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# Electro-photocatalytic degradation of methylene blue dye using various nanoparticles: A demonstration for undergraduates

## Abstract

In this study, we have designed a bench-scale, electro-photocatalytic (EPC) reactor system consisting of a glass beaker, electrolytic cell, aluminium wires and nanoparticles as photocatalysts. Various nanoparticles as types of photocatalysts were utilized for the degradation of methylene blue (MB) by using electro-photocatalysis (EPC) method. The photocatalysts used were pre-synthesized CdS, TiO2 and Ag nanoparticles in the presence of UV-light source (long UV=365 nm) and commercial battery (9 V) to perform electro-photocatalytic (EPC) experiments. For the purpose, different band gap nanomaterials such as CdS quantum dots, TiO2 and Ag nanoparticles were selected to compare their photocatalytic activity. The in-depth comparative study of EPC degradation of methylene blue dye was performed and the results of EPC degradation experiments revealed highest efficiency of 86% in 4 hours. The effect on photo degradation efficiency of these nano-photocatalysts in presence of commercial electronic battery was studied in detail by a high school student under supervision for demonstration of concept that has potential to handle water pollution.

**Keywords:** Electro-photocatalysis, Methylene Blue, semiconductors, nanoparticles, photocatalysts

Volume 7 Issue 4 - 2018

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**Received:** June 28, 2018 | **Published:** September 5, 2018

**Abbreviations:** EPC, electro-photocatalytic; MB, methylene blue; NP, nanoparticles; SPR, surface plasmon resonance

## Introduction

Due to rapid industrialization, the lives of living cells including human has been threatened by all sorts of toxic and hazardous chemicals released from the manufacturing units. This has caused much water pollution globally.[1] In day to day processing in various chemical industries that include paper, textile, leather, food, hair dyes etc., large amount of organic dyes are used and much of the quantity is un-consumed during the processing.[2] The excess contaminated water therefore is released in large amount as effluent including synthetic/organic dyes in water resources thus causing serious water pollution.[3] Therefore, there is a need of removal of these organic dyes from polluted water.[4] The removal of such pollutants from water although sounds as a simple process however; practically it is highly challenging in the current era of nanotechnology. The overall question is to make the polluted water free from toxicity so as to utilize it again for human consumption as well as for other living organism.

Till date, various methods like, adsorption, biological treatment, oxidation, photocatalytic degradation, electrochemical oxidation and coagulation, etc. have been studied in detail and often have been demonstrated at commercial level.[5–10] Photocatalytic degradation process has numerous advantages over other existing methods e.g. it is less hazardous and time saving process. Similarly, electro-photocatalysis (EPC) method is the also highly promising method. This can be executed even by an undergraduate student without much of the sophistication. In such a process a bias potential is applied to the liquid medium that contain organic molecules (typically dyes). Direct electrical current can cause breaking of the chemical bonds of a given organic dye however this can be further enhanced by combining with photon energy. Such a process then can be termed as electro-photocatalysis and in presence of a suitable catalyst, it can increase the rate of degradation tremendously. Electro-photocatalysis (EPC) method is considered as clean process for degradation of organic effluents.[11] In the electro-photocatalytic degradation phenomenon, when a material is irradiated by UV light it generates electron-hole pair via undergoing a second order reaction kinetics with formation of free radical. These free radicals are considered as powerful oxidizing agents to degrade the toxic organic pollutants and micro pollutants present in the water.

The nano-sized particles having large surface area due to their extremely smaller size are significant materials for photocatalysis as well as electro-photocatalysis. In particular, various materials like zinc oxide (ZnO), titanium dioxide ($TiO_2$), tungsten trioxide ($WO_3$), cadmium sulphide (CdS) etc. have been widely employed as photocatalysts for degradation of organic dyes.[12–15] Among all the photocatalysts, $TiO_2$ is considered as effective due to ability to act in UV region and has been reported as the most suitable photocatalysts due to its low-cost, non-toxicity, stability and robust nature.[16,17] Due to wide band gap, $TiO_2$ is only active in UV region and suffers from limited photocatalytic efficiency in the visible region. The metal nanoparticles (NPs) like silver (Ag) NPs have been considered as a potential photocatalysts due to its high redox potential and photonic light absorption in the visible region.[18] Similarly, II-VI semiconducting materials such as CdS quantum dots have been considered as effectual photocatalytic material operating in the visible region.[19,20] Also, CdS can enhance photocatalytic efficiency due to good carrier transportation capacity of photo generated electrons

and holes.[21] In the present work, we have demonstrated to a high school student where the student has performed these experiments for concept learning and the results obtained from such basic studies following the concept of electro-photocatalysis for the degradation of methylene blue dye, is presented. For the purpose, three different types of photocatalysts such as $TiO_2$ NPs, Ag NPs and CdS QDs were used according to their absorbance capacity in different region. We therefore present a comparative photocatalytic behavior of these materials for degradation of MB dye by using as designed bench-scale photo-reactive system under 8 Watt long UV light irradiation to the dye solution under the impact of a external bias electrical current generated through a commercial battery of 9 volts.

## Experimental

### Preparation of TiO2 NPs:

The TiO2 NPs were prepared by reported method using sol-gel concept with PVP as capping agent.[22] Here, the appropriate amount of titanium tetrachloride ($TiCl_4$) was added to 2-propanol with a molar ratio of 1:6 along with PVP under ice bath at ambient conditions. The obtained white colored titanium dioxide nanoparticles were the result of solution-gelation process over a period of 8-10 hrs.

### Preparation of Ag NPs:

Silver nanoparticles were prepared following the reported method by Khanna[23] According to this method, citrate capped silver nanoparticles can be generated from use of tri-sodium citrate and silver nitrate in aqueous medium. The grey free flowing silver powder can be obtained after centrifugation (small amount) or vacuum filtration (large amount). Such silver nano-powder can be re-dispersed in water to up to about 25 wt.%.

### Preparation of CdS QDs:

The CdS QDs used for the electro-photocatalytic degradation were prepared by the earlier reported method.[24] For this purpose, cadmium chloride ($CdCl_2$) was dissolved in DI water followed by addition of 2- mercaptopropionic acid with stirring. Later, the aqueous solution of sodium sulphide ($Na_2S$) was added drop-wise to the above reaction mixture at room temperature with constant stirring. The yellow colour precipitate was obtained after centrifugation for further use.

### Construction of bench-scale electro-photocatalytic (EPC) reaction system:

For the construction of bench-scale system, commercial batteries (9V) were used as it is. The aluminium wires were fixed at both the positive and negative ends of the battery by tin-soldering. The whole battery system was then fixed on 50 ml glass beaker with the help of adhesive tape to make it as one part of photo-reactor. The dye containing water in appropriate concentration was poured into this reactor. A certain photo catalyst (CdS, $TiO_2$ or Ag nanoparticles) was added to the beaker which was then kept under UV irradiation without stirring. The system together was considered as EPC reactor system for electro-photocatalytic activity (Figure 1).

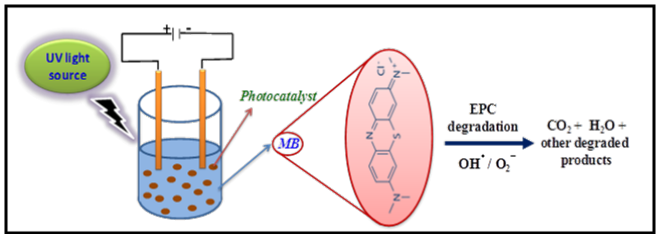
### Experimental procedure for electro-photocatalytic (EPC) degradation of MB Dye using various catalysts:

The electro-photocatalytic degradation experiments for all the samples along with plain MB dye (50 ppm) were carried out under UV light (365 nm) without stirring. In the beaker designed with bench-scale photo reactive system, 20 ml of MB dye solution (50 ppm) was prepared and to this solution 20 mg of photocatalysts was added. In a simultaneous experiment with four different catalysts, the beakers were placed under UV irradiation for 4 hours. The observations were made before and after irradiation of the solution under UV light to note the visual colour change of the solution. The photocatalytic degradation of MB dye was investigated and monitored by using UV-Visible spectroscopy. During the experiments, after the interval of 1 hour, 200 µl of MB dye solution was diluted with 2.5 ml of DI water and monitored by using UV-Visible spectroscopy.


**Figure 1** Photograph of as constructed photo reactive system for degradation of MB dye.

## Result and Discussion

Scheme 1 represents the electro-photocatalytic degradation of MB dye by using various photocatalysts ($TiO_2$, Ag NPs and CdS). We believe that, after irradiation of UV light MB dye undergoes degradation by elimination of different by-products. The photocatalysts utilized for the experiments were already reported as explained in synthesis section, therefore the characterization part is not included in this article. Here, we performed the electro-photocatalytic experiments to educate the undergraduate students as they can learn the basic concepts of electrochemistry and photocatalysis through this modified experiment. The current article therefore discusses the UV-Visible spectroscopy-based results related to degradation MB dye (Scheme 1).




**Scheme 1** Schematic illustration of electrophotocatalytic activity against MB dye.

### Electro-photocatalytic activity against MB dye

The electro-photocatalytic degradation of MB dye was performed using three different photocatalysts (i.e. $TiO_2$, Ag NPs and CdS) along with one reference system which does not contain any catalyst (i.e. plain). The MB dye which is commonly used dye in textile industries shows absorption in visible region of 550 to 700 nm. Therefore, we believe it is an ideal dye to study and demonstrate the photocatalytic activity of the above mentioned photocatalysts.

The bench-scale photo reactive system containing 50 ppm solution along with 20 mg catalysts were kept under UV irradiation with 365 nm light and the experiments were monitored by using UV-Visible spectrophotometer.

**Citation:** Hiragond CB, Kshirsagar AS, Khanna DP, et al. Electro-photocatalytic degradation of methylene blue dye using various nanoparticles: A demonstration for undergraduates. *J Nanomed Res.* 2018;7(4):254–257. DOI: 10.15406/jnmr.2018.07.00195

The results of UV-Visible monitoring of MB degradation are shown in Figure 2. Additionally, EPC degradation efficiencies for all the samples were calculated by using equation 1.[25]

$$Degradation\ (\eta\%) = \frac{C_0 - C}{C_0} \times 100 \qquad (1)$$

Here, % η is photo degradation efficiency, $C_0$ initial concentration of dye before illumination and C is concentration of dye after a certain time irradiation under light respectively (Figure 2).

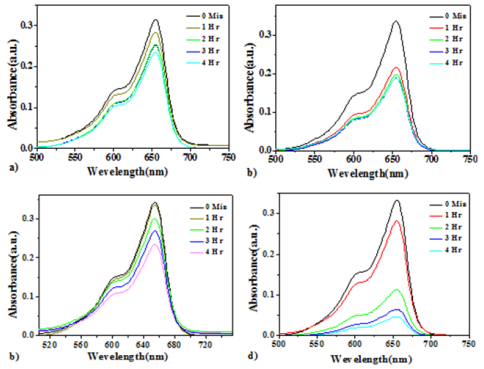



**Figure 2** UV-Visible monitoring of MB degradation via electro-photocatalytic process under UV light irradiation by employing various photocatalysts a) Plain (without catalysts i.e. only 50 ppm MB) b) TiO2 c) Ag NPs and d) CdS.

Initially, photocatalytic activity of pristine 50 ppm concentration MB solution was carried out and result is shown in Figure 2a. It was observed that, plain sample (i.e. without catalyst) gives only 30% photocatalytic degradation efficiency after four hour EPC process Figure 3. As it is known that, MB does not undergo self degradation therefore we believed as obtained activity could be due to the electrolytic cell (Figure 3).

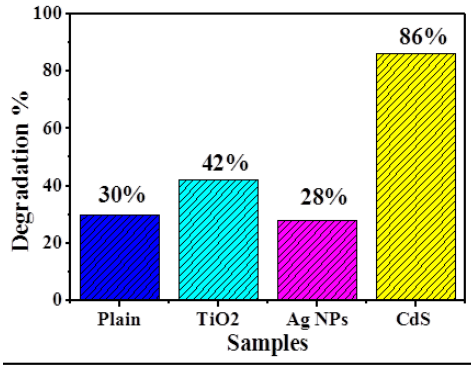



**Figure 3** Graph showing dye degradation percentage of the photocatalytic activity.

Then after, the sample containing $TiO_2$ NPs showed 42% degradation efficiency after 4 hour (Figure 2b and Figure 3). Thus, the increase in photo degradation efficiency clearly indicates the significant role of TiO2 nanoparticles. As presented in Figure 2c the EPC degradation of MB by using Ag NPs showed 28% Figure 3 efficiency which is less than that of plain (without photo catalyst) system. Since, the light source used for the experiment was of 365 nm while Ag NPs absorbs light in visible region of more than 400 nm due to surface plasmon resonance (SPR). The SPR phenomenon is not sufficiently capable of releasing the free electrons to promote the oxidation or reduction as the electrons are not transferred unlike in semiconductors. Therefore, it is believed that it does not promote photo degradation however; observed degradation efficiency could be due to electrolytic reaction. Further, the reactive system containing CdS QDs despite absorbing in visible region showed the highest degradation efficiency of 86% after 4 hours Figure 2d. In the present case, CdS QDs absorbs light in the region of 370-420 nm since 365 nm UV light was used; it is enough energy to cause the excitation of electrons from valence band to conduction band thus causing the transfer of electronic via electron hole formation mechanism. This leads to most efficient degradation and highest photo degradation efficiency is due to rapid electro-photolysis. It is thus stated that CdS QDs promotes redox reaction and generate electrons and holes via electro-photo energy leading to higher degradation efficiency. Figure 4 represents the changes in initial and final concentration of the MB ($C/C_0$) with respect to time (t). It indicates that, in case of plain, $TiO_2$, Ag and CdS system the gradual decrease in concentration of MB with respect to time was observed (Figure 4) (Table 1).

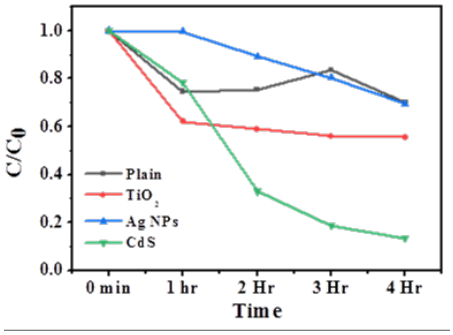



**Figure 4** Photodegradation plot of MB dye with respect to time using different catalysts.

**Table 1** Table showing comparative study of photo degradation efficiency (Ƞ %), rate constant (k) and energy of activation (Ea) of EPC reaction.

| Parameters | Plain | $TiO_2$ | Ag NPs | CdS |
|---|---|---|---|---|
| Ƞ % | 30 | 42 | 28 | 86 |
| k ($min^{-1}$) | 0.04585 | 0.04794 | 0.04440 | 0.05110 |
| $E_a$ (J/mol) | 7676.16 | 7565.49 | 7756.54 | 7406.52 |

The dye degradation under UV light is considered as pseudo-first order reaction equation 1. Therefore, the rate constant of reaction was calculated by employing pseudo-first order kinetic formula equation 2.

$$-In\left(C / C_0\right) = kt \qquad (2)$$

Here, C = concentration at time t in minute, $C_0$ = initial dye concentration in ppm, k = rate constant in min-1 and t = time in min. Also, energy of activation required for dye degradation was calculated by using equation 3 and the results were shown in Table 1.

$$log\ k = -E_a / 2.303RT \qquad (3)$$

Where, k = rate constant, $E_a$ = energy of activation, R = gas constant (8.314 $Jmol^{-1}\ K^{-1}$) and T = temperature at which reaction proceeded (300 K). The values of as calculated degradation efficiency (%η), the rate constant (k) and the activation energy ($E_a$) were shown in table. It can be seen that, CdS catalyst containing reactive system delivered

86% of maximum efficiency which required minimum energy of activation i.e. 7406.52 J/mol with 0.05110 ($min^{-1}$) rate constant. While the least degradation efficiency (i.e. 28%) was obtained using Ag NPs containing reactive system and required highest activation energy (7756.54 J/mol)

## Conclusion

Herein, we have demonstrated bench-scale photo reactive system for electro-photocatalytic experiments. The different types of photocatalysts in the form of CdS QDs, $TiO_2$ and Ag nanoparticles were employed for the degradation of methylene blue (MB) by using electro-photocatalysis method. The results of electro-photocatalysis degradation showed that, plain sample which does not contain any catalyst gives 30% degradation efficiency after 4 hours irradiation under UV light (365 nm). The reactive system containing CdS QDs catalyst showed superior activity with 86% attributed due to photo-generated electron-hole pair in energy band level of CdS. Therefore we believe that, electro-photocatalysis (EPC) method is the most promising alternative where a bias potential is applied in the photocatalytic degradation using different photocatalysts considered as clean process for degradation of organic effluents.

## Acknowledgement

None.

## Conflict of interest

Authors declare that there is no conflict of interest.

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