Removing colour pollutants from wastewater: Use of a novel nanosized ternary semiconductor Ba$_3$Y$_2$WO$_9$ and measurement of kinetic parameters

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Abstract
Photocatalysis, a part of advanced oxidation technology is considered as a promising technology for waste water treatment. In the present work attempt is made to degrade a dye Azure B using Barium Yttrium tungsten Oxide, as a photocatalyst. Effect of various rate affecting parameters like pH, concentration of dye, amount of semiconductor, intensity of light etc. have been investigated. The rate is monitored spectrophotometrically and on the basis of observed data, a tentative mechanism has been proposed which proves the reaction to be a photocatalytic one. Optimum conditions (pH 7.3, concentration of the dye 5x10$^{-6}$M, amount of semiconductor 0.12, light intensity 37mW/cm$^2$) for maximum degradation are extracted. The kinetic study suggests that the reaction follows pseudo-first order rate law. Formation of nontoxic degraded products like NO$_2$, CO$_2$, H$_2$O etc. make the process of immense importance. Participation of OH free radical is confirmed by use of scavenger. The process is found beneficial for cleaning the hazards from environment that too in an eco friendly manner as it uses solar light and the semiconductor is in heterogeneous phase and is recovered back for further studies.

Citation:

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1. Introduction

As we stepped into the twenty first century, we faced the challenge of purification of water and air resource. Colour compounds like pigments and dyes are used widely in textile, plastic, food, and dyeing, paper, printing, pharmaceutical and cosmetic industries. These compounds affect the life in many ways. Many of these are toxic, carcinogenic, mutagenic or even stable to biological degradation (Wong et al., 2003).

1.1 Methods for removal of pollutants
Several methods have been developed for the removal of dyes from effluents including physical methods employing precipitation, adsorption, and reverse osmosis, chemical methods via oxidation (using air oxygen, ozone, NaOCl, and H$_2$O$_2$ as oxidants), reduction (e.g. Na$_3$S$_2$O$_4$) and biological methods including aerobic and anaerobic treatment. The disadvantages of these conventional methods are sludge formation, waste disposal, high operation cost, time consuming and ineffectiveness in cases where complicated aromatic compounds are presented (Entezari et al. 2007, Lachheb et al., 2002; Ladakowicz et al., 2001; Robinson et al., 2001; Zamora et al., 1999).

1.2 Advanced oxidation process
Among chemical technologies, a novel method that has been growing in recent decades is the advanced oxidation processes (AOPs) which are very potent in oxidation, decolorization, mineralization, and degradation of organic pollutants. AOPs were based on the generation of very reactive species such as hydroxyl radicals (OH$^-$) that oxidize a broad range of pollutants quickly with no selectively. AOPs such as Fenton and photo-Fenton catalytic reactions (Balanosky et al.,1999; Feng et al.,1999; Morrison et al.,1996; Kang et al.,2000).
**1.3 Heterogeneous photocatalysis**
Among AOPs, heterogeneous photocatalysis has been reported as an efficient water treatment technology, especially for organic dyes, since it is cost effective, highly efficient, low energy-consuming, moderate conditioned, extensively applicable and show reduced secondary pollution. Photocatalysis gained attention of the researchers in the field of environmental remediation when the photo-electrochemical splitting of water on titanium dioxide electrodes took place. It was reported that semiconductors such as nanosized TiO$_2$ (Fujishima et al., 1972; Wang et al., 2005; Wang et al., 2011) and ZnO (Percheranie et al., 2005; Sharma et al., 1995; Neppolian et al., 1999; Lizama et al., 2002) are most promising photocatalysts for the degradation of organic dyes in aqueous media in presence of solar/ultraviolet (UV) illumination.

**1.4 Semiconductors used as photocatalysts**
Many investigations have been carried out under ultraviolet/ visible radiation using different semiconductor like Nb$_2$O$_5$ (Prado et al., 2008), Ta$_2$O$_5$ (Zhu et al., 2005), Ga$_2$O$_3$ (Hou et al., 2007), Sb$_2$S$_3$ (Sun et al., 2008), BiVO$_4$ (Kohtani et al., 2003), Bi$_2$WO$_6$ (Fu et al., 2008), SrTiO$_3$ (He, 2009), ZnWO$_4$ (Huang et al., 2007), CaIn$_2$O$_4$ (Tang et al., 2003), ZnIn$_2$S$_4$ (Chen et al., 2009), Pb$_3$Nb$_2$O$_13$ (Li et al., 2007), Ag$_2$ZnGeO$_4$ (Li et al., 2008), La$_2$Ti$_2$O$_7$ (Ku et al., 2007), Y$_2$InSbO$_7$ and Y$_2$GdSbO$_7$ (Luan et al., 2011) etc.

Besides all these studies it was observed that less attention is paid on the studies carried out with ternary semiconductors. Thus an attempt in present work is made to reduce environmental pollution with help of a new nano photocatalyst Ba$_5$Y$_2$WO$_9$. It was found to show most promising results as compared to other catalysts.

**2. Objective of Research**
In current era environmental pollution has become a global issue. The matter is being discussed in various meetings and summits. Polluted water can cause many problems in living beings and plants. It may also cause death. Thus it becomes one moral duty to act towards the removal of such pollution causing elements so that pure water may be made available for all. An attempt in our work is made to remove some pollutants for one of the essential environmental resource i.e. water. The treated water then can be used for many other purposes like irrigation, cleaning, as coolant, as lubricant in machines etc. This process may provide an alternative path for purifying water. Use of solar energy and semiconductor, which can be recovered back, reduces the cost of the process and makes it economic. Thus it may be considered as an excellent process for water purification.

**3. Experimental**
In many industrial areas like paper mills, yarn industries, plastic industries etc. where dyes are used for coloring purpose, it is observed that effluents contain a remarkable amount of these dyes as these are not consumed completely. These dyes when excreted in environment with water, air or on land pollute them and degrade their quality. Thus it becomes necessary to remove these carcinogenic pollutants from water. The present work emphasises on degradation of such dye namely Azure B. It was degraded with help of solar light and semiconductor to a considerable extent. The formed products were not harmful to the environment.

A stock solution of Azure-B (0.030583g/100 ml=1x10$^{-3}$M) was prepared in doubly distilled water. The photo catalytic degradation was initiated by adding 0.12g of Ba$_5$Y$_2$WO$_9$ to the dye solution. Irradiation was carried out keeping whole assembly exposed to a 200W tungsten lamp (Philips). The intensity of light at various distances from the lamp was measured with the help of solarimeter (CEL201). The pH of the solution was measured by a digital pH meter (Henna imported pen type). The desired pH of the solution was adjusted by addition of prestandardized HCl and NaOH solutions. The progress of photocatalytic reaction was followed by recording optical density at regular time intervals using a spectrophotometer (Systronics 106). A water filter was used to cut off the heat reaction. Use of scavenger suggested the participation of OH free radical in the reaction. This free radical is found strong enough to break the different bond of dye (N=N, C=N, C-N, C=C, C=C etc). Controlled experiments proved the reaction neither to be photo degradation nor to be catalytic degradation rather it was a photo catalytic degrading process.

Graph between time and 1+log O.D. was found to be a straight line suggesting the reaction to follow pseudo first order kinetics. The rate constant was determined by –

\[ K=2.303 \times \text{slope} \]

**4. Result and Discussion**

4.1 Effect of Irradiation time
The relation between time and percentage degradation is shown in table-1 and figure-2. It is observed that percent degradation increases with irradiation time. The process slows down with time because it stands difficult to convert N-atoms into nitrogen compounds (Bandara et al. 1997). The difficulty in breakdown of C-N bond was also discussed (Maillard et al.1992). The dye is degraded by formation of OH\(^\cdot\) free radical whose presence was confirmed by study carried out in presence of scavenger that almost ceased the reaction.

**Figure 1:** Structure of Azure B

![Image of Azure B structure]

**Figure 2:** A typical run

![Graph showing percentage degradation versus time]

**Figure 3:** Effect of variation of pH

![Graph showing pH variation]

**Figure 4:** Effect of variation of dye concentration

![Graph showing dye concentration variation]

**Figure 5:** Effect of variation of amount of semiconductor

![Graph showing semiconductor variation]

**Figure 6:** Effect of variation of light intensity

![Graph showing light intensity variation]

**Table 1:** A typical run
[Azure B] = 5×10^{-6} M, pH = 7.3, Ba_3Y_2WO_9 = 0.12 g, light intensity = 37 mW/cm^2

<table>
<thead>
<tr>
<th>Time (Min.)</th>
<th>O. D.</th>
<th>14 log O.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.275</td>
<td>0.4393</td>
</tr>
<tr>
<td>2.00</td>
<td>0.240</td>
<td>0.3802</td>
</tr>
<tr>
<td>4.00</td>
<td>0.232</td>
<td>0.3654</td>
</tr>
<tr>
<td>6.00</td>
<td>0.204</td>
<td>0.3096</td>
</tr>
<tr>
<td>8.00</td>
<td>0.182</td>
<td>0.2600</td>
</tr>
<tr>
<td>10.0</td>
<td>0.167</td>
<td>0.2227</td>
</tr>
<tr>
<td>12.0</td>
<td>0.150</td>
<td>0.1760</td>
</tr>
<tr>
<td>14.0</td>
<td>0.138</td>
<td>0.1398</td>
</tr>
<tr>
<td>16.0</td>
<td>0.126</td>
<td>0.1003</td>
</tr>
<tr>
<td>18.0</td>
<td>0.119</td>
<td>0.0755</td>
</tr>
</tbody>
</table>

K = 8.44 × 10^{-3} (Sec^{-1})

**Table 2:** Effect of variation of pH
[Azure B] = 5×10^{-6} M, amount of semiconductor = 0.12 g, light intensity = 37 mW/cm^2

<table>
<thead>
<tr>
<th>pH</th>
<th>Rate constant×10^{-3} sec^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3</td>
<td>4.83</td>
</tr>
<tr>
<td>5.8</td>
<td>5.05</td>
</tr>
<tr>
<td>6.3</td>
<td>5.26</td>
</tr>
<tr>
<td>6.8</td>
<td>6.63</td>
</tr>
<tr>
<td>7.3</td>
<td>8.44</td>
</tr>
<tr>
<td>7.8</td>
<td>6.19</td>
</tr>
<tr>
<td>8.3</td>
<td>5.83</td>
</tr>
<tr>
<td>8.6</td>
<td>4.99</td>
</tr>
</tbody>
</table>

**Table 3:** Effect of variation of dye concentration
pH = 7.3, amount of semiconductor = 0.12 g, light intensity = 37 mW/cm^2

<table>
<thead>
<tr>
<th>Dye Concentration×10^{-6}M</th>
<th>Rate constant×10^{-3} sec^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>5.21</td>
</tr>
<tr>
<td>4.0</td>
<td>6.35</td>
</tr>
<tr>
<td>5.0</td>
<td>8.44</td>
</tr>
<tr>
<td>6.0</td>
<td>5.59</td>
</tr>
<tr>
<td>7.0</td>
<td>5.21</td>
</tr>
<tr>
<td>8.0</td>
<td>4.73</td>
</tr>
<tr>
<td>9.0</td>
<td>3.70</td>
</tr>
</tbody>
</table>

**Table 4:** Effect of variation of amount of semiconductor
[Azure B] = 5×10^{-6} M, pH = 7.3, light intensity = 37 mW/cm^2

<table>
<thead>
<tr>
<th>Amount of Semiconductor (g)</th>
<th>Rate constant×10^{-3} sec^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>4.90</td>
</tr>
<tr>
<td>0.06</td>
<td>5.19</td>
</tr>
<tr>
<td>0.08</td>
<td>7.93</td>
</tr>
<tr>
<td>0.12</td>
<td>8.44</td>
</tr>
<tr>
<td>0.14</td>
<td>7.24</td>
</tr>
<tr>
<td>0.16</td>
<td>6.70</td>
</tr>
<tr>
<td>0.18</td>
<td>6.42</td>
</tr>
<tr>
<td>0.20</td>
<td>5.40</td>
</tr>
</tbody>
</table>

**4.2 Effect of pH**
The most important factor affecting degradation is pH as it governs the formation of OH free radical which is found responsible for the reaction. Thus the effect of pH on the photocatalytic degradation of Azure B is carried out and is reported in table-2 and figure-3.

**Table 5:** Effect of variation of amount of semiconductor
[Azure B] = 5×10^{-6} M, amount of semiconductor = 0.12 g, pH = 7.3

<table>
<thead>
<tr>
<th>Intensity of light (mW/cm^2)</th>
<th>Rate constant×10^{-3} sec^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>37</td>
<td>8.44</td>
</tr>
<tr>
<td>34</td>
<td>4.56</td>
</tr>
<tr>
<td>30</td>
<td>3.46</td>
</tr>
<tr>
<td>27</td>
<td>2.53</td>
</tr>
<tr>
<td>23</td>
<td>2.22</td>
</tr>
</tbody>
</table>

All other factors were kept constant. It is observed that rate of degradation increases with varying pH. It may be explained that as the pH rises, concentration of OH^- ions rises which may support increase in number of OH' free radicals. Beyond a particular pH (7.3), if pH is increased further, the rate decreases. This is because of repulsion between excessive OH ions generated by the base and electrons on the semiconductor surface.

**4.3 Effect of Dye Concentration**
Dye concentration is likely to affect the rate of degradation and so by keeping all other factors constant, concentration of dye was varied (3.0×10^{-6} to 9.0×10^{-6} M) and its effect on rate was studied. The data are recorded in table-3 and figure-4. The rate of photocatalytic degradation is found to increase with increase in the concentration. This is because the rate of reaction is directly proportional to the molar concentration of dye. With further increase in concentration of dye (above 5×10^{-6} M), rate of reaction decreases. It is due to the fact that more concentration of dye imparts darker color to the solution and may act as filter to the incident light reaching the semiconductor surface. As a consequence the pathway of other molecules gaining the light and attaining excited state is interrupted and this results in the decrease in degradation.

**4.4 Effect of Catalyst loading**
Keeping all other parameters constant, amount of semiconductor was also varied (0.04 g to 0.20 g). The data are recorded in table-4 and figure-5. It was found that up to a limited weight of semiconductor (0.12 g), the rate of photocatalytic degradation increases. It may be due to more surface area available of semiconductor to catch hold the light and generate the excited state. Addition of photocatalyst increases the number of active site and number of OH' free radicals (Bajpai et al., 2006). After this limit substrate molecules are not sufficient to fill the active site of semiconductor and simultaneously increases in turbidity reduces the light intensity reaching the base of the vessel. Thus further addition of photo catalyst causes decrease in rate of reaction.

**4.5 Effect of light intensity**
Variation of light intensity is one of the major factors affecting the degradation. Thus the experiments were performed by varying it from 23mWcm$^{-2}$ to 37mWcm$^{-2}$ and with keeping all other factors constant. The results are reported in table-5 and figure-6. It was observed that increase in light intensity increases the rate of degradation (Kew et al. 2001, Chakrabarti et al. 2004). It is due to increase in number of photons striking per unit area of the photocatalyst. Higher intensities were not studied as increase in intensity may cause thermal reaction instead of photo catalytic one.

**Conclusion**

It is concluded here by that dyes are being degraded, with the help of photocatalyst and in presence of visible light, into fragments and no harmful products are formed. In presence of light, dye molecule gets excited to its singlet state. Then by losing some energy through inter system crossing (ISC), it get converted to its triplet state.

On the other hand semiconductor absorbs photon and an electron from its valence band jumps to the conduction band leaving a hole behind. The hole abstracts an electron from OH$^-$ ion generating OH$^˙$ free radical and the hole is quenched. This OH$^˙$ free radical abstracts an electron from weaker site of the dye and a sequence of break down starts finally converting the dye into fragments like H$_2$O, CO$_2$, NO$_2$, NH$_3$ etc. products. These products are of no harm or less harm to the environment. The photocatalyst is recovered which makes the process cost effective and useful.

**Research Highlights**

Present work incorporates use of natural inexhaustible energy resource that is the solar energy which makes the process of immense importance. Furthermore the process involves heterogeneous photocalysis where the photocatalyst is recovered back and can be used further for same purpose. This proves the process to be economic one.

Major factors affecting the rate of degradation were varied and the optimum conditions were extracted. Selected pH was 7.3 which is nearer to normal pH and so does not add another pouting factor that is the base to the water.

**Limitations**

Due to environmental factors, the work faced some limitations which were as follows:

The pH variation was limited to avoid the cause of secondary pollution as addition of base will make water more basic and another problem of removal this base will occur.

Higher light intensities were not used as the make the reaction occur through thermal way instead of photocatalytic one.

Higher concentrations of dye were not studied due to limitations of instrument which was not able to record the optical density above 0.9999.

Higher amount of semiconductor generated a problem of turbidity and was found floating on the surface. Thus weight was restricted.

**Recommendations**

Higher light intensities can be used if some arrangements can reduce the reaction caused by heat. Further semiconductors can be used with higher density so that they may settle down reducing the turbidity problem.

**Funding and Policy Aspects**

As the present work is an excellent addition to the way of cleaning the pollution in environment, it should be exposed and sent to several desks to gain attention and funds from various agencies. Various sectors must work in the path of removal of pollution through environmental factors like water, air, land etc.

**Authors’ Contribution and Competing Interests**

It seems to be a great contribution in the field of removal of pollutants. One may carry out similar kind of work for removal of other kinds of pollutants like metal ions in water, organic living pollutants like bacteria etc. and may also study the effect of various other factors on the efficient removal of these pollutants. Use of sources other than solar light can also be incorporated. Instead of using inorganic semiconductors one can also use organic semiconductors and some natural substances like ash, charcoal etc.

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**References**


