nitrophenol under UV exposure in presence of combustion synthesized TiO_2 (CST) and Degussa P-25.

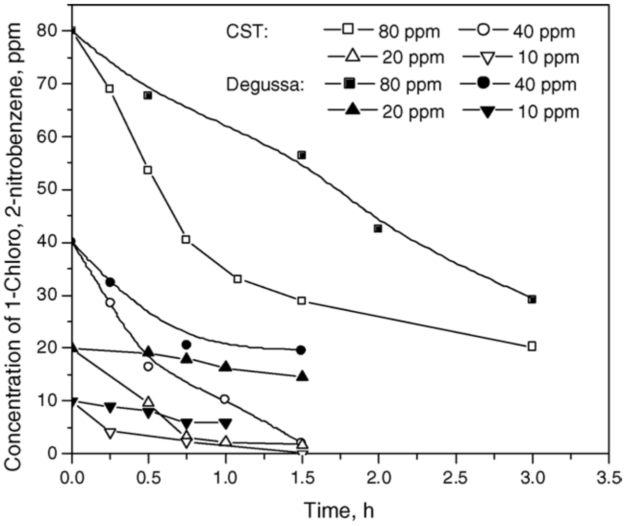


Fig. 5. Degradation profile for 1-chloro,2-nitrobenzene under UV exposure in presence of combustion synthesized TiO_2 (CST) and Degussa P-25.

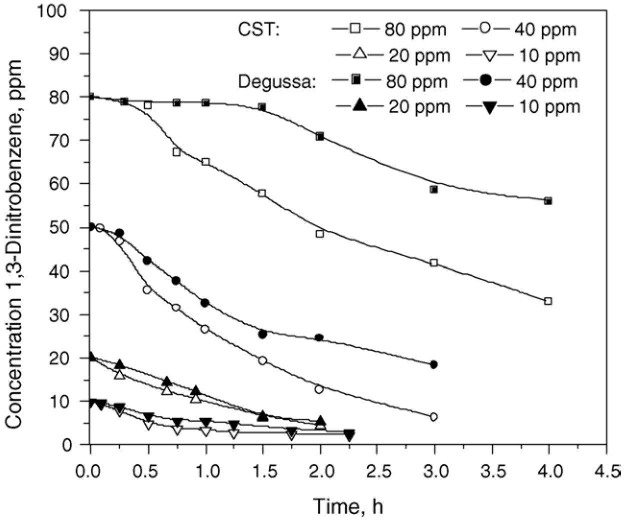


Fig. 7. Degradation profile for 1,3-dinitrobenzene under UV exposure in presence of combustion synthesized TiO_2 (CST) and Degussa P-25.

than 2-nitrophenol, which is consistent with an another study [26].

Though chloro substitution is a ortho- and para-directing group, it is a weakly deactivating group unlike hydroxy substitution, which is a strongly activating group. Therefore, the increase in degradation rate in presence of chloro substitution is less than that of the rate in the presence of hydroxy group. Thus, the degradation of chloronitrobenzene is less than that for nitrophenol. This is in congruence to an other study [9] on the degradation of chlorophenol, where it was found that the rate of secondary hydroxylation (i.e. degradation of dihydroxybenzene) was about twice than that of the primary hydroxylation reaction (i.e. degradation of chlorophenol (chlorohydroxybenzene)). Similar to the above observation, wherein 4-nitrophenol degraded faster than 2-nitrophenol, 1-chloro,4-nitrobenzene degraded faster than 1-chloro,2-nitrobenzene.

In 1,3-dinitrobenzene, the presence of two nitro groups (strongly deactivating group) deactivates the aromatic ring for electrophilic attack [17,19] and, therefore, a reduced rate of degradation was observed compared to that of nitrobenzene. The rate of degradation of 2,4-dinitrophenol was slower compared to that of all the three isomers of nitrophenol, which is in agreement with other studies [16,20,25,27]. As in case of nitrophenol and nitrobenzene, the presence of hydroxy group enhanced the degradation rate and, therefore, the rate of degradation of 2,4-dinitrophenol was nearly twice than that of 1,3-dinitrobenzene.

As discussed above, the rates of degradation of 1,3-dinitrobenzene and 2,4-dinitrophenol are slower than that

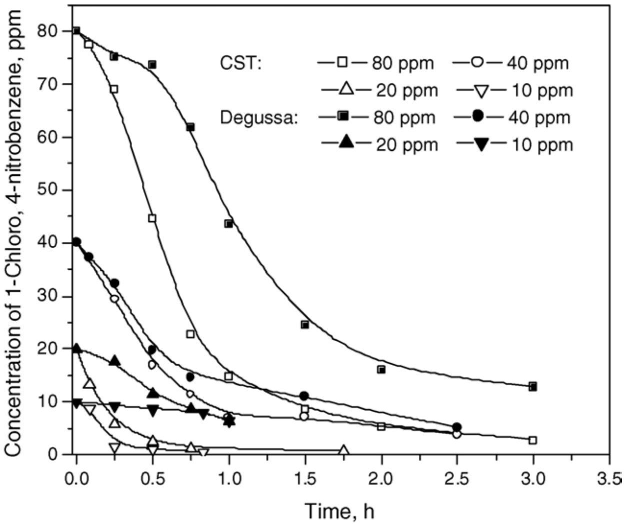


Fig. 6. Degradation profile for 1-chloro,4-nitrobenzene under UV exposure in presence of combustion synthesized TiO_2 (CST) and Degussa P-25.

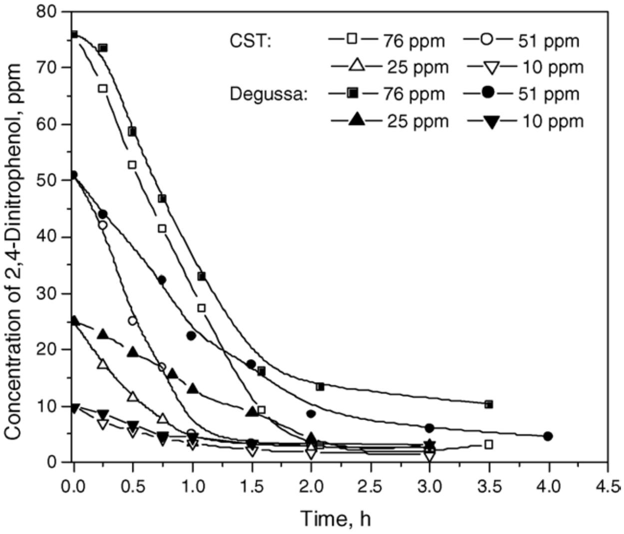


Fig. 8. Degradation profile for 2,4-dinitrophenol under UV exposure in presence of combustion synthesized TiO_2 (CST) and Degussa P-25.

Table 2
First order rate constants for the degradation of various organics catalyzed by combustion synthesized TiO_2 and Degussa P-25

Compound	k_{CST} ($\times 10^3$ min^{-1})	$k_{Degussa}$ ($\times 10^3$ min^{-1})	Enhancement ratio, $k_{CST}/k_{Degussa}$
Nitrobenzene	8.5	6.3	1.35
2-Nitrophenol	17.5	10.6	1.65
3-Nitrophenol	13.9	10.0	1.39
4-Nitrophenol	23.8	16.5	1.44
1-Chloro,2-nitrobenzene	10.1	6.8	1.49
1-Chloro,4-nitrobenzene	16.0	14.3	1.11
1,3-Dinitrobenzene	6.2	3.9	1.59
2,4-Dinitrophenol	11.3	7.3	1.55
1-Chloro,2,4-dinitrobenzene	24.9	16.6	1.50

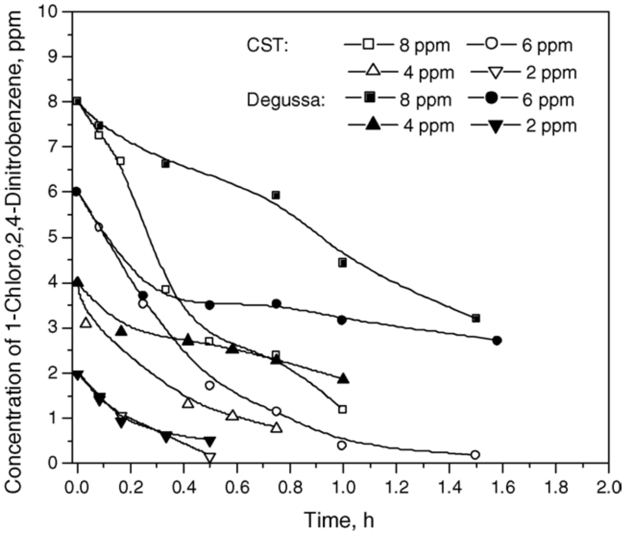


Fig. 9. Degradation profile for 1-chloro,2,4-dinitrobenzene under UV exposure in presence of combustion synthesized TiO_2 (CST) and Degussa P-25.

of nitrobenzene and nitrophenol, respectively. However, the degradation of 1-chloro,2,4-dinitrobenzene was higher than that of 1-chloro,2-nitrobenzene and 1-chloro,4-nitrobenzene and other dinitro compounds. The reason for this discrepancy is not clear and it is speculated that the mechanism of degradation of chlorodinitrobenzene is different from that of dinitrophenol and dinitrobenzene. It has been reported that degradation of dinitrophenol and dinitrobenzene involves removal of nitro group from aromatic ring resulting in the formation of nitrocatechol/nitrohydroquinone and nitrophenol, respectively [17,25,27]. This is in contrast to the hydroxyl radical directly attacking benzene ring as in the case of nitrophenol and nitrobenzene. Because the chloro group is more bulky than the nitro group, it may detach preferentially and faster compared to nitro group and, therefore, chlorodinitrobenzene degrades faster than other dinitro compounds. The presence of two nitro groups in chlorodinitrobenzene could accelerate the detachment of chloro group compared to chloronitrobenzene and thus chlorodinitrobenzene degrades faster compared to chloronitrobenzene.

Overall, it was observed in the study that CST is superior to Degussa P-25 for the catalytic degradation of nitro-aromatic compounds. This can be attributed to the higher surface area, lower band gap and higher hydroxyl species content of CST compared to that of Degussa P-25. The influence of hydroxy, nitro and chloro substitution on the degradation of nitrobenzene was investigated and plausible mechanisms were suggested.

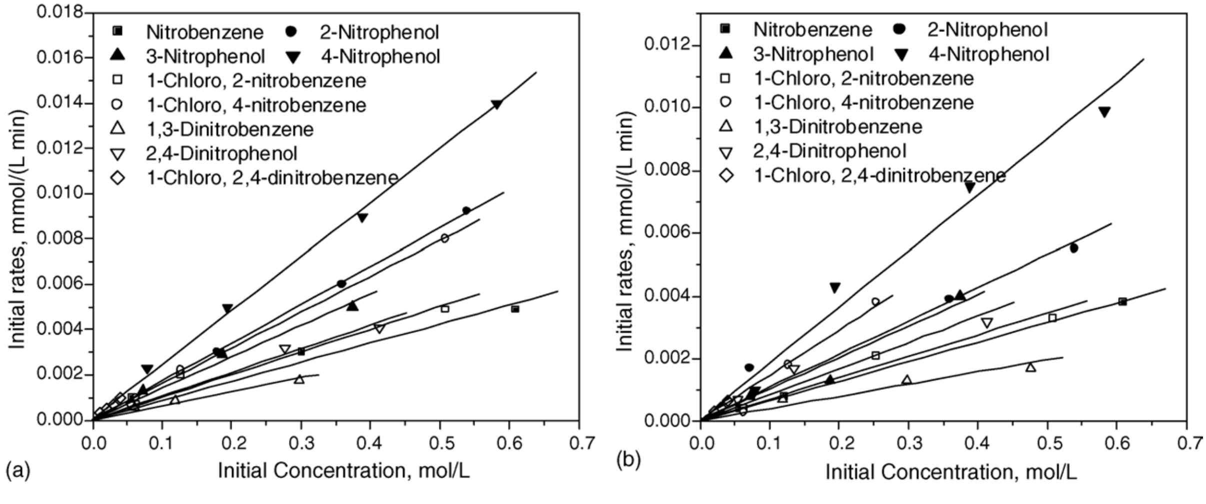


Fig. 10. Variation of initial rates, r_0, with the initial concentration, C_0, for various pollutants using (a) combustion synthesized catalyst (CST); (b) Degussa P-25.

4. Conclusions

The photocatalytic degradation of nitrobenzenes, nitrophenols, chloronitrobenzenes was studied over combustion synthesized catalyst and Degussa P-25. The organics degraded faster when catalyzed by combustion synthesized catalyst TiO_2 compared with that of Degussa P-25. The concentration of pollutants decreased to less than 10% of its original concentration within 2–3 h when catalyzed by combustion synthesized nano-TiO_2. The concentration reached a saturation value beyond which there was no appreciable degradation when the reaction was catalyzed by Degussa P-25. The influence of hydroxy, chloro and nitro substitution on nitrobenzene was also investigated. In general, hydroxy and chloro substitution on nitrobenzene accelerated the degradation rate while nitro substitution on nitrobenzene decelerated the degradation rate. The position of substitution also influenced the rate of decomposition. The rate of degradation of 4-nitrophenol and 1-chloro,4-nitrobenzene was higher than 2-nitrophenol and 1-chloro,2-nitrobenzene, respectively, while 3-nitrophenol degraded the slowest among nitrophenols.

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