

# Photodegradation of Organic Dyes Using CdSTe Quantum Dots

C. Aviles-Martin\*, L. Alamo-Nole\*

\*Chemistry Department, Pontifical Catholic University of Puerto Rico, USA, luis\_alamo@pucpr.edu

## ABSTRACT

The inappropriate disposal of organic dyes used in a variety of industrial applications has become a contamination source of many water sources. Photodegradation techniques have the advantage to degrade organic contaminants completely. This project evaluates the photodegradation capacity of CdSTe quantum dots (QDs) synthesized in an aqueous medium using microwave heating at 180°C. QDs were characterized optically and structurally using UV-Vis spectroscopy, photoluminescence, and HR-TEM. Photodegradation experiments were done using methylene blue (MB), and Victoria blue (VB) dyes. The concentration of both dyes was analyzed by HPLC-VWD. MB was not photodegraded because of it induces a quenching effect on the QDs fluorescence. In contrast, 91% of VB concentration was degraded using 200 mg/L of QDs even though a slight decrease in fluorescence was observed when VB was mixed with the QDs.

**Keywords:** Quantum dots, CdSTe, photodegradation, quenching, methylene blue, Victoria blue

## 1 INTRODUCTION

Contamination of water sources have begun to rise due to the large amount of improper disposal of organic dyes. Textile and paper industries are associated with the discharge of organic dyes into water bodies producing colored effluents with the potential risk to living organisms. Coagulation, sorption, and membrane processes are used to remove the dyes from industry effluents. These technologies are expensive due to the use of activated carbon, special membranes, and coagulants. Also, the saturated material must be disposed. The development of new or more efficient removal methodologies is necessary.

Photodegradation techniques have the advantages that they can mineralize organic components under favorable conditions. Photocatalyst agents can degraded the contaminants decreasing the residues and they can be reused multiple times. The photodegradation process include the capacity of the photocatalyst to produce radicals during the irradiation with natural or artificial sources. In this regard, quantum dots (QDs) are a viable solution for this problem. Since QDs possess exceptional optical properties, they can be suitable for photodegradation experiments [1].

QDs are semiconductor nanocrystals that are smaller than 10 nm in at least one dimension. Due to their size, their optical properties are easily modified. The band gap and fluorescence emission wavelength are properties that can be

modified changing their crystal size. When QDs are irradiated, an electron from the valence band (HOMO band) jumps to the conduction band (LUMO) producing a hole (h<sup>+</sup>) and an electron (e<sup>-</sup>). This electron/hole pair has the capacity to produce free radicals that are the responsible for the photocatalytic effect. The radicals can be produced by the interaction with water molecules or directly with organic dyes molecules. An important step in the photodegradation process is the adsorption of the organic dye on the surface of the catalyst that facilitates the production of free radicals. The small size of the QDs offers an advantage over other catalyst because they have a large surface area per mass, exposing more adsorption points. Although, the dye adsorption on the QDs is important, the capacity to produce electron/hole pairs should not be affected during this step, for a success photodegradation process. An interruption on the excitation stage (jump of the electrons) or increasing the velocity of the recombination of the electron/hole could affect the photodegradation efficiency. A loss of fluorescence (quenching) can be an indicative that the production of electron/hole pairs (and the photocatalysis) will decrease.

In this project, the photocatalytic activity of CdSTe QDs was evaluated. Although, the use of QDs have been reported to be used to eliminate dyes from water solutions, we found that the quenching of the fluorescence should be considered to develop a very efficient photocatalyst.

## 2 METHODS

### 2.1 CdSTe Synthesis and Characterization

The CdSTe nanoparticles were prepared using a method previously published in our research group.[2] A typical synthesis consists of mixing thioglycolic acid and a CdNO<sub>3</sub> precursor solution in deionized water. Then, the solution is degassed with N<sub>2</sub>. Simultaneously, a solution of elemental tellurium reduced with NaBH<sub>4</sub> is prepared, and both solutions are transferred into a glovebox under a flow of UHP Nitrogen to avoid oxidation of the precursors. In the oxygen free atmosphere, the telluride solution is added to the samples and the final solution is transferred to a microwave reactor system and heated at 180°C for 15 minutes. The resulting solution is purified by centrifugation with isopropanol. This step yield an orange colored solid which was later dispersed in deionized water.

The optical properties of a QDs aqueous solution were evaluated spectroscopically using a Lambda 35 UV-Vis Spectrophotometer - Perkin Elmer and the fluorescence using a FP-6200 spectrofluorometer - Jasco exciting with a

386 nm excitation wavelength. The structural properties were evaluated using a JEM-ARM200CF HR-TEM- JEOL operated at 200KV.

## 2.2 Photodegradation Experiment

Aqueous solutions of methylene blue and Victoria blue were prepared for analysis. A 1.0 mM stock solution was prepared for both dyes. Calibration standards of 1.0, 5.0, 10, and 20  $\mu\text{M}$  were prepared and analyzed with an Agilent 1100 series HPLC system. 10  $\mu\text{M}$  solutions of the dyes were prepared and mixed with the CdSTe QDs (200 mg/L final concentration). The samples were placed in a rotatory mixer and irradiated with a UV lamp with a 302nm wavelength. Samples were withdraw at specific times until 300 minutes (5 hours) and the concentration was quantified by HPLC. All experiments were done in triplicates.

Dark experiments were also done to evaluate the adsorption of the Victoria blue on the QDs. Working solutions (10  $\mu\text{M}$ ) of Victoria blue was contacted with CdSTe (200 mg/L) in a dark environment to avoid photodegradation. After 24 hours, the solutions were centrifuged and the concentration of the dye in the supernatant was quantified.

## 3 RESULTS AND DISCUSSION

### 3.1 CdSTe QDs Characterization

Fig. 1 shows the High-Resolution Transmission Electron Microscopy (HR-TEM) of the CdSTe QDs synthesized at 180° C. The image confirms the nanometric size of the crystals. The average crystal size was around 7 nm. The blurring around the edges of the nanoparticle can corresponded to the organic layer of thioglycolic acid which allows the stability of the nanoparticle in water.

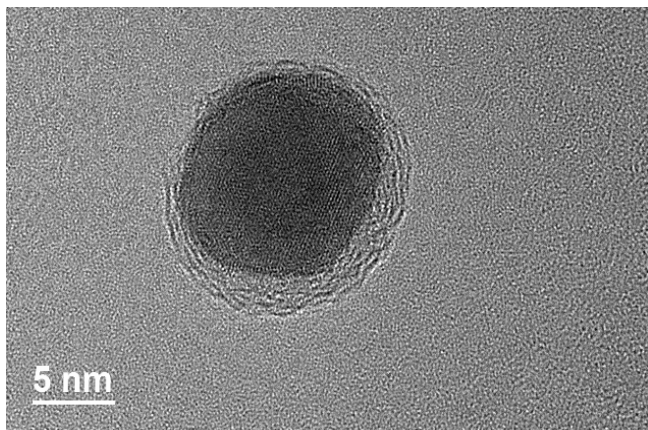


Figure 1. HR-TEM image of the CdSTe QDs synthesized at 180° C

The florescence (using a blue laser diode) of a dilute and colorless solution (100 mg/L) of CdSTe QDs synthesized at 180° C has a high red fluorescence that can be observed with the naked eye (Fig. 2).

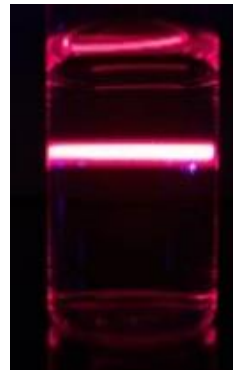


Figure 2: CdSTe QDs emission (640nm wavelength) when excited with a 5mW 405nm laser diode

The emitted red color coincides with the emission peak of the QDs observed in the photoluminescence analysis (Fig. 3). The emission peak centered at 642 nm correspond to a red color in the light spectrum. The absorption spectra (Fig. 3) shows that the QDs can be excited with visible light which explain the fluorescence observed with a laser diode of 405 nm. The capacity of the CdSTe QDs to absorb in the visible region of the spectrum open the possibility to use visible light to induce a photodegradation process. The spectrophotometric analysis also indicates that the exciton is located around 386 nm. This wavelength was used for excitation in the photoluminescence analysis.

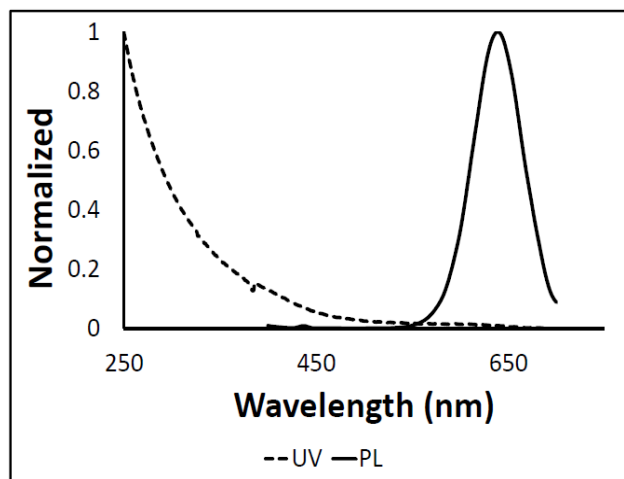


Figure 3: UV-VIS Spectrophotometric and Photoluminescence analysis of CdSTe QDs

### 3.2 Organic Dye Quenching Effect

The fluorescent emission of the CdSTe QDs was analyzed before and after mixing it with the MB (Fig. 4). The results show high decrease of the CdSTe emission after mixing with the dye. The loss of the fluorescence can occur

for two principal processes: collisional quenching and static quenching [3]. The collisional quenching is produced when the fluorophore (QDs) is in contact with a molecule (MB) that facilitates a non-radiative transition. In the static quenching, the fluorophore (QDs) forms a stable link with a molecule (MB) and the new complex does not produce fluorescence. Apparently, the quenching of the CdSTe QDs produces a fast recombination of the electron/hole pair that affects the production of radicals and the photodegradation process. This effect was confirmed in the photodegradation experiments. There was no decrease in MB concentration when the solution of MB and CdSTe QDs was mixed and irradiated (Results not shown).

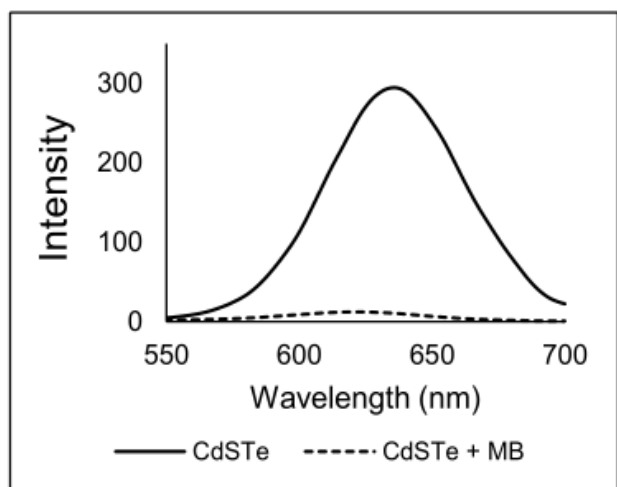


Figure 4: Fluorescence spectrum of CdSTe QDs mixed with Methylene Blue

Fig. 5 shows the fluorescence of the CdSTe QDs before and after being contacted with a Victoria blue dye solution. There is a slight decrease of the intensity indicating that the production of radicals could be slightly affected.

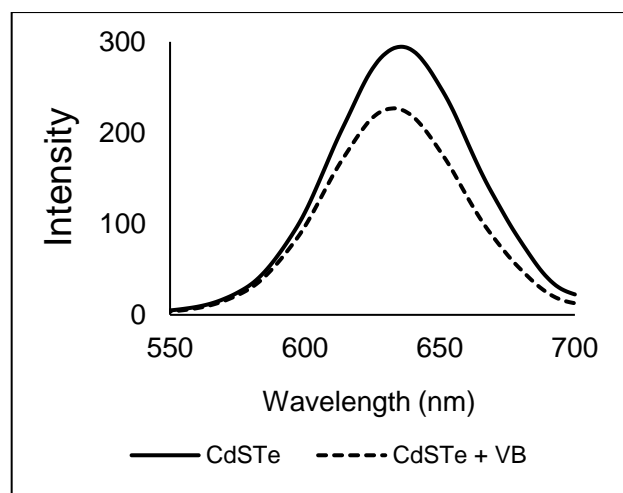


Figure 5: Fluorescence spectrum of CdSTe QDs mixed with Victoria blue

### 3.3 Photodegradation of Victoria Blue

Fig. 6 shows the chemical structure of Victoria Blue. The photodegradation of n-substituted dyes like methylene blue and Victoria blue have been studied by other authors [4]. The process should start with the n-des-ethylation of the amine groups of the VB followed by the degradation of the aromatic rings.

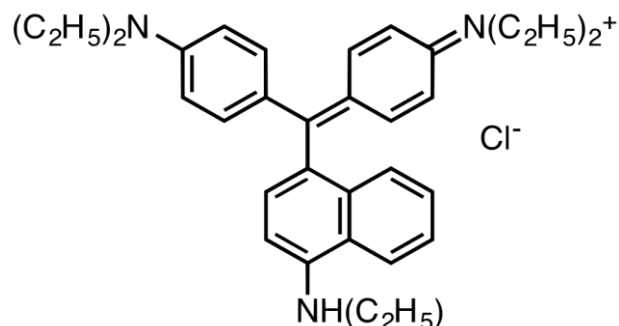


Figure 6: Chemical structure of Victoria blue

The concentrations of the solutions of MB and VB were 10  $\mu\text{M}$ . Higher concentrations of the dyes decrease the photodegradation process because of the dye molecules can absorb the light impeding that it reaches the QDs surface. If low quantity of photons reach the catalyst, it produces low quantity of free radicals. Radicals like  $\text{OH}^*$  can be produced by the interaction of the water with the electron/hole pair on the surface of the QDs. Also, radicals can be generated directly on the MB or VB molecules when they are in contact with the QDs.

Interactions between the QDs and the dyes is expected to be generated for a successful degradation. It is important that the dye be near the QDs because the half-life of the radicals is very short.

There was no photodegradation of the MB using CdSTe QDs due to a quenching effect, so that, the results are not reported.

Table 1 shows the average concentration of VB analyzed by HPLC monitoring at 600 nm. The samples were analyzed after irradiation at different periods using an 8 watt UV-lamp with a wavelength of 302 nm. The presence of other peaks was observed in the chromatograms that indicates the presence of photodegradation products principally by the n-des-ethylation of the VB. Our group has observed the presence of these peaks when other quantum dots were used [5]. A blank solution of VB irradiated for the same period was used to evaluate the effect of the irradiation on the dye without the presence of QDs. Less than 85% of the dye was photodegraded in the blank solution.

Fig. 7 shows the photodegradation percentage of VB at different irradiation periods. The final concentration was around 0.74  $\mu\text{M}$  representing more than 99% of degradation that confirms the capacity of the CdSTe QDs to be used as photocatalyst. A fast decrease of the concentration was observed at time 0 (after mixing VB with CdSTe QDs) that indicates a fast adsorption of the VB on the CdSTe QDs.

Time	Concentration ( $\mu\text{M}$ )
0	$8.3 \pm$
15	7.2
30	6.6
60	6.0
90	5.6
120	5.2
150	4.9
180	3.8
210	2.8
240	1.7
270	0.74

Table 1: Concentration of Victoria blue in the samples at each period of irradiation.

This initial adsorption is important to assure the photodegradation. The proximity of the VB on the QDs surface favors the interaction with the radical produced on the surface.

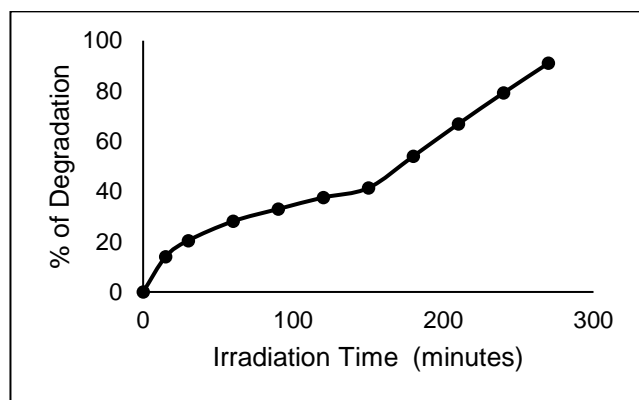


Figure 7: Degradation percentage of VB across the irradiation periods.

The photodegradation pattern (Fig. 7) shows a two-step process. The initial step (approximately until 180 minutes) can indicate the combination of an adsorption and photodegradation processes occurring at the same time. The second step can be due to the photodegradation process. The dark experiments (Fig. 8) indicated that VB is adsorbed on the CdSTe QDs surface producing the precipitation of the nanomaterial probably by neutralization of the negative charge of the thiols on the QDs surface by the positive charge of the protonated amines from the VB. The blue color of the precipitate indicates that VB is adsorbed but no degraded. The photodegraded solutions showed a very slightly blue color (approximately 1 % of dye) and the precipitate was not observed.

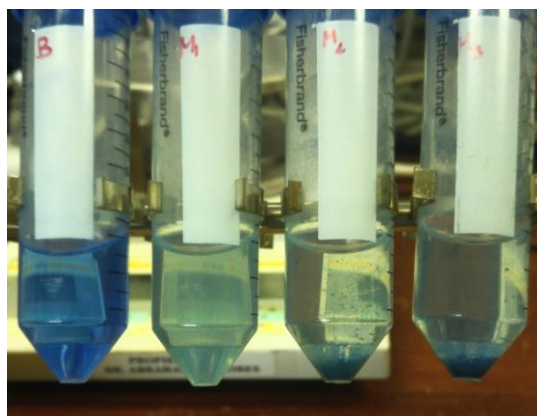


Figure 8: Samples of the dark experiments after 24 hours of mixing. The 3 samples on the right contain CdSTe QDs.

## 4 CONCLUSIONS

The photocatalytic activity of water stable CdSTe QDs with an average crystal size of 7 nm was evaluated using methylene blue and Victoria blue dyes. The QDs were not able to degrade methylene blue due to a quenching of the fluorescence. The photodegradation of the VB by the QDs shows a two steps process which are influenced by the adsorption of VB on QDs. The photocatalytic capacity of CdSTe QDs was confirmed.

## 5 Acknowledgments

The authors would like to thank the Padre Tosello Research Center of the Pontifical Catholic University of Puerto Rico (PUCPR) for support and PCUPR for institutional seed grant funds. The TEM work was performed at the National High Magnetic Field Laboratory, which is supported by NSF DMR-1157490 and the State of Florida.

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