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Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/



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Photocatalytic degradation mechanism of Amaranth, a recalcitrant carcinogenic azo dye, was investigated using mesoporous anatase TiO₂ under sunlight. Mesoporous anatase TiO₂ of high photocatalytic activity has been synthesized using sol-gel method and its photocatalytic activity for degradation of Amaranth dye has been evaluated with respect to Degussa P25. Effect of bi-dentate complexing agents like oxalic acid, ethylene glycol and urea on surface properties of TiO₂ catalyst has been investigated using TG-DTA, FTIR, HR-TEM, SAED, PXRD, EDS, UV-DRS, PL, BET N₂ adsorption-desorption isotherm studies and BJH analysis. The influence of catalyst properties such as mesoporous network, pore volume and surface area on kinetics of degradation of Amaranth as a function of irradiation time under natural sunlight has been monitored using UV-Vis spectroscopy. The highest rate constant value of 0.069 min⁻¹ is obtained for the photo catalytic degradation of Amaranth using TiO₂ synthesized via urea assisted sol-gel synthesis method. The effect of reaction conditions such as pH, TiO₂ concentration and Amaranth concentration on photo-degradation rate has been investigated. The enhanced photocatalytic activity of synthesized TiO_2 in comparison to P25 has been attributed to mesoporous nature of the catalyst leading to, increased pore diameter, pore volume, surface area and enhanced charge carrier separation efficiency. New intermediates of photo catalytic degradation of Amaranth namely, sodium-3-hydroxynaphthalene-2.7disulphonate, 3-hydroxynaphthalene, sodium-4-aminonaphthalenesulphonate and sodium-4-aminobezenesulphonate have been identified using LC-ESI-MS for the very first time, providing direct evidence for simultaneous bond cleavage pathways (-C-N-) and (-N=N-). A new plausible mechanism of TiO2 catalysed photo-degradation of Amaranth along with the comparison of its toxicity to that of its degradation intermediates and products is proposed.

1 Introduction

Organic azo dyes are one of the most common persistent organic pollutants, directly emitted to the environment by industries such as textile, leather, food and cosmetic ^{1,2}. It is now established that, these untreated dyes pose a great hazard to environment as their complex aromatic structure, stability and low-biodegradability results in their accumulation in natural water bodies and causes biochemical and morphological effects on biological systems³. Amaranth is one such widely used azo dye, used in food and cosmetic industry ⁴. Food additives and contaminants committee has restricted the use of fifteen synthetic dyes out of which, Amaranth is one of the most toxic, mutagenic and carcinogenic in nature ^{5,6}. Owing to its harmful effect on biological systems, many conventional and biological methods like coagulation, membrane separation, adsorption etc. have been investigated for removal of Amaranth from water bodies³. However, due to its high solubility in water, these methods are ineffective for complete separation or mineralization. The photocatalytic dye degradation using TiO₂ has emerged as one of the most promising route, due to its low band gap, inertness, economic viability, insolubility in water, stability to photo corrosion and its effectiveness towards the degradation of aqueous organic contaminants^{6,7}. Crystalline anatase TiO₂ in particular, has been found to exhibit higher photo catalytic activity

as compared to rutile due to increased rate of photo generated electrons and holes. Induction of mesoporosity in crystalline TiO_2 results in improved photocatalytic efficiency due to availability of greater specific surface area for effective dye adsorption and mass transport to the reactive sites, leading to enhancement in photo degradation rate. Various methods such as hydrothermal, combustion, co-precipitation, sol - gel etc.⁸⁻¹¹ have been proposed, to prepare crystalline mesoporous anatase TiO_2 with very high surface area of 234 m²g⁻¹. When compared to former methods of synthesis, sol-gel method has been found to be the most promising, due to its low processing temperature, homogeneity and stoichiometric synthesis control ¹¹. In most of these synthesis methods, the surface morphologies of TiO_2 are usually modified using expensive long chain complexing agents or surfactants via a modified sol-gel process for better photo degradation efficiency.

Photocatalytic degradation of Amaranth using TiO₂ in UV light in presence of strong oxidizing agents such as H_2O_2 , enhances the rate of formation of oxidants i.e. holes, OH and HO₂ radicals which leads to effective degradation (Gupta et al.¹³). However, efficiency and safety in handling and implementing such a process for practical applications depends on complete knowledge of dye degradation intermediates products and their toxicity evaluation^{4,5,12,13}. No such analysis on intermediates products have been provided in the work of Gupta et al.¹³ Moreover, due to handling problem with bulk H_2O_2 , more focus has been directed towards enhancing the photocatalytic properties of TiO₂. Researchers have also investigated the rate of degradation of Amaranth by doping

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transition metals like Cu, Ag on TiO₂ surface⁴. Jain et al. ¹⁴ investigated the enhancement of photocatalytic degradation of Amaranth by doping N and S onto TiO₂ using thiourea as surface modifier. However, these studies use methods such as hydrothermal and combustion synthesis which lack practical application for bulk catalyst synthesis. Moreover the metal loaded catalysis leads to leaching of active metals from the surface of catalyst which in turn leads to decrease in catalytic efficiency. Therefore facile methods of synthesis, use of low cost templates or complexing agents which are cost effective, economical and provide appreciable photocatalytic activity of TiO₂ are desired.

While the research on development of cost effective and efficient synthesis of TiO₂ or supported TiO₂ has gained large interest, less focus has been channelled towards identification of degradation products of Amaranth, various possible degradation pathways and mechanisms. According to the studies of Karkmaz et al.¹⁵ degradation of aqueous Amaranth dye solution is assumed to occur via the C-N bond cleavage leading to direct mineralization of azo group to $N_{\rm 2}$ gas, while the ring rupture process under mild acidic condition leads to formation of products such as organic acids which further mineralize to CO₂. On the contrary, in a sono-electrochemical experiment of Steter et al. 16 , the degradation of Amaranth is suggested to be initiated by the N=N (azo bond) cleavage leading to sodium-4-aminonaphthalenesulfonate and sodium-4-imino-3-hydroxynaphthalene-2,7-disulfonate. Further conversion of sodium-4-imino-3-hydroxynaphthalene-2,7disulfonate into 1-aminonaphthalene-2-ol, Sodium-4-amino-1naphthalenesulfonate which further convert to organic acids is proposed and not via direct mineralization to N₂ pathway. However, in both the above studies, the primary intermediates of C-N and N=N cleavage pathways namely, sodium-3hvdroxynaphthalene-2.7-disulphonate.sodium-4-

aminonaphthalenesulphonate and sodium-4-imino-3hydroxynaphthalene-2,7-disulfonate respectively, which provide direct evidence for the two independent cleavages have not been measured. Hence, the exact degradation mechanism of Amaranth is yet to be fully understood. Moreover, 1-aminonaphthalene-2-ol is a common stable undesired carcinogenic product of degradation of various dyes such as Yellow 14, Solvent Orange 7, Solvent Red 24 and Pigment Red 3 including Amaranth. Identification of such intermediates and products of photo catalysed dye degradation would provide a better insight into the degradation mechanism, which is extremely essential for the photo catalysis technology implementation to safely treat waste water polluted with Amaranth dye.

In the present study, we use a modified sol-gel method to prepare highly active mesoporous anatase TiO_2 nanocatalyst using Ti-isopropoxide precursor and cost effective bi-dentate complexing agents such as urea, ethylene glycol and oxalic acid. A comparative study of photo catalytic activity of synthesized TiO_2 catalyst for degradation of Amaranth dye under various experimental conditions of pH, TiO_2 concentration and Amaranth concentration in comparison to Degussa P25 is investigated. The identification of new degradation products, evidence for C-N and N=N bond cleavages along with a plausible mechanism of Amaranth degradation has been presented.

2 Experimental

2.1 Materials and methods

Amaranth dye (85%) was purchased from LobaChem and has been used without any further purification. Other chemicals such as titanium isopropoxide (98%), urea (99.5%), oxalic acid (99.5%), ethylene glycol (99.5%) and 10% aqueous ammonia solution were obtained from Spectrochem and were used without any further purification.

2.2 Catalyst synthesis

Mesoporous TiO₂ catalyst has been synthesized by using sol gel method. To 50 mL of Titanium isopropoxide-ethanol mixture at 8°C, 10% ammonia solution (200 mL) was added for the formation of metal hydroxide (at pH = 8). The metal hydroxide solution was then peptized using 1N HNO₃ followed by addition of 16 g of structure directing agents (SDA) such as urea, oxalic acid and ethylene glycol under constant stirring. The mixtures were stirred for 1 hour, aged and dried at 100 °C to form dry solid/semi solid. These as-synthesized mixtures were subjected to calcination in air at 550°C for 5 hours to obtain mesoporous TiO₂ catalyst. The synthesized pale yellow coloured catalysts were labelled as: TU= TiO₂ using urea, TOA= TiO₂ with oxalic acid, TEG= TiO₂ using ethylene glycol.

2.3 Catalyst characterization

The thermal decomposition behaviour of as-prepared mixtures was analysed using TG-DTA thermal analyser (NETSTA409 PC Luxx). Phase and structure of as-synthesized TiO₂ catalyst were investigated by powder X-ray diffraction (PXRD, Philips PW-1840) with Cu K alpha (k= 0.1540 nm) and nickel as filter over the 2θ range of 10-80°. The surface functionalities of the synthesized TiO₂ were evaluated using FTIR spectroscopy (Shimadzu IR- Prestige-21). The light absorption properties of the photo catalyst were investigated using UV-diffuse reflectance spectroscopy and solid state photoluminescence spectroscopy (PL). The morphology of the catalyst was determined by using Transmission Electron Microscopy (TEM, Microscopy JEOL). The porosity measurements using N₂ adsorption - desorption isotherm studies (Autosorb IQ QUA 211011) and BET, BJH analysis methods were used for determination of surface area, pore size distribution and total pore volume.

2.4 Photocatalytic activity

Amaranth stock solution of 30 ppm was prepared. Calibration plot for the dye solution has been obtained by varying the concentration from 10 - 100 ppm. 50 mg of the catalyst was dispersed in 200 mL (30 ppm) dye solution and the pH of the solution was recorded (pH = 5.7). The mixture was exposed to natural sunlight (12:00-2:00 pm, IST) under constant stirring condition for 90 minutes. The decrease in absorbance at 520 nm with increase in time was noted. The influence of various experimental parameters such as pH, dye concentration and catalyst concentration on the rate of photo degradation of Amaranth were investigated. The preliminary products of photo degradation of Amaranth were identified using LC-ESI-MS (Agilent 6520). The HPLC analysis (Agilent 1200) were performed using PhenomenexKinetex XB C18 column (length 30 mm, internal diameter 3.0 mm). Impurity profiling of

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Amaranth stock solution was performed using LC-ESI-MS and UPLC-ESI-MS technique (Acquity SDS Mass Spectrometer from Waters). The eluent gradient conditions used for separation are as listed in table ST1 in supplementary material. The mass parameters were optimized using a dual spray (ESI) with positive/negative polarity, operated under full scan mode with gas temperature of 350 $^{\circ}$ C and a flow rate of 10 Lmin⁻¹.

3 Results and discussion

3.1 TG-DTA and FTIR analysis

The representative TG-DTA curves of as-synthesized mixture of titanium isopropoxide with urea (TU), ethylene glycol (TEG) and oxalic acid (TOA) as a function of calcination temperature are presented in SF1 in supplimentary material. In brief, all as synthesized mixtures showed initial weight loss below 150 °C attributed to the loss of physically adsorbed water. With increase in calcination temperature, the decomposition of organic moety with loss of CO/CO₂, NOx occurs untill final transformation into stable oxide of titanium at 550°C. Samples calcined at higher temperatures resulted in decrease in the intensity of the IR vibrational peaks of NH, CH, C=O. Complete elimination of NH, CH, C=O and appearance of intense and broad absorption band due to Ti-O-Ti stretching and bending vibration modes in the region 800-400 cm⁻¹ confirms complete removal of organic moeity and formation of oxide of Titanium¹⁹ at 550 °C, in good agreement with TG studies see SF2 in suplementary materials.

3.2 PXRD analysis

The powder X-ray diffraction pattern of all the three synthesized catalysts (Figure 1) shows the formation of pure anatase phase of TiO₂ with peaks at 20 value 25.3°, 37.81°, 48.0°, 53.9°, 55.06°, 62.7°, 68.7° and 70.2° confirmed by comparing with the standard pattern (JCPDS number, 84-1286). The presence of sharp diffraction peaks indicates high crystallinity of the catalyst. Diffractogram of TU, TOA and TEG did not present any peak at 20 = 27.3° which indicates absence of rutile phase in the as-synthesized sample, in good agreement with the reports by Munner et al. ²⁰. The crystallite size of the synthesized nanoparticles has been calculated by using Scherer equation. Average crystallite size of the TiO₂ catalyst was estimated to be in the range of 10 -20 nm (see Table 1).

| Catalyst | Crystallite size | Band Gap | BET Surface | BJH Surface | Pore volume | Pore diameter |
|----------|---------------------|-------------|----------------------------------------|---------------------------|-------------------|------------------|
| | nm | eV | area m ² g ⁻¹ | area m²g ⁻¹ | ccg ⁻¹ | nm |
| DEG | 10.0 | 3.20 | 50 | | | |
| τu | 17.6 | 3.21 | 77.5 | 69.0 | 0.20 | 12.2 |
| TEG | 18.3 | 3.27 | 51.7 | 40.0 | 0.09 | 10.1 |
| ТОА | 15.0 | 3.32 | 30.0 | 23.7 | 0.08 | 3.0 |

Table 1: Comparison of properties of synthesized TiO_2 to that of Degussa P25



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Figure 1: Powder X-ray diffraction pattern of synthesized TiO₂ catalyst with different SDA.

3.3 Optical properties



Figure 2: A) PL spectra of TU and DEG, B) UV-DRS spectra of assynthesized TiO_2 catalysts.

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Figure 2 B shows UV-DRS plots of synthesized TiO₂ catalyst using different structure directing agents. The band gap of TiO₂ has been determined by plotting $F\infty^2 v/s eV$ (inset), along with absorbance v/s wavelength plot. Using the wavelength of absorption (λ), the value of E (eV) has been calculated using the following equation:

$$E(eV) = \frac{1240}{\lambda}$$

The band gap of the synthesized TiO₂ samples were found to be in the range of 3.20-3.33eV (see Table 1) with the lowest band gap of TU and the highest of TOA. In earlier studies, it has been reported that TiO₂ synthesized using urea generally leads to N doping in TiO₂, leading to a decrease in band gap and a shift in absorption band to visible region above 400 nm^{21, 22}. However, the obtained band gap in case of TU is similar to Degussa P25. In order to evaluate the possibility of N-doping and the origin of pale yellow colour in TU, photoluminescence measurement on DEG and TU were performed (see Figure 2 A). The PL emission spectrum of TiO₂ was recorded at an excitation wavelength of 220 nm (high absorption region). The PL emission spectra of both P25 and TU were found to be similar with major peaks at 361, 421, 461, 491, 535 and 604 nm. The 361 nm peak (lower than the band edge emission) is due to band to band transition ²³. Emission peaks at longer wavelengths in the visible region 421, 461, 491, 535 and 604 nm are attributed to surface state emissions which are located within the band gap of TiO2²⁴. The oxygen vacancies and surface hydroxyl groups present on the TiO₂ surface are known to act as excellent traps for charge carries, reducing the electron-hole recombination rate ^{23,24,25,26,27}. The major difference between the PL spectra of P25 and TU is observed in the emission intensity at 460 nm. The ratio of emission intensities at 460 to 421 nm decreases to 0.73 in TU compared to 0.97 in P25. This is because of the presence of oxygen vacancies that form shallow- trap states near the absorption band edge and acts as efficient electron trap centres or colour centers^{26,27}. The PL emission intensity decreases with increase in magnitude of F centres. On the contrary, N-doping on TiO₂ surface generally acts as a deep trap state for positive charge carriers (holes) and the PL emission intensity increases with increase in the amount of Ndoping ^{28,29}. Hence, the PL measurements indicate that the Ndoping has probably not occurred or is insignificant in the synthesized TU and the pale yellow colour of the synthesized TiO₂ powders is therefore attributed to the presence of F centers (F or F1+ or F2+) in TU.

3.4 HR-TEM, SAED and EDS analysis

For the synthesized TiO₂ catalyst, the surface morphology, particle size and shape has been investigated by using HR-TEM analysis. The HR-TEM images in Figure 3 are of TiO₂ samples obtained using urea, ethyleneglycol and oxalic acid after calcination in air at 550°C, which illustrates the formation of nano size TiO₂ particles. The average particle size was around 30 nm. HR-TEM images indicate the formation of aggregates of cuboidal shaped nanoparticles.

The selected area electron diffraction pattern of TU, TEG and TOA, is shown as an inset in Figure 3. The intensity and brightness of the polymorphic rings in the case of TEG and TOA was found to be weak whereas in the case of TU bright spots were observed which indicates enhanced poly crystallinity of TU catalyst. The 'd' values obtained from the electron diffraction pattern, 0.351 nm, 0.233 nm, 0.186 nm and 0.170 nm, corresponds to the planes (101), (004), (200) and (105). The 'd' spacing at 0.351 nm corresponding to (101) plane is the highest intensity peak in XRD at $2\theta = 25^{\circ}$ and is the characteristic peak of anatase phase of TiO₂. EDS surface analysis of TU, TOA and TEG (Figure 3) showed peaks corresponding to Ti and O with no other impurity peaks within the EDS detection limit. The XRD, SAED and EDS analysis are in good agreement and confirms the formation of high purity anatase TiO₂^{30, 31}.



Figure 3: HR-TEM images with selected area diffraction pattern of TiO_2 catalyst synthesized using Urea (TU), Ethylene glycol (TEG) and oxalic acid (TOA) after calcinations in air at 550°C

3.5 N₂ adsorption-desorption

Mesoporous TiO₂ prepared using sol gel method displayed type IV isotherms with hysteresis loop, typical of mesoporous adsorbents as shown in Figure 4. The initial part of the isotherm (low pressure) represents the monolayer-multilayer adsorption on to the mesoporous walls followed by capillary condensation/pore filling mechanism³². A pronounced effect of different SDA on the mesoporous structure of the synthesized catalyst was observed. Catalyst TU displayed H2a hysteresis with a characteristic step in desorption curve indicating the existence of complex pore structure with interconnected pore network. Such a phenomenon occurs when the wide pores have to access the external surface only through narrow necks.

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Figure 4 : N₂ adsorption-desorption isotherms and corresponding pore size distribution of mesoporous TiO₂ catalyst synthesized using 1)Urea (TU), 2) Ethylene glycol (TEG) and 3)Oxalic acid (TOA)

Hence, desorption through large pores is not possible until the condensate from narrow pores is desorbed, resulting in a H2a hysteresis. This is understandable, as urea acts as a fuel during heat treatment of the as-synthesized samples, resulting in rapid liberation of gases such as CO/CO₂, NOx etc. This may result in the observed complex pore structures with interconnected network of pores. On the other hand, the H1 hysteresis observed in the case of TEG indicates the formation of cylindrical or tubular uniform pores. The hysteresis loop observed in case of TOA is more similar to H3 hysteresis with the only difference being the extension of hysteresis even to low pressure region, indicating the presence of microporous-mesoporous structure ³². Both TU and TEG displayed a narrow pore size distribution in the range of 5-30 nm. The average pore diameter and pore volume for all three catalysts are as listed in Table 1. The highest surface area, pore size and pore volume were recorded for catalyst TU.

3.6 Percentage Purity and Impurity profiling of Amaranth dye

The LC-ESI-MS analysis of Amaranth stock solution showed major peak on chromatogram due to Amaranth dye with minor unresolved impurity bands which were below the mass detection limit (SF5 in supplementary material). Hence, further analysis were performed with Ultra Performance LC-ESI-MS under positive scan mode. Two impurity peaks at retention time 0.18 mins (11%) and 1.27 (7%) corresponding to m/z peaks of 144.2 and 301.3 respectively were detected (see SF6 and SF7 in supplementary material). The former impurity was identified to be α naphthylamine, however, no particular structure could be assigned to the second impurity.

3.7 Photocatalytic activity of synthesized TiO₂ catalysts

Amaranth belongs to the azo family of dyes with typical absorption peaks at 520 nm due to the π electron delocalization in the chromophore (azo group) and four absorption bands at 216, 242,

282 and 330 nm due to the π electron excitation on the naphthalene rings substituted with SO₃- and OH groups. The dye degradation reactions were performed under following reaction conditions: (i) Adsorption in dark with catalyst (ii) photolysis without catalyst and (iii) photo-catalytic degradation using synthesized TiO₂ catalysts. The initial reaction conditions were set to [Amaranth] = 30 ppm, pH = 5.6, TiO₂ = 50 mg at 30 °C and reaction time of 90 mins. The change in absorbance as a function of adsorption time or photocatalytic reaction time was noted using UV-Vis spectrometer at 520 nm.

During the photo degradation experiment in natural sunlight without catalyst, an insignificant decrease in the absorbance of <4% from the initial value was observed after 90 minutes of irradiation time. The corresponding change in the dye concentration was estimated by establishing the calibration plot of absorbance versus dye concentration. On the contrary, the addition of TiO₂ catalyst and irradiation in sunlight resulted in continuous decrease in intensity of absorption bands of Amaranth without appearance of new absorption bands. The colour of the solution changed from an initial pink to colourless at the end of 90 minutes. Accordingly, % degradation was calculated. Typical UV-visible spectra depicting the decrease in absorbance of the dye as a function of irradiation time using TU catalyst is presented in Figure 5. It was observed that the pH of the dye solution after the photocatalytic reaction decreases to 4.51 from an initial pH of 5.6, the change in the absorbance due to this pH change was accounted and % degradation due to photocatalytic reaction was corrected, more detailed in section 3.10. Among the various structure directing agents used to obtain TiO₂, the photo-catalyst TU showed the highest decrease in dye concentration (82.6%) after 90 minutes of reaction time. The lowest decrease in dye concentration was observed (62.3%) for TOA as shown in Figure 6A. In order to account for the change in photon flux of the solar radiation during a typical reaction run of 90 minutes on different days, every set of dye degradation experiment was performed with reference to the degradation experiment using commercially available Degussa P25 catalyst. The corresponding relative variation in the percentage conversion of the synthesized TiO₂ catalyst was accordingly recalculated.



Figure 5 : UV-Visible spectra depicting a decrease in absorbance of Amaranth dye as a function of photo-catalytic reaction time in presence of sunlight.



The bands at 1195, 1168 and 1040 cm⁻¹ are due to asymmetric stretching vibration in $SO_2 Na^+$ and the coupling between benzene mode and $v(SO_3)^{33}$ as seen in Figure 7B. The peak at 1340cm⁻¹ is due to O-H bending vibrations or it may also be attributed to SO2-O fingerprint¹⁵. The two intense peaks at 1496 and 1370 cm⁻¹ were attributed to -N=N- bond and the aromatic ring vibrations sensitive to the azo group 33 . The band at 1614 cm⁻¹ are linked to C=C aromatic skeletal vibrations. It is evident from Figure 7B that, the ratio of intensities of the peaks at 1195 cm⁻¹ to that of 1496 cm⁻¹ is 0.95 in solid Amaranth, while the ratio decreases to 0.89 in case of Amaranth adsorbed on TiO2, indicating that Amaranth undergoes adsorption on TiO₂ surface via interaction through SO₃⁻ group.



Figure 7 : IR spectra depicting the adsorption of Amaranth dye on to the surface of TiO₂ catalyst.

DOI: 10.1039/C7PP00090A

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Figure 6 : A) Kinetics profiles of photocatalytic degradation of amaranth over TiO₂ catalyst, B) Linear fits to the logarithmic ratio of initial concentration of Amaranth at time '0' to concentration at time 't'. [Amaranth]₀ = 30 ppm, TiO₂ = 50 mg, solution pH = 5.7 at 30°C.

Previous studies on photo degradation of Amaranth dye have reported pseudo first order reaction kinetics ^{2, 4}. A similar conclusion was drawn from our studies as the photo degradation kinetics of Amaranth were found to be best described by pseudo first order kinetic model, given by equation (In[Amaranth]₀/[Amaranth]_t=kt). А plot of In[Amaranth]₀/[Amaranth]_t gave a straight line fit, from the slope of which the rate constant k was calculated (see Figure 6B). Table 2 presents a list of calculated rate constants along with degradation efficiency of each of the synthesized TiO₂ catalyst. The TiO₂ catalyst synthesized using urea showed the highest photo degradation efficiency of 82.6% after 90 minutes of reaction time with a pseudo first order rate constant of 0.042 min⁻¹. The decreasing order of degradation efficiency of TiO₂ catalyst is as follows, TU>DEG>TEG>TOA.

3.8 Adsorption efficiency

As compared to the photo degradation efficiency of the synthesized catalyst, the adsorption efficiencies measured in dark for a comparable time period showed ~30% adsorption on TU. The decreasing adsorption efficiency trend was similar to that observed

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Since the average adsorption capacity in the dark is ~30% after 90 minutes for TU, the observed 82.6 % decrease in Amaranth concentration at pH=5.6 for a similar irradiation time period has to be the synergistic effect of the presence of interconnected porous network in TU with average pore diameter of 12.2 nm, large pore volume of 0.20 ccg⁻¹ leading to significantly large surface area of 77.5 m²g⁻¹ and greater dye adsorption efficiency, as well as low band gap which facilitates rapid degradation of dye and easy desorption of degraded products from the mesopores, thus regenerating the active surface for new dye molecules to be adsorbed. The apparent rate constant (k_{app}) for degradation of dye was found to be ~10 times greater than that of adsorption rate constant as listed in Table 2.

3.9 Effect of catalyst concentration

The study was carried out using catalyst amount of 30, 50, 80, 110, 140, 170 mg at pH = 5.6. Figure 8 shows the percentage degradation efficiency of Amaranth dye with varying catalyst amount. It can be observed from the graph that the degradation efficiency of the catalyst increases with increase in catalyst amount up to 110 mg. This could be due to increase in number of active sites and available total surface area for adsorption and light induced degradation. At this catalyst amount almost 99.1% of the Amaranth dye is decolourized within 60 minutes. When the loading of catalyst was less than the optimal value, the generation of \bullet OH and \bullet O₂⁻ superoxide radical anions is proportionally decreased which results in low catalytic activity. With further increase in catalyst above the optimum value, either leads to saturation or has a slight negative effect on the degradation efficiency which

| *Catalyst | Degradation Rate constant min ⁻¹ k _{app} | Adsorption Rate constant min ⁻¹ k_{ads} | % Ads | % Degd | % [#] Degd corrected for pH change |
|-----------|--------------------------------------------------------------------------|------------------------------------------------------------------|----------|-----------|---------------------------------------------------------|
| Blank | | | | 3.7 | |
| DEG | `0.031 | 0.0033 | 22.4 | 92.3 | 76.61 |
| TU | 0.042 | 0.0043 | 30.1 | 99.1 | 82.60 |
| TEG | 0.021 | 0.0014 | 9.0 | 83.3 | 69.14 |
| ТОА | 0.015 | 0.0015 | 11.0 | 75.0 | 62.25 |

*Catalyst amount = 50 mg, [Amaranth] = 30 ppm and total reaction time = 90 minutes at pH = 5.6 [#] % Degradation is corrected of the change in absorbance due to pH change at the end of photocatalytic reaction. Ads = Adsorption, Degd = Degradation.

Table 2 : Comparative analysis of degradation efficiency and degradation rate constants of synthesized TiO₂ vs Degussa P25.

could be due to less penetration of light due to the turbidity formed from increased amount of catalyst³⁴. The corresponding pseudo first order rate constant also shows almost linear increase with increase in catalyst amount up to 110 mg. An optimum value of k = 0.051 mins⁻¹ at [TU] = 110 mg at pH= 5.6 after 60 minutes of irradiation in sunlight of catalyst has been estimated. The above estimated value is ~2 times greater than the reported value by Karmaz et. al (k= 0.027 mins⁻¹ using 375 mg of TiO₂ and similar Amaranth concentration) at pH= 5.6.



Figure 8 : Variation in % degradation efficiency as a function of catalyst loading.



Figure 9 : Effect of initial dye concentration on photo catalytic degradation rate

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3.10 Effect of dye concentration

It has been observed that lower the initial concentration of the dye, faster is the degradation rate (see Figure 9). This is because, with optimum catalyst amount available, the dye molecules easily adsorb on the catalyst surface. However as the dye concentration increases, the rate of dye adsorption overrides the rate of photo degradation. With further increase in dye concentration, the dye itself acts as an internal filter for incident light and hence the light photons cannot reach the catalyst surface which in turn reduces the formation of *****OH and O_2 ***** radicals ^{13, 28}. (Kinetics plots along with rate constant and % degradation using TU catalyst are presented in SF4 and ST2 in supplementary material).

3.11 Effect of pH on degradation rate

The effect of pH on the rate of degradation of Amaranth was investigated in the pH range 2.0 - 11.0. In the first step, the initial absorbance of the dye solution (in dark, without catalyst) at different initial pH (2, 3, 5.6, 7, 8, 9 and 11) was recorded (marked as 'A' in Table 3). It was observed that the pH of the solution after photocatalytic reaction (in sunlight) decreases (see Figure 10A) to lower values (marked as 'B' in Table 3) as compared to the initial pH, possibly due to the formation of organic/inorganic acids. A typical plot of change in pH during the photocatalytic reaction and the corresponding change in absorbance is presented in Figure 10A. In order to account for the change in absorbance due to this pH change, the pH of the dye stock solution was adjusted to the values listed as 'B' in Table 3 and the corresponding decrease in absorbance was noted (marked as 'C' in Table 3 and presented in Figure 10B). The % degradation due to photocatalytic reaction was calculated as [(C/A)-(B/A)]×100. The estimated values of % rate constants at each initial reaction pH are listed in Table 3.

It can be seen that the highest degradation efficiency of 97.14% with an optimum rate constant of 0.069 mins⁻¹ has been estimated with 110 mg of catalyst TU at pH = 2 and 30 ppm dye solution under sunlight. On the contrary at pH 11, % degradation due to photocatalytic reaction is almost negligible. This could be due to fact that with the increase in pH the TiO₂ band edge positions shifts to more negative values, thereby resulting in the decrease in oxidation potential. Furthermore, the dissociation of TiOH into H⁺ and TiO⁻ results in decrease in adsorbed hydroxyl groups and hence a decrease in hydroxyl radical concentration. In addition to this, under extreme basic conditions, the TiO₂ surface becomes negatively charged and hence would repel the negatively charged dye (R-SO₃⁻) leading to lower adsorption rate and reduced degradation efficiency

3.12 Regeneration of catalyst

After every run of degradation experiment, the catalyst was kept in hot boiling deionised water under constant stirring for 1 hour and washed with deionised water before reactivation at 400°C. The catalytic efficiency of the activated catalyst was re-measured. This procedure was repeated 4 times. The observed decrease for every cycle is as follows: C1= 96.8%, C2= 96.7%, C3 = 96.3%, C4 = 96.3%.

6.0 1.0 D— pH change during photocatalytic reaction Absorbance of pH adjusted solution (in dark) Absorbance during photocatalytic reaction 0.8 5.7 0.6 5.4 Absorbance 편 5.1 0.4 0.2 4.8 Α 0.0 4.5 20 60 80 100 0 40 Time (minutes) After photocataytic 0.9 reaction (in light) Absorbance for adjusted pH (in dark) Initial absorbance (in dark Absorbance 0.6 0.3 В 0.0 10 8 12 14 6

Figure 10 : Efffect of pH on photo catalytic degradation rate.

pН

3.13 Photocatalytic degradation mechanism

Н

$$\begin{aligned} \text{TiO}_2 + \text{h}\nu \rightarrow \text{e}^- + \text{h}^+ \\ \text{(O}_2)_{ads} + \text{e}^- \rightarrow \text{O}_2^{\bullet^-} \\ \text{H}_2\text{O} + \text{h}^+ \rightarrow \text{OH} + \text{H}^+ \end{aligned}$$

Two possible mechanisms have been suggested in the literature 15 , 16 . According to the studies of Karkmaz et al. 15 , under acidic conditions, the surface of TiO₂ is positively charged,

$Ti-OH + H^+ \leftrightarrow Ti-(OH_2)^+$.

Adsorption of Amaranth on the surface of Ti-(OH₂)⁺ occurs via interaction of sulphonyl group in the ortho position with respect to the OH group on the naphthalene ring. The formation of OH radicals and h^+ on the catalyst surface are believed to initiate the radical degradation of Amaranth according to following reactions:

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| Initial pH of the dye solution | Initial dye [#] Abs | Final pH after photocatalytic reaction | Abs at final pH after photocatalytic | Initial dye pH adjusted to B value | Abs at pH adjusted to B value | % Degd due to photocatalytic reaction | Degd Rate constant min ⁻¹ |
|--------------------------------------|---------------------------------|----------------------------------------------|--------------------------------------------|---------------------------------------|----------------------------------|---------------------------------------------|--------------------------------------------|
| (dark) | (dark) A | (light) | reaction (light) B | (dark) | (dark) C | [(C/A)-(B/A)]x100 | k _{app} |
| | | | | | | | |
| 2 | 0.70 | 1.78 | 0.01 | 1.78 | 0.69 | 97.14 | 0.069 |
| 3 | 0.66 | 2.89 | 0.01 | 2.89 | 0.65 | 96.96 | 0.051 |
| 5.6 | 0.75 | 4.51 | 0.01 | 4.51 | 0.63 | 82.66 | 0.040 |
| 7 | 0.60 | 6.71 | 0.15 | 6.71 | 0.58 | 71.66 | 0.035 |
| 8 | 0.57 | 6.50 | 0.17 | 6.50 | 0.55 | 66.66 | 0.030 |
| 9 | 0.56 | 5.92 | 0.28 | 5.92 | 0.55 | 48.21 | 0.020 |
| 11 | 0.55 | 10.76 | 0.43 | 10.76 | 0.46 | 5.5 | 0.009 |

*Catalyst = TU, Catalyst amount = 110 mg, [Amaranth] =30 ppm and total reaction time = 60 minutes. [#]Abs= Absorbance

Table 3 : Effect of pH on degradation efficiency of TU.

 $R-SO_{3}^{-} + OH \rightarrow R + HSO_{4}^{-} (\rightarrow H^{+} + SO_{4}^{2-})$ $R-SO_{3}^{-} + h^{+} \rightarrow R-SO_{3}^{\bullet}$

Where R-SO₃ represents Amaranth dye. The radical reactions of R[•] initiates dye degradation process via ring rupture, leads to formation of organic acids such as lactic acid and malic acid both of which transform to formic acid before converting to gaseous CO₂ along with direct mineralization of azo group to gaseous N2. On the contrary, Steter et al. 16 performed sonoelectrochemical degradation of Amaranth and product identification by LC-MS and suggested that, the Amaranth degradation occurs by cleavage of the -N=N- (pathway B' in Figure 11) leading to sodium-4-amino naphthalenesulphonate sodium-4-imino-3-hydroxynaphthalene-2,7-(B1) and disulfonate (B'1) and not via direct mineralization to N₂ gas. Further conversion of (B'1) into 1-aminonaphthanlene-2-ol (B'2) which converts to naphthalene-1,2-diol tautomer (B'3) is assumed to form salicylic acid via ring rupture, followed by conversion to phenol, oxalic acid and malic acid etc. Hence, different intermediates and products in these individual studies suggest contradictory bond cleavage pathways. Moreover, the primary intermediates A1, B1 and B'1 of C-N and N=N bond cleavage steps respectively, have not been detected so far, to the best of our knowledge.

The present study reports qualitative identification of primary intermediates and products using LC-ESI-MS technique. The detected m/z values and their comparison with the proposed mechanisms by Steter et al. and Karkmaz et al. leads to an interesting observation. The various products detected using LC-ESI-MS in our study, can be explained only if two simultaneous bond cleavage pathways, i.e. C-N bond cleavage

(marked as cleavage-A) and N=N cleavage (marked as cleavage-B and B') respectively in Figure 11, are considered, (mass spectra are presented in supplementary material). Cleavage-B leads to formation of two primary intermediates B1 and B'1 as explained earlier. B'1 transforms into 1aminonaphthalen-2-ol (m/z = 216) via loss of two SO_3^- groups, which further converts into phenol (m/z = 117) and malic acid (m/z = 135) via ring rupture mechanism of 1,2dihydroxnaphthalene-1,2-diol tautomer (m/z = 191), in agreement with Steter et al. ¹⁶. However, the formation of phenol can also be explained via intermediate B1 which transforms in to sodium-4-aminobenzenesulphonate (B2, m/z = 172) that undergoes loss of SO₃ and NH₂ groups via oxidative OH addition leading to phenol. Moreover, C-N cleavage (cleavage-A) leads to formation of sodium-3hydroxynaphthalene-2, 7-disulfonate (A1, m/z = 365), which losses two SO_3 groups to form 3-hydroxynaphthalene (m/z = 162).3-hydroxynaphthalene may undergoing rupture mechanism to form phenol. It is important to note here that this is the first study on identification of four probable new intermediates namely, sodium-3-hydroxynaphthalene-2,7disulphonate (A1), 3-hydroxynaphthalene (A2), sodium-4aminonaphthalene sulphonate (B1) and sodium-4aminobezenesulphonate (B2) formed during photocatalytic degradation of Amaranth to the best of our knowledge. Two new plausible pathways A and B leading to formation of phenol are presented in Figure 11. Moreover, there were some other fragmentation patterns observed in mass spectra which were complex to assign any particular structure. The two impurities detected in Amaranth stock solution in UPLC-ESI-MS, will be negligible and unresolved in LC-ESI-MS as discussed earlier and does not influence the proposed mechanism of Amaranth degradation. The above discussion is therefore restricted to qualitative identification only. Nonetheless, the degradation kinetics and identification of degradation intermediates and products provide a better insight into the various possible degradation pathways simultaneously operating on TiO₂surface.

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Figure 11 : Plausible mechanism of Amaranth degradation

3.14 Toxicity of Amaranth versus photocatalytic degradation products.

Literature reports on toxicological impact of Amaranth dye tested on albino rats confirm that Amaranth at 10 times ADI (Acceptable Daily Intake) leads to fatal abnormalities and doses of 47 mg/kg by weight of Amaranth could impair hepatic function³⁵. Meanwhile, the literature studies on the degradation products and intermediates of Amaranth dye detected in this study such as, sodium-3-hydroxynaphthalene-7-disulphonate, 3-hydroxynaphthalene, sodium-4-2. aminonaphalenesulphonate, sodium-4aminobezenesulphonate, phenol, malic acid indicate that they are comparatively far less damaging. Tests performed by Safety Assessment Laboratory, Panapharm Laboratories Co. Ltd, report sodium-3-hydroxynaphthalene-2,7-disulphonate to be non-mutagenic and non-toxic. 1-aminonaphthalene-2-ol is reported to be a carcinogen when tested on rats $^{\rm 36,37}.$ 1aminonaphthalene-2-ol is observed to be the stable end product of chemical reduction of many dyes such as Solvent Yellow 14, Solvent Orange 7, Solvent Red 24 and Pigment Red 3^{38} . It is also the product of anaerobic metabolism of azo dyes such as Sudan I, Sudan II, Sudan III, Sudan IV and Para Red³⁹.However, in our study, 1-aminonaphthalene-2-ol is only an intermediate which is transformed into less toxic products such as malic acid, phenol etc. Phenol is known to be nongenotoxic and thus it is not considered to be direct cancer risk⁴⁰.No reports on carcinogenicity of malic acid is available in the literature to the best of our knowledge. From the above

comparisons it can be concluded that, photocatalytic degradation of amaranth using TiO_2 under natural sunlight can be safely implemented as a pre-treatment procedure to decolourize waste water contaminated with Amaranth. However, for complete water purification, total mineralization of Amaranth is desired.

4 Conclusions

Nano sized mesoporous anatase TiO₂ catalysts were synthesized using a sol gel method. A pronounced effect of SDA on porous nature of synthesized TiO₂ catalyst leading to high surface area of 77.5 m^2g^{-1} (using urea) was observed. Amaranth, one of the food dyes which is prohibited due to its carcinogenic effect, was effectively decolorized to less hazardous products using synthesized mesoporous TiO₂ catalysts under natural sunlight in water. Mesoporous TiO₂ obtained using urea showed better photo catalytic activity with highest rate constant of 0.069 min⁻¹ for the degradation of Amaranth as compared to the rest of SDA's and commercially available Degussa P-25, which was attributed to the synergistic effect of mesoporous nature of TiO₂ leading to reduction in electron-hole recombination rate, increased dye adsorption rate, efficient photo degradation on TiO₂ due to low band gap and ease of desorption of degradation products from mesopores, leading to regeneration of active surface. New intermediates of photocatalytic degradation of Amaranth namely, sodium-3-hydroxynaphthalene-2,7-disulphonate, 3-

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hydroxynaphthalene, sodium-4-aminonaphalenesulphonate and sodium-4-aminobezenesulphonate were identified for the very first time, providing the evidence for two simultaneous bond cleavage pathways (-C-N-) and (-N=N-) leading to degradation of Amaranth. The toxicity comparison between Amaranth dye and the identified degradation products suggest that, mesoporous TiO_2 nano catalyst can be used effectively and safely to pre-treat coloured waste water contaminated with Amaranth dye.

Acknowledgements

This work has been funded by the UGC-BSR start-up research grant project No. F.30-102/2015 and SERB ECR award project No. ECR/2015/000047. Authors would like to thank NCCR, IITM for extending facilities for catalyst characterization. We owe our sincere gratitude to Prof. B. Viswanathan (NCCR, IITM-India), Prof. J. B. Fernandes, Prof. K. Priolkar and Dr. P. Samant (Goa University-India) for their guidance, valuable suggestions and constant encouragement throughout the work.

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Graphical Abstract



Highlights

- > Urea assisted sol-gel synthesis of mesoporous anatase TiO₂ of high photo catalytic activity
- ➢ Highest photocatalytic Amaranth degradation rate constant of 0.069 min⁻¹
- Identification of novel intermediates viz sodium-3-hydroxynaphthalene-2,7-disulphonate,
 3-hydroxynaphthalene, sodium-4-aminonaphthalenesulphonate and sodium-4-aminobezenesulphonate
- Evidence of C-N and N=N bond cleavages and new plausible mechanism of Amaranth degradation.