

# Treatment of industrial effluent by synthesized Nano-composite ZrCdPbO<sub>4</sub> through solar energy

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## Research Article

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# Abstract

Water is the most essential natural resource for living beings, animals and plants but unfortunately it is being polluted by various means. Coloured pollutants, mainly dyes contribute maximum to this. Thus an attempt is made to remove such pollutants in an eco friendly manner. Novel nano sized composite material  $ZrCdPbO_4$  is synthesized by coprecipitation method, characterized by UV-vis, IR, FESEM, XRD, XPS and EDX analysis methods and is used for removing such pollutants from water. The emphasis of the present work is to use the prepared material as photocatalyst for degradation of various pollutants. Experimental details of degradation of a common industrial effluent, Azure-A dye as role model are discussed. Number of factors are varied to obtain maximum degradation rate through pseudo first order kinetic study. Hydroxyl radicals are found to play important role in cleavage of various bonds of the pollutant and is endorsed by scavenger study. LCMS/MS analysis is carried to rule out the route of the degradation. Final products are ascertained by laboratory tests.

## Introduction

Water is the essential natural resource for life on earth. Now a day, through release of different pollutants, the availability of potable water has decreased and if available, is adversely affecting the health of living beings. Some human activities like constructions, release of various industrial wastes like clothes, paper, printing, dye waste, agricultural and pharmaceutical waste, excavation, cutting of tree etc has harmed the nature and has disturbed the natural balance. One of such activities that had polluted water is synthesis of colours and dyes. These colour pollutants when excreted directly into water, without any treatment, cause harm to the resource ending into dangerous outcomes. Thus need of the hour is to treat such resources by any mean and remove these pollutants. Various treatment methods are available to treat pollutants in wastewater like foam separation, electrode materials, bio-adsorption technologies, Tailoring nanofiltration membranes, Fenton-flocculation process etc (Fei et al. 2018; Yang et al. 2019; Li et al. 2019; Cao et al. 2020; Xiao et al. 2017). Beside these methods, photocatalysis is an emerging technology for degradation of pollutants. Some pollutants like pharmaceuticals and diagnostic agents, different pesticides (alachlor, atrazine, chlorfenvinphos, diuron, isoproturon and pentachlorophenol), refractory organics, organic contaminants etc. were removed through various methods [Doll et al. 2005; Hincapie et al. 2005; Xiao et al. 2015; Pelizzetti and Minero 1993; Goetz et al. 2009]. Photocatalytic degradation gives almost complete decolourization of dyes and removal of total organic carbon [Gouvêa et al. 2000; Kuo 2009; Bizani et al. 2006; Andriantsiferana et al. 2014; Sacco et al. 2012]).

Various types of photocatalyst are synthesized and are found to have high degradation efficiency towards organic dyes.  $Ca_4Fe_9O_{17}$ ,  $CuInSe_2/TiO_2$  hybrid hetero-nanostructures,  $Fe_3O_4/ZnO$  nanoparticles,  $CaMoO_4$ /electroconductive geopolymers composite,  $Fe_3O_4-TiO_2$ ,  $CdBiYO_4$ , tungsten containing nanoparticles etc are some examples of such photocatalysts (Chatterjee and Chakraborty 2021; Kshirsagar et al. 2017; Długosz et al. 2021; He et al. 2019; Zazouli et al. 2017; Du et al. 2012; Vijay and Bhardwaj et al. 2015). Doping of photocatalysts also enhances the rate of degradation like zinc sulfide doped with manganese, nickel and copper etc (Pourererdal et al. 2009).

It is observed that hydroxyl radicals play a significant role in heterogeneous photocatalysis and in degradation of dyes (Daneshvar et al. 2004; Raizada et al. 2014). Transition metal oxides like Al-based  $\text{Fe}_2\text{O}_3$  nanostructures generate these radicals during photocatalysis (Shinde et al. 2013). The yield of hydroxyl radicals on photocatalyst surface was determined at the rate of 35.6  $\mu\text{M}/\text{hr}$ , 0.28  $\mu\text{M}/\text{h}$  and 0.88  $\mu\text{M}/\text{h}$  for P25 (standard commercial catalysts),  $\text{WO}_3$  and Pt-C<sub>3</sub>N<sub>4</sub> photocatalysts respectively (Nagarajan et al. 2017). Photocatalytic system,  $\text{MoO}_3/\text{g-C}_3\text{N}_4$  composite works in acidic medium suggesting participation of superoxide radicals and holes instead of hydroxyl radicals (Xue et al. 2019). Pathways of degradation of dyes and intermediate molecules formed within the path were determined through study of peaks in LCMS/MS analysis (Shen et al. 2021; Zhong et al. 2009; Mittal et al. 2020; Chen et al. 2009; Jo et al. 2016). Studies were carried out with various types of doped transition metals to improve the photocatalytic activities especially in  $\text{TiO}_2$  (Gracien et al. 2007; Wong et al. 2005). Joshi et al. 2015 carried out degradation study using  $\text{Li}_2\text{CuMo}_2\text{O}_8$  as a photocatalyst.

Present investigations deal with synthesis of a novel nano composite material  $\text{ZrCdPbO}_4$ . Numerous beneficial properties of prepared photocatalyst make it suitable for degradation of pollutants in water, especially dye molecules. Azure A dye is considered as a role model. Different factors like pH, dose of photocatalyst, concentration of dye, light intensity etc. are varied to extract the maximum degradation conditions. Participation of hydroxyl free radical is ruled out by scavenger study. A tentative mechanism for degradation is proposed through LCMS/MS peak analysis and intermediates are also determined.

## Materials And Methods

Zirconyl nitrate, lead nitrate and cadmium nitrate were used as precursors (Merck) for synthesis of the photocatalyst, sodium hydroxide was used as precipitating agent (CDH) and Azure A (Otto) was used as the model pollutant. HCl (CDH) and NaOH (CDH) were used for adjusting the pH of the solutions and pH was recorded by pH meter (Heraeus imported pen type). Optical density of solutions at different time intervals was recorded by UV-Vis spectrophotometer (CHINO). A 200 Watt lamp (Philips) was used for irradiation and the intensity of light was measured by solarimeter (CEL-201). KI, EDTA and isopropyl alcohol (Merck) were used as scavenger to trap the active species. All chemicals were used in approximately 95-99% pure form and of LR grade. LCMS/MS technique on instrument XEVO-TQD#QCA1232 with ESI type, source temperature 144°C, mass range 125 to 1000, duration time 15 minutes and collision energy 3.0 was employed.

## Experimental

The photocatalyst  $\text{ZrCdPbO}_4$  was synthesized by using precursors- zirconyl nitrate, lead nitrate and cadmium nitrate. Solid co-precipitation method was employed and sodium hydroxide was used as precipitating agent under controlled conditions. Solid off white coloured material was obtained after calcination with yield of 71.73%. The material was then characterized by XRD to obtain crystal size of  $21.59 \pm 6.15$  nm. EDX analysis proved the presence of Zr, Cd, Pb and O elements in ratio 1:1:1:4. XPS

analysis determined the oxidation states as +4 for Zirconium, +2 for cadmium, +2 for lead and -2 for oxygen. The molecular formula of the prepared photocatalyst was thus confirmed to be  $\text{ZrCdPbO}_4$ . FE-SEM analysis showed homogeneous cluster form of the material and IR study showed bonding and vibrations (bending and stretching) correlated to  $\text{CdO}$ ,  $\text{PbO}$  and  $\text{ZrO}_2$  molecules. UV-VIS spectral study was used to determine the band gap and peak at 229 nm suggested it to be 5 eV. The results are reported earlier (Lohar et al. 2021). Larger band gap ensured higher photo-quantum efficiency of the prepared material because of greater life time of photo-generated electrons and holes, thus having enough time to degrade pollutants. Participation of OH free radical was ascertained by scavenger study. Further the analysis for degradation of Azure A was carried out through LC/MS technique to determine the intermediated formed and path way of degradation.

## Photocatalytic study

Stock solution of the dye of concentration  $1 \times 10^{-3}$  M (0.288 g/L) was prepared in doubly distilled water. This was further diluted to obtain desired concentration. Dye solution of concentration  $0.2 \times 10^{-4}$  M was taken, pH was adjusted to 8.0 by adding pre standardized NaOH solution and 0.22 g of  $\text{ZrCdPbO}_4$  photocatalyst was added. The reaction mixture was then exposed to a tungsten lamp at the intensity of 74.0 mW/cm<sup>2</sup> and a water filter was used to cut off thermal side reactions. 2-3 mL of aliquot was drawn from the reaction mixture after particular time intervals during the progress of the reaction and optical density was recorded at  $\lambda_{\text{max}}$  600 nm. It was observed that presence of light and the photocatalyst both was necessary to bring the degradation of dye, suggesting the reaction to be a photocatalytic one.

## Results And Discussion

### Typical Run

A typical run is plotted between  $1 + \log$  of optical density (O.D.) and time. The observation data are given in Table 1 and graphically represented by figure 1. A straight line in the plot indicates the rate of reaction to follow pseudo first order kinetics. Kinetic models, pseudo-first-order and pseudo-second-order (Type-1, Type-2, Type-3, Type-4 and Type-5) were selected to explain the degradation data and it was found that pseudo-first-order kinetic model prevailed in degradation process. (Zulfiqar et al. 2021). The reaction conditions obtained for maximum degradation of the dye Azure A are at pH 8.0, dose of photocatalyst 0.22 g, concentration of Azure A  $0.2 \times 10^{-4}$  M and light intensity 74.0 mW/cm<sup>2</sup>.

Percentage of dye degradation at optimum conditions of parameters is given by:-

$$\text{Degradation Efficiency(DE)(\%)} = \frac{A_0 - A_t}{A_0} \times 100 = 75.31 \quad (1)$$

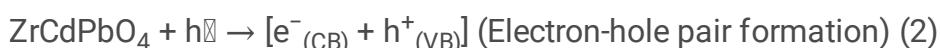
It is observed that absorbance of the dye solution decreases with time. The maximum rate of degradation is found to be  $k = 7.67 \times 10^{-4}$  (sec<sup>-1</sup>) and 75.31% degradation of the dye is observed in 40 minutes.

## **Effect of pH**

One of the major factors affecting the rate of degradation of the dye is pH of the solution. Thus it was varied by adding pre standardized NaOH and HCl and all other factors were kept constant. It was observed that with change in pH, the initial optical density of the solution changes, which can also be observed in multiline graphs, suggesting the pH sensitive nature of dyes. The effect of pH was studied in range 5.0 to 10.0 with difference of 0.5, results of which are reported in figure 2 and table 2.

It was observed that rate of photocatalytic degradation increased with increase in pH up to 8.0 and then gradually decreased. It is explained by following reactions.

Electron hole pairs are generated at photocatalyst surface by absorption of photons from light.



The increase in rate is attributed to the availability of more concentration of OH<sup>-</sup> ions in the solution. Holes abstract electrons from hydroxyl anions generating hydroxyl free radicals which are the responsible species causing degradation.



After pH 8.0, decrease in reaction rate is observed because repulsion amongst OH<sup>-</sup> ions and electrons on photocatalyst surface dominated due to crowd created at the surface. This repulsion forces the recombination of electrons and holes, besides abstracting electrons from OH<sup>-</sup> species. Thus a decrease in the rate of degradation is observed.

## **Effect of Dose of Photocatalyst**

The effect of dose of photocatalyst is studied by varying its weight and with keeping all other factors constant. The range is considered from 0.06 g to 0.26 g having difference of 0.02 g. Figure 3 represents the effect of variation graphically and the data are given in Table 3.

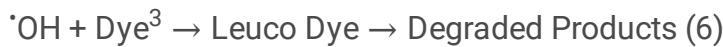
Maximum rate of degradation is observed at 0.22 g of photocatalyst. Further increase in dose of photocatalyst, reduces the rate of reaction. It is explained on the basis that with increase in dose of photocatalyst surface area of particles exposed to light increases and thus formation of number of electron-hole pairs increases. These holes are found responsible for abstraction of electrons from the hydroxyl ion (OH<sup>-</sup>), producing hydroxyl free radicals ( $\cdot\text{OH}$ ), the responsible species for degradation of the dye. Thus increase in rate is observed. After attaining maximum value (0.22g), rate of reaction decreases because of formation of multilayer of photocatalyst and it forces the recombination of electrons and holes. Thus reduction in rate of degradation is observed.

## **Effect of Dye Concentration**

The effect of concentration of dye on degradation is studied ranging from  $0.08 \times 10^{-4}$  to  $1.4 \times 10^{-4}$  M. The resulting data are shown graphically in figure 4 and tabulated in Table 4. All other factors were kept constant. Dye molecules absorb the light radiations and get excited to singlet state during the reaction and convert to triplet state by inter system crossing.



Dye molecules are attacked by OH free radicals at weaker bond site and breakdown of the molecules is observed.



The observations show that with increase in concentration of dye, rate of reaction increases. The reason behind is with increase in concentration, more dye molecules are available to absorb photons from light and get excited. Thus rate of degradation increases. After attaining maximum value ( $0.2 \times 10^{-4}$  M), increase in concentration of the dye decreases the rate of degradation because beyond the concentration, addition of dye imparts darker colour to the solution and starts acting as filter to the incident light. Thus the desired amount of incident light is not able to reach up to the photocatalyst surface at the base of the vessel; as a result the rate of reaction decreases.

## Effect of Light Intensity

Variation of light intensity is carried out in the range 7.0 to 74.0 mW/cm<sup>2</sup>. The observation data are graphically represented in figure 5 and tabulated in Table 5. All other factors are kept constant.

The rate of photocatalytic degradation increases with increase in intensity of light. This is explained by the fact that with increase in light intensity, number of photons striking per unit area per unit time increases. This increases the number of excited dye molecules and increase in generation of electron hole pair at the surface of photocatalyst is also observed. Thus rate of degradation increases. The rate of degradation is found maximum at light intensity 74.0 mW/cm<sup>2</sup>. Further rise in intensity of light causes heating of the solution and thus is avoided.

## Scavenger study

Scavenger study is carried out to find out the role of active species that cause degradation. Different scavengers like benzoquinone, EDTA, KI and isopropyl alcohol are used and are graphically reported in figure 6. It is evident from the data that addition of isopropyl alcohol (hydroxyl radical scavenger) ceases the reaction and significant reduction in the rate of degradation (up to 82%) is observed proving that the dye degradation is caused by hydroxyl radicals.

## LCMS/MS Analysis for Determination of Degradation Pathway

Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS) is an analytical method in which fragmentation of any molecule is analyzed by trapping separated ions (Chen et al. 2008). The mechanistic path in degradation of dyes like Methylene Blue, Orange G etc was studied using LCMS technique (Rauf et al. 2010; Meetani et al. 2011; Hisaindee et al. 2013; Kushwaha et al. 2018; Sinha and Ahmaruzzaman. 2015).

LC/MS analysis for degradation of Azure A is carried out on instrument XEVO-TQD#QCA1232 with ESI type, source temperature 144°C, mass range 125 to 1000, duration time 15 minutes and collision energy 3.0. The dye solution with pH 8.0, dose of photocatalyst 0.22 g, concentration of dye  $0.2 \times 10^{-4}$  M, is exposed to the light with intensity 74.0 mW/cm<sup>2</sup> and 10 mL of the solution at different time intervals (7, 14 and 21 minutes) are quenched and separated from the reaction system. These are then subjected to LC-MS analysis. The data are given in Table 6 and figure 7, 8, 9 and 10. The values of m/z are calculated to obtain possible degradation pathway and tentative fragmentation of dye molecule. Further formation of smaller gaseous fragments is ascertained through laboratory experiments.

LC/MS peak analysis suggested that during degradation process, the dye molecules are attacked by 'OH free radicals several times, at the weaker bond site and a breakdown of ring as well as of conjugation is observed resulting in formation of smaller fragments.

Initially attack of hydroxyl free radicals at the parent dye molecule generates molecule 4 (m/z 311.05 via 2 and 3 of m/z 257 and 229 respectively, figure 8b). Further attack results in breakdown of the central ring into two fragments 5 and 6 (m/z 203.2 and 159.1 respectively, figure 8a, 8c). Molecule 5 is further attacked by hydroxyl free radicals converting into 5" (m/z 185.3, figure 8c) and total double bond break down (TDBB) is observed to form smaller molecules. Molecule 5 also gets converted to molecule 6 and further attack of 'OH free radicals causes removal of H<sub>2</sub>O from the unstable fragment producing molecule 7 (m/z 159.1) followed by break down of ringed species to form molecule 8 (m/z 160, figure 8c) and into smaller fragments like CO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>O etc is observed.

Simultaneously, following other path, molecule 4 breaks into two fragments that are molecule 5' (m/z 221.2) and molecule 6' (m/z 130.3, figure 8a, 8c). Molecule 5' then gets converted to molecule 7' (m/z 195.2) via molecule 6', by removal of unstable fragment (figure 8b). Further attack of free radical breaks the ring to form molecule 8' (m/z 210.1, figure 9). Elemental test in the residual solution proved that no element is left behind, suggesting complete breakdown of the dye molecules in smaller fragments like CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>O etc.

Numbers of peaks are observed at higher m/z values suggesting the formation of unstable polymeric molecules by recombination of fragments which readily break down into smaller ones. A tentative route is drawn for the same (figure 10). Some molecules with higher mass values 349, 456, 762, 963 etc are constructed through azo linkage, ether linkage and through release of small fragments like H<sub>2</sub>O, CO<sub>2</sub>, H<sub>2</sub> etc.(figure 9). Lower intensity of these peaks suggested their lower stability and their instantaneous breakdown into other fragments.

# Conclusions

It is concluded here by that a novel nanosized quaternary photocatalyst is synthesized and is characterized. Band gap energy of the photocatalyst comes out to be 5 eV, which makes the material suitable for photocatalytic activities as recombination of electrons and holes is reduced. The photocatalyst is further used for removal of dye Azure A from water. A mechanistic pathway is proposed where degraded fragments are identified by considering m/z peaks through LC-MS spectra. Complete degradation of the dye molecules into smaller harmless fragments is observed. The process is found beneficial for the society in numerous ways. Use of solar radiations, simple process of regeneration and reusability of photocatalyst, treatment of polluted water to make it useful, less time and energy consuming process etc. makes the process economic one. The process does not add any other material to the resource or environment and so is an eco-friendly process. Thus the process can be used at larger scale for purification of water in eco-friendly manner.

# Declarations

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## Author Contributions

All the authors have been working with equal efforts on the project and have contributed equally.

## Conflicts of interest

There are no conflicts of interest to declare.

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## Tables

**Table 1** Typical run

Time (min.)	Optical Density (O.D.)	1+log O. D.
00	0.470	0.6720
05	0.354	0.5490
10	0.277	0.4424
15	0.221	0.3443
20	0.187	0.2718
25	0.162	0.2095
30	0.138	0.1398
35	0.128	0.1072
40	0.116	0.0644
$k = 7.67 \times 10^{-4} (\text{sec}^{-1})$		

**Table 2** Effect of pHDose of photocatalyst = 0.22 g, [Azure A] =  $0.2 \times 10^{-4}$  M, Light intensity = 74.0 mW/cm<sup>2</sup>

pH	Rate constant $\times 10^4$ (sec <sup>-1</sup> )
5.0	0.77
5.5	2.68
6.0	3.97
6.5	4.24
7.0	4.24
7.5	5.94
<b>8.0</b>	<b>7.67</b>
8.5	5.94
9.0	5.94
9.5	5.10
10.0	5.10

**Table 3** Effect of dose of photocatalystpH= 8.0, [Azure A] =  $0.2 \times 10^{-4}$  M, Light intensity = 74.0 mW/cm<sup>2</sup>

Dose of photocatalyst (g)	Rate constant $\times 10^4$ (sec $^{-1}$ )
0.06	1.86
0.08	2.11
0.10	3.61
0.12	4.48
0.14	5.38
0.16	5.82
0.18	6.31
0.20	6.31
0.22	7.67
0.24	6.72
0.26	5.06

**Table 4** Effect of dye concentration

pH= 8.0, Dose of photocatalyst = 0.22 g, Light intensity = 74.0 mW/cm $^2$

[Azure A] $\times 10^{-4}$ M	Rate constant $\times 10^4$ (sec $^{-1}$ )
0.08	6.38
0.10	6.38
0.20	7.67
0.40	5.96
0.60	3.40
0.80	2.76
1.00	1.90
1.20	1.27
1.40	1.05

**Table 5** Effect of light intensity

pH= 8.0, Dose of photocatalyst = 0.22 g, [Azure A] = 0.2 $\times 10^{-4}$  M

Light intensity (mW/cm $^2$ )	Rate constant $\times 10^4$ (sec $^{-1}$ )
07.0	1.11
14.0	2.26
40.0	4.22
67.0	6.80
74.0	7.67

**Table 6** Mass to charge ratio in LC-MS/MS spectra during cleavage of Azure A

Structure no.	Chemical Formula	Exact Mass	MS/MS Fragments	% Mass Error
1	C <sub>14</sub> H <sub>14</sub> ClN <sub>3</sub> S	291.06	289.3	0.99
2	C <sub>14</sub> H <sub>14</sub> N <sub>3</sub> S <sup>+</sup>	256.09	257.3	1.00
3	C <sub>12</sub> H <sub>10</sub> N <sub>3</sub> S <sup>+</sup>	228.07	229.2	1.00
4	C <sub>12</sub> H <sub>13</sub> N <sub>3</sub> O <sub>5</sub> S	311.06	311.1	1.00
5	C <sub>6</sub> H <sub>9</sub> NO <sub>5</sub> S	207.02	203.2	0.98
5'	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> O <sub>5</sub> S	220.02	221.2	1.00
5''	C <sub>6</sub> H <sub>15</sub> NO <sub>5</sub>	181.09	185.3	1.02
6	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>	156.05	159.1	1.01
6'	C <sub>6</sub> H <sub>7</sub> NO <sub>2</sub>	125.05	130.3	1.04
7	C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>	154.03	159.1	1.03
7'	C <sub>6</sub> H <sub>9</sub> NO <sub>4</sub> S	191.03	195.2	1.02
8	C <sub>6</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub>	158.06	164.1	0.96
8'	C <sub>6</sub> H <sub>11</sub> NO <sub>5</sub> S	209.03	210.1	1.00

## Figures

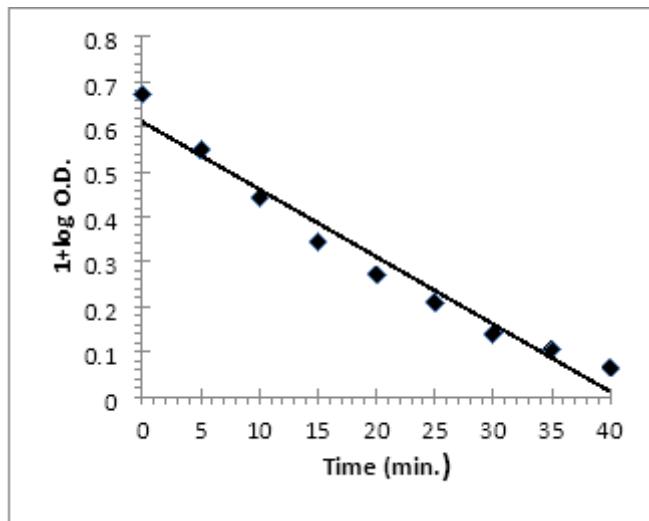


Figure 1

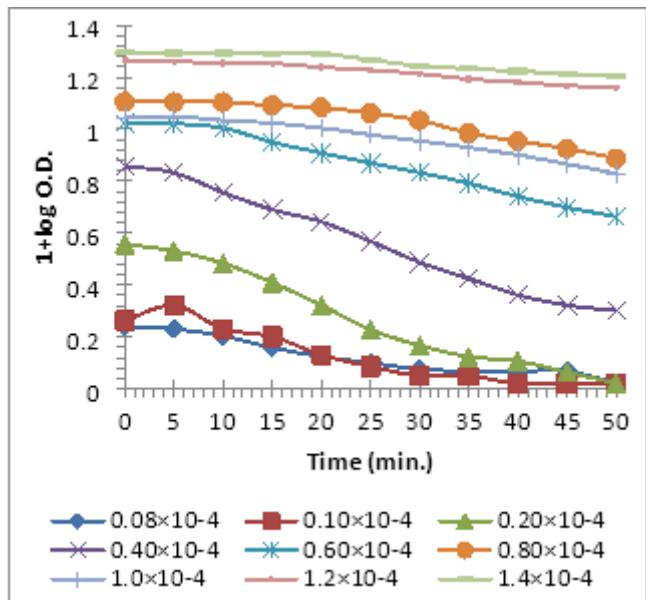
A typical run

Figure 2

Effect of variation of pH

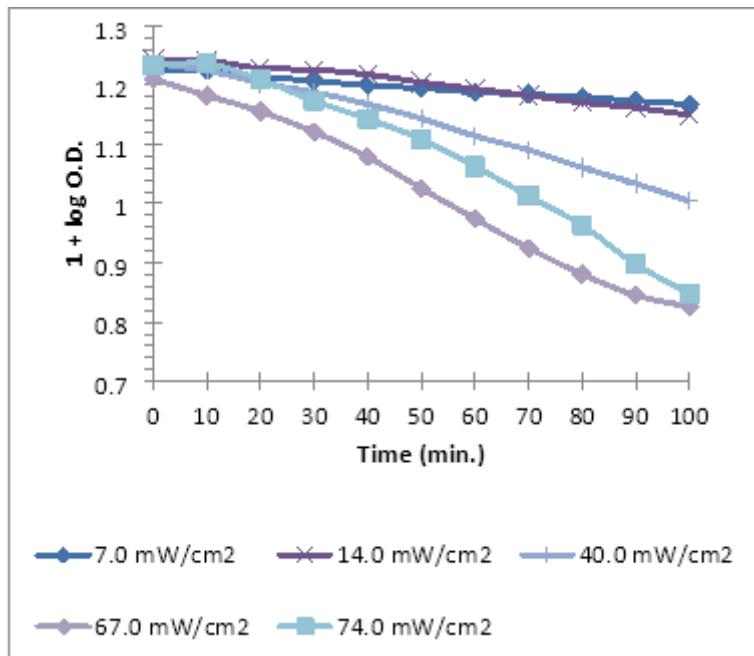
**Figure 3**

Effect of variation of dose of photocatalyst



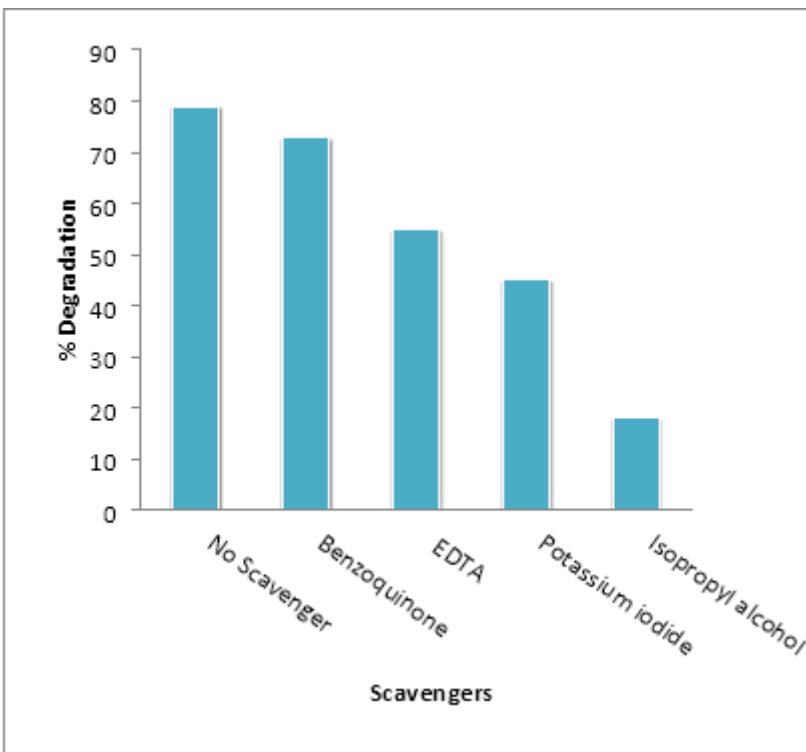
**Figure 4**

Effect of variation of dye concentration (Moles/Litre)



**Figure 5**

Effect of variation of light intensity ( $\text{mW/cm}^2$ )

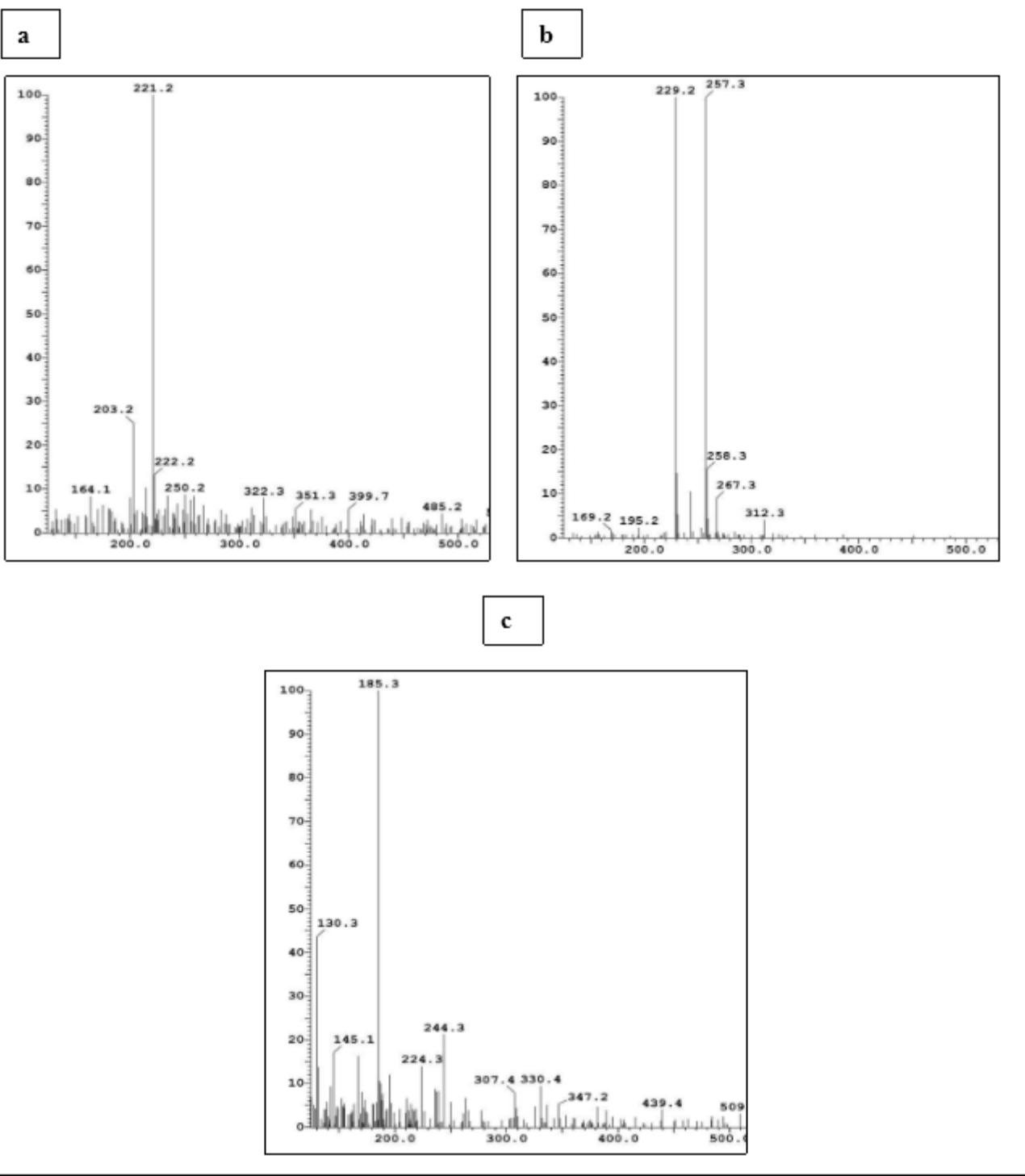


**Figure 6**

Scavenger study

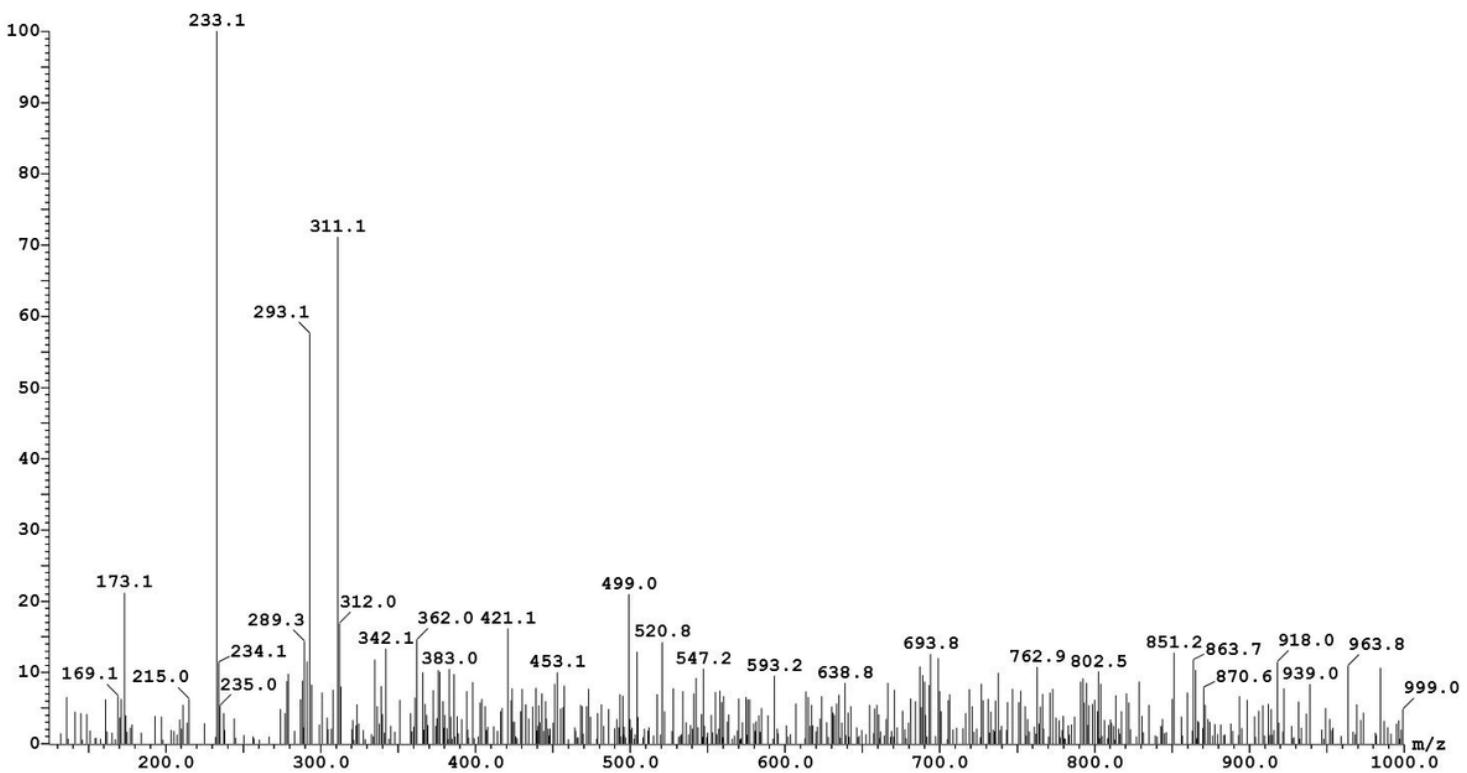
**Figure 7**

Mechanistic pathway proposed for degradation of Azure A



**Figure 8**

LCMS spectra of Azure A cleavage



**Figure 9**

LCMS spectra of Azure A cleavage and peaks at higher m/z

**Figure 10**

Mechanistic pathway of intermediates with high molecular mass fragments