Int. J. Electrochem. Sci., 15 **(2020)** 1206 – 1217, doi: 10.20964/2020.02.11

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

CdS Quantum Dots as Photocatalyst for Methylene Blue and Methyl Red Degradation and its Electrochemical Properties

Lebogang L. R. Mphahlele and Peter A. Ajibade[*]

School of Chemistry and Physics, University of KwaZulu-Natal, Private Bag X01, Scottsville,
Pietermaritzburg, 3209 South Africa
[*]E-mail: ajibadep@gmail.com

Received: 15 July 2019 / *Accepted:* 7 October2019 / *Published:* 31 December 2019

The study reports the use of oleylamine (OLM), hexadecylamine (HDA) and octadecylamine capped cadmium sulphide (CdS) quantum dots as photocatalyst for the decomposition of methylene blue (MB) and methyl red (MR) illuminated by visible light and their electrochemical properties. The effect of irradiation time and type of nano photocatalysts were investigated on the decomposition efficiency of both cationic (MB) and anionic (MR) dyes. The degradation efficiency and the chemical oxygen demand reduction of methylene blue (MB) and methyl red (MR) are 93% and 83% for OLM-CdS, 75% and 48% for HDA-CdS and 70% and 52% for ODA-CdS respectively. Cyclic Voltagram of the CdS quantum dots were used to study the relationship between the electrochemical band energies and the optical band gaps. Electrochemical band energies were found to be 1.64 V for OLM-CdS 1.92 V for HDA-CdS and 1.90 V for ODA-CdS which are comparable to those obtained from the calculated optical band gaps.

Keywords: CdS quantum dots; Photodegradation; Electrochemical behaviour; cyclic voltammetry

1. INTRODUCTION

Semiconductor metal sulphide quantum dots have characteristics which are noticeably different from those of macroparticles due to size confinement, quantum effect, and high surface area to mass ratio [1, 2]. The size dependent properties of quantum dots rise to numerous applications such as photocatalysis, photoelectrochemistry, etc. The use of quantum dots as photocatalysts have received great attention because of their degradation efficiency, major photostability, and high quantum yields [3, 4]. There are reports on the use of semiconductor nanoparticles such as CdS as photocatalyst [5, 6] to degrade organic compounds such as dyes. Anandan *et al*. [5] reported that semiconductors nanocatalysts are better under visible light irradiation to eliminate organic dyes from water effluents [2, 6]. The photodegradation of organic pollutants is achieved by illuminating semiconductor pollutants solution by visible light but the energy of the irradiated light must be higher than the energy of the desired band gap to produce better results. During illumination, the full valence band (VB) and unoccupied conduction band (CB) promotes the light redox processes of the semiconductors because they can act as sensitizers and catalyst due to their electronic properties [5, 7] and the reaction produces electron-hole pair [8-10]. The resulting pair have very high reduction and oxidation ability with, migration of electrons from VB to CB that result in reduction process [11,12]. These produce free radicals within the system of oxidoreduction of the substrate. The ensuing free-radicals (·OH) are economical oxidizers of organic materials [13, 14]. The reduced band gap (Eg = 2.4 eV) of CdS makes materials much less stable than most wide band-gap semiconductors, particularly with the involvement of surface charge [15, 16]. However, the composition of semiconductor quantum dots determines their electrochemical properties due to band structure dependent parameters such as, physical phenomenon band edge, valence band edge and quasiparticle gap and introduction of charge induced phenomena [17, 18]. Thus, the properties of quantum dots make them useful for the development of devised based primarily on quantum dots. Numerous methods such as photoelectron spectroscopy (PS) [19], scanning tunnelling microscopy (STM) [20] and cyclic voltammetry (CV) [21] have been used for the determination of band structure parameters, however the preferred techniques is cyclic voltammetry [17]. CdS quantum dots display impact of quantum confinement once prepared with a crystallization size below Bohr exciton radius of the macroparticles [22]. Quantum confinement effects and electrochemical behaviour result in distinctive size-dependent electro-optical properties that can be tuned for different, applications [17, 23]. Herein, we report the use of amine capped CdS quantum dots as nanocatalysts for photodecomposition of methylene blue (MB) and methyl red (MR) using sodium lamp as light source. The electrochemical properties of the as-prepared CdS quantum dots are also presented.

2. EXPERIMENTAL

2.1. Material and physical characterization

Methylene blue, methyl red, dichloromethane (DCM), tetrabutylammonium hexafluorophosphate ($TBAPF_6$), acetone, and ethanol were purchased from Merck and used as obtained without purification. Cadmium sulphide quantum dots were prepared as reported in our previous work [24]. Perkin-Elmer Lambda 25 UV-Vis Spectroscopy was utilized to evaluate the decay of the dye, at 664 nm for methylene blue (MB) and 550 nm for methyl red (MR), Auto Lab Potentiostat/Galvanostat was used for electrochemistry.

2.2. Photocatalytic decomposition of methylene blue and methyl red dyes

Aqueous solution containing 10-ppm methylene blue dye was prepared and stirred in the dark for 15 min to reach equilibrium. Cadmium sulphide quantum dot was then added to the dye solution to catalyse the photocatalytic degradation. The solution with the CdS nanocatalyst was stirred in the dark for 15 min to reach equilibrium so that the loss of compound due to adsorption can be considered. It was then irradiated with OSRAM VIALOX (65600 lumens) high-pressure sodium lamp. The degradation process was continued for 3 h to achieve complete degradation. Samples were removed at regular time intervals of 30 min to measure any decrease in dye concentration. The absorbance and concentration of the sample were monitored using a UV-Visible spectrophotometer at the maximum wavelength of the dye. The experiment was repeated using methyl red solution prepared with 6:4 ratio of alcohol to water [25, 26].

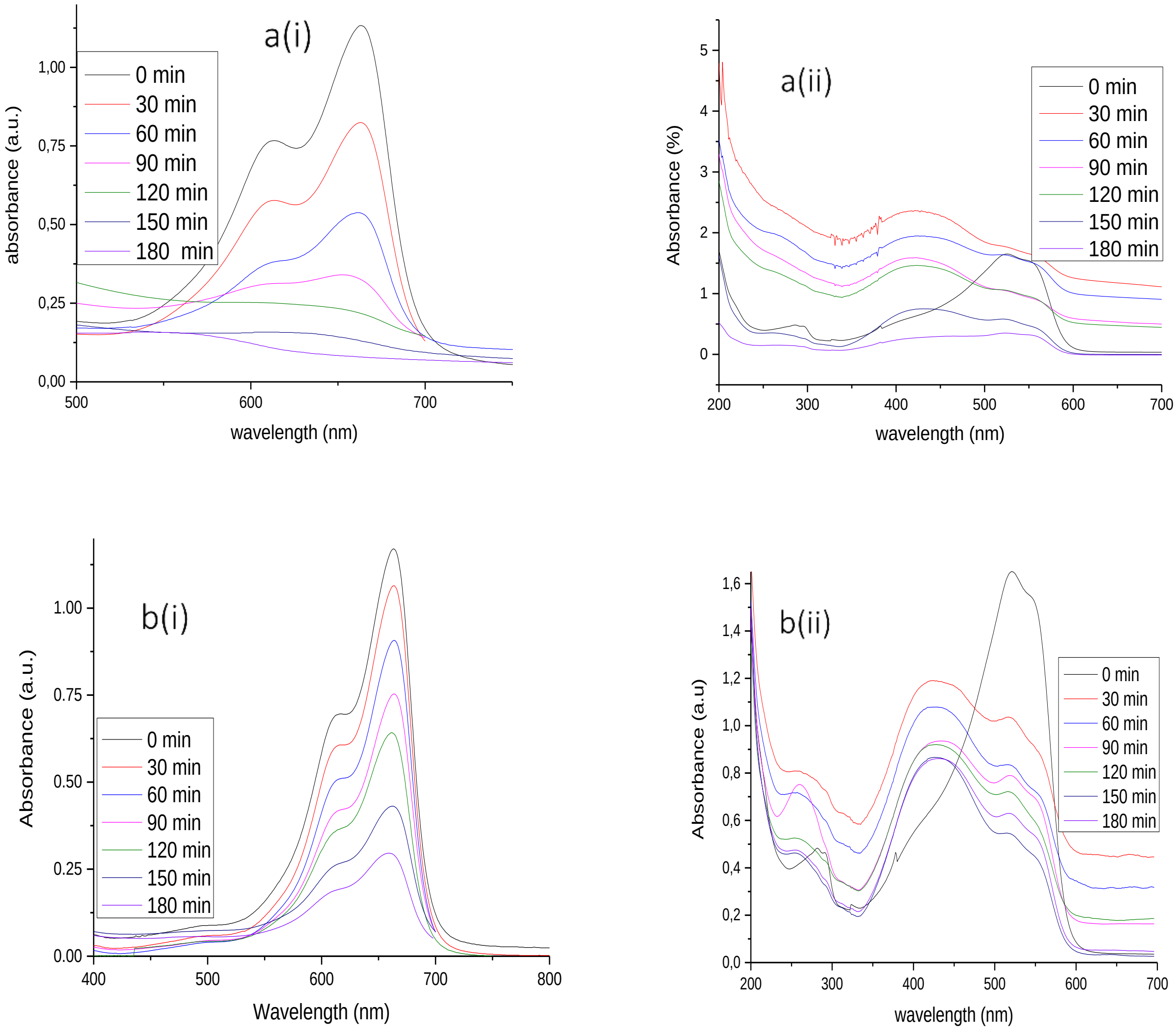
2.3. Electrochemical properties of the CdS quantum dots

The electrochemical properties of the CdS quantum dots were studied by Auto Lab Potentiostat/Galvanostat (with Nova 3.2 software). The measurements were carried out by three-electrode system, glassy carbon working electrode (GCWE), Ag/AgCl reference electrode and platinum counter electrode. Activation of the working electrode was performed by 2 mM solution of the CdS quantum dots and the supporting electrode was prepared using 0.1 M of the electrolyte (tetrabutylammonium hexafluorophosphate (TBAPF6)), both solutions were prepared in dichloromethane (DCM). After the electrodeposition the electrochemical properties were studied using the cyclic voltammetry (CV), using five different scan rates [17, 27].

3. RESULTS AND DISCUSSION

3.1. Influence of CdS photocatalysts and time on the photodegradation of methylene blue (*MB) and* methyl red *(MR) dyes*

The photocatalytic activities of the as-prepared CdS quantum dots were assessed by degrading organic cationic methylene blue (MB) and organic anionic methyl red (MR) in aqueous solutions under visible light irradiation, respectively. The evaluation of the photocatalytic activity of as-synthesized CdS photocatalysts on both dyes is presented in Fig. 1. Fig. 1a(i), b(i), and c(i) showed the absorption spectra of MB, the absorption peak corresponding to methylene blue at 664 nm diminished gradually during the illumination [28]. The organic dye decomposition technique is more complimentary under photochemical condition. Correspondingly, the photocatalyst utilized impacts the decomposition procedure, the photocatalytic procedure is affected by the energy measurements, (3 mg) was the best concentration of the CdS quantum dot catalyst for the study. The longer the irradiation time the higher the decomposition. It has been established that the band gap of semiconductor quantum dot photocatalyst influences their response to visible light and the narrower the band gap the higher the ability to absorb light [29]. The percentage photocatalytic degradation (Fig. 2 a, b, and c) of MB was found to be 93% for OLM-CdS, 75% for HDA-CdS and 70% for ODA-CdS after 180 min. From the results, it is suggested that the higher the photo-degradation, the slower the recombination of electron-hole pair [30]. The irradiation with visible light produces electron-hole pair at the tail states of the conduction and valence bands. Methylene blue (MB) is a cationic dye, thus the electrons generated are transferred upon the adsorption of MB molecules on the surface of the quantum dots. The excited electrons disrupt MB conjugated coordination which then leads to the decomposition of the dye [31, 32]. The absorption spectra of methyl red (MR) Fig. 1a(ii), b(ii), and c(ii) indicate that the concentration of MR decreases as the irradiation time increases due to radiolysis. However, the position of absorption maxima changes in the optical absorption spectrum from 510 to 450 nm in the presence of the CdS quantum dots catalysts due to shifts in pH to the basic region [26]. The percentage degradation of MR dye is 83% for OLM-CdS (Fig. 2a), 48% for HDA-CdS (Fig. 2b) and 52% for ODA-CdS (Fig. 2c) after 180 min. The degradation demonstrates that the number of photons consumed, and the number of dye particles adsorbed increases with the amount of CdS quantum dots photocatalyst consumed



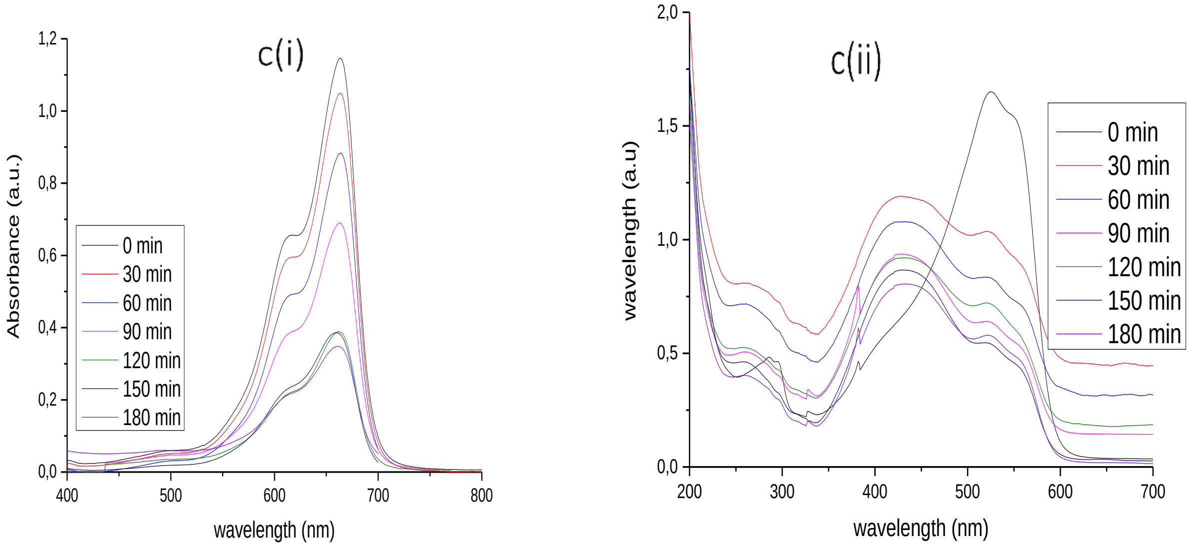
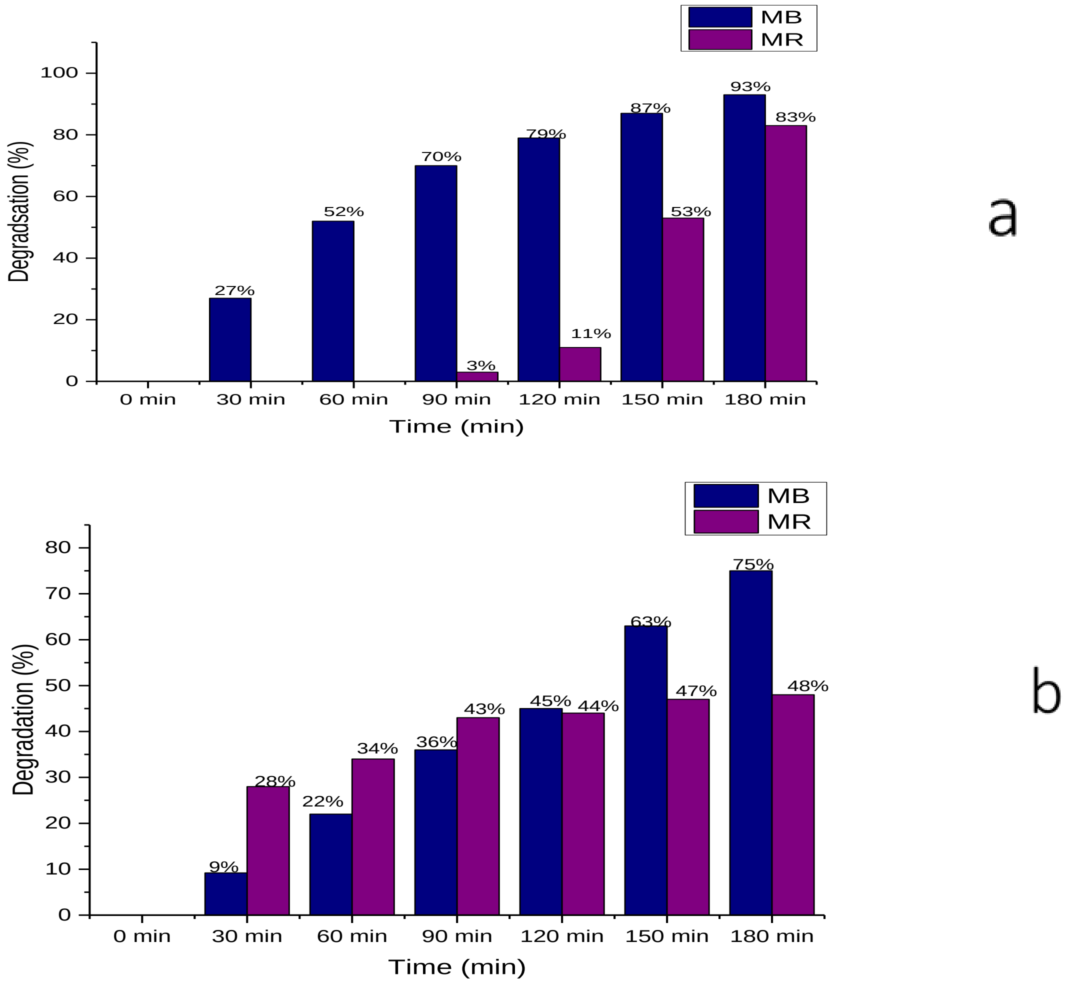


Figure 1. Photocatalytic degradation of both methylene blue (i) and methyl red (ii) dye using 3 mg of nana catalyst (a(i), a(ii) for OLM-CdS, b (i), b (ii) for HDA-CdS and c(i), c(ii) for ODA-CdS quantum dots.



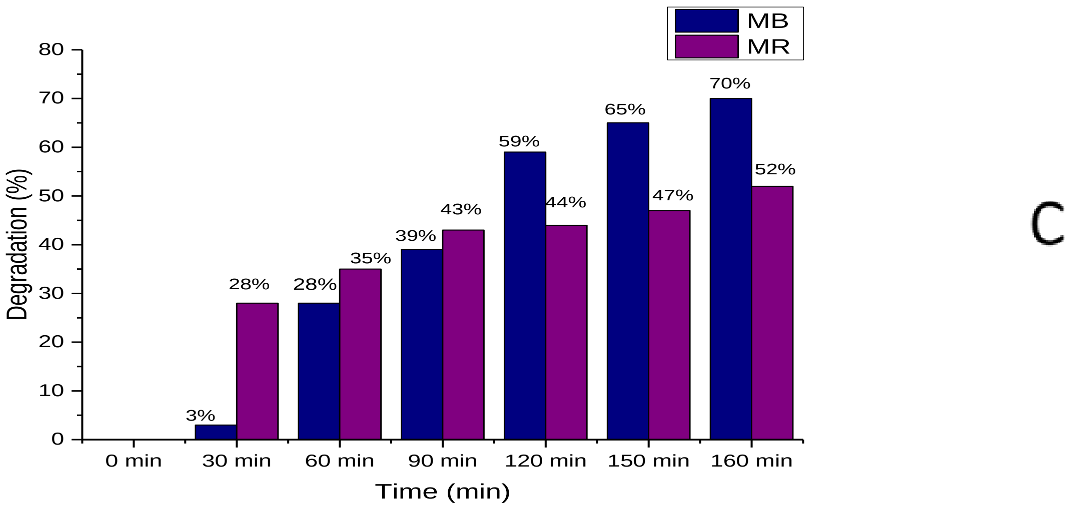
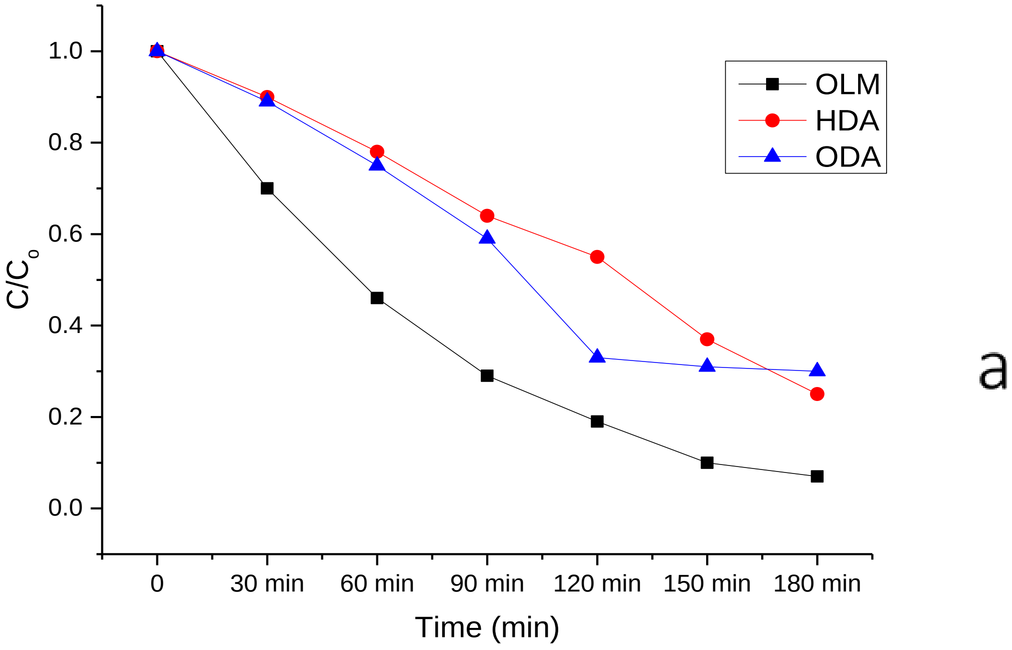


Figure 2. Percentage degradation efficiency of MB and MR dye under light irradiation (a- OLM-CdS, b-HDA-CdS and c-ODA-CdS) quantum dots.

Increase in the concentration of the irradiated atom increases the rate of degradation. When the concentration of the dye reaches the induced level, the dye molecules available are not enough for adsorption [33]. The OLM-CdS catalyst changes the concentration of the dye, it turned out that the absorbance of the dye increased with time of UV-photoreaction.



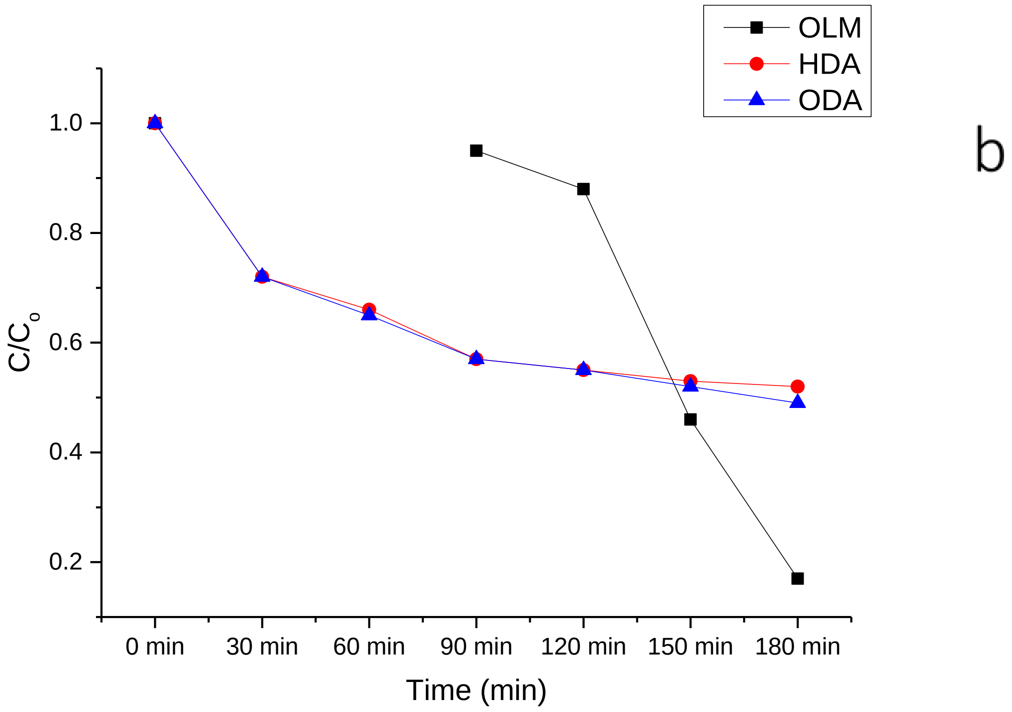


Figure 3. Photocatalytic degradation selectivity by MB (a) and MR (b) under light using as-prepared OLM-CdS, HDA-CdS and ODA-CdS quantum dots.

This could be due to the concentration of the catalyst versus saturation of the dye, however another catalyst only changed the pH of the dye, thus with OLM-CdS, it decomposes after long exposure to light and again it still has better decomposition efficiency. The results suggest that the as-obtained CdS quantum dots exhibit outstanding photocatalytic activity for both the dyes. To determine the selectivity of the dyes by the CdS quantum dots, the plot of ln(C/Co) vs Time (Fig. 3) shows that MB (Fig. 3a) has comparable degradation efficiency to MR (Fig. 3b) when using CdS quantum dots. HDA-CdS and ODA-CdS quantum dots photocatalyst have comparable degradation of MR because their optical band gaps are comparable as well.

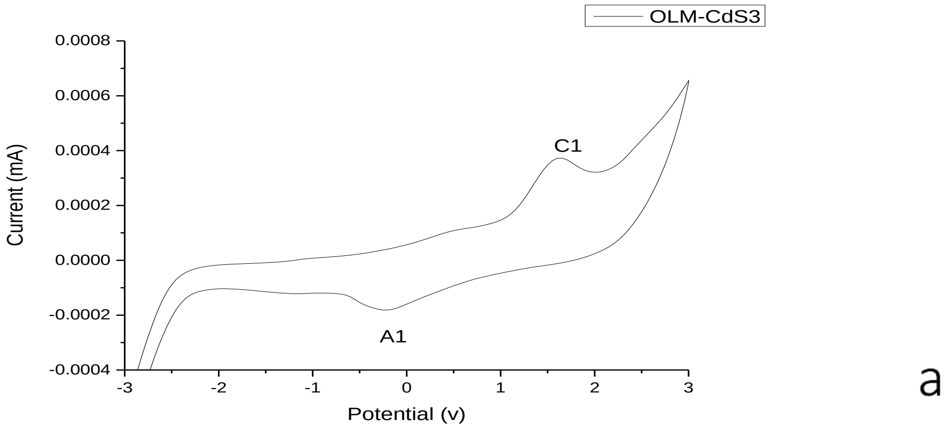
3.2. Electrochemical properties of the CdS quantum dots

Table 3.1. Relationship between the Optical and electrochemical band gaps for fractions 0.25-1.25 mV/s scan rate

compounds	1.25 mV/s –0.25 mV/S	the band gap (eV) [24]	Size (nm)
OLM-CdS	1.64	1.59	5.70
HDA-CdS	1.92	1.65	5.96
ODA-CdS	1.90	1.62	5.83

Electrochemical measurements of CdS quantum dots were carried out using cyclic voltammetry (CV). The CV was obtained with a glass electrode to determine the electronic band gap between anodic and cathodic electrode to validate Brus model [17]. The results show that the three CdS quantum dots displays similar features. Clear oxidation (C1) and reduction (A1) peaks appeared at different regions depending on the CdS quantum dots used. The oxidation peak appeared between ~ 0.92-2.12 V and reduction process was observed between ~ -0.34 to -1.34 V. Additional peaks were observed only on scan reversal after traversing either from oxidation to reduction (Fig. 4(a), (b), and (c)). The resulting peaks are from solution diffusion of CdS quantum dots to the electrode resulting in response to redox reaction. During the reduction process, the prospective scan moves towards the cathodic direction and the other scan moves towards the anodic direction. At the point when the decay of the clusters happens, the multi-electron moves to an environment where they are consumed, during this procedure electron move and charge move were pursued by chemical response (EC) system.

The physical separation between the oxidation and reduction peaks is identified with an electrochemical band gap, and the qualities attained for the three CdS quantum dots studied are presented in Table 3.1. The band gaps were comparable to those obtained from the absorption studies [24] but still higher. The band gap results proved that the band gap increases with increase in particle size, the origin of this difference can be due to the fast-following reactions which cause the peaks to shift to less extreme potential. As expected, the smaller nanocrystals are oxidized at increasingly positive possibilities and diminished at progressively negative possibilities, because the highest point of the valence band is moved in the direction of lower energies and the base of the conduction band shifts to the opposite direction with decreasing particle size. However, the outcomes repudiate the usual meaning. In addition, the charge moves to CdS quantum dots were viewed, at that point the electrons are disbursed by quick coupled substance reaction due to decay of the group [17, 34]. The increase in the scan rate decreases the reduction peak (Fig. 5). Fig. 5(c) showed the disappearance of reduction peak with the increase of the scan rate.



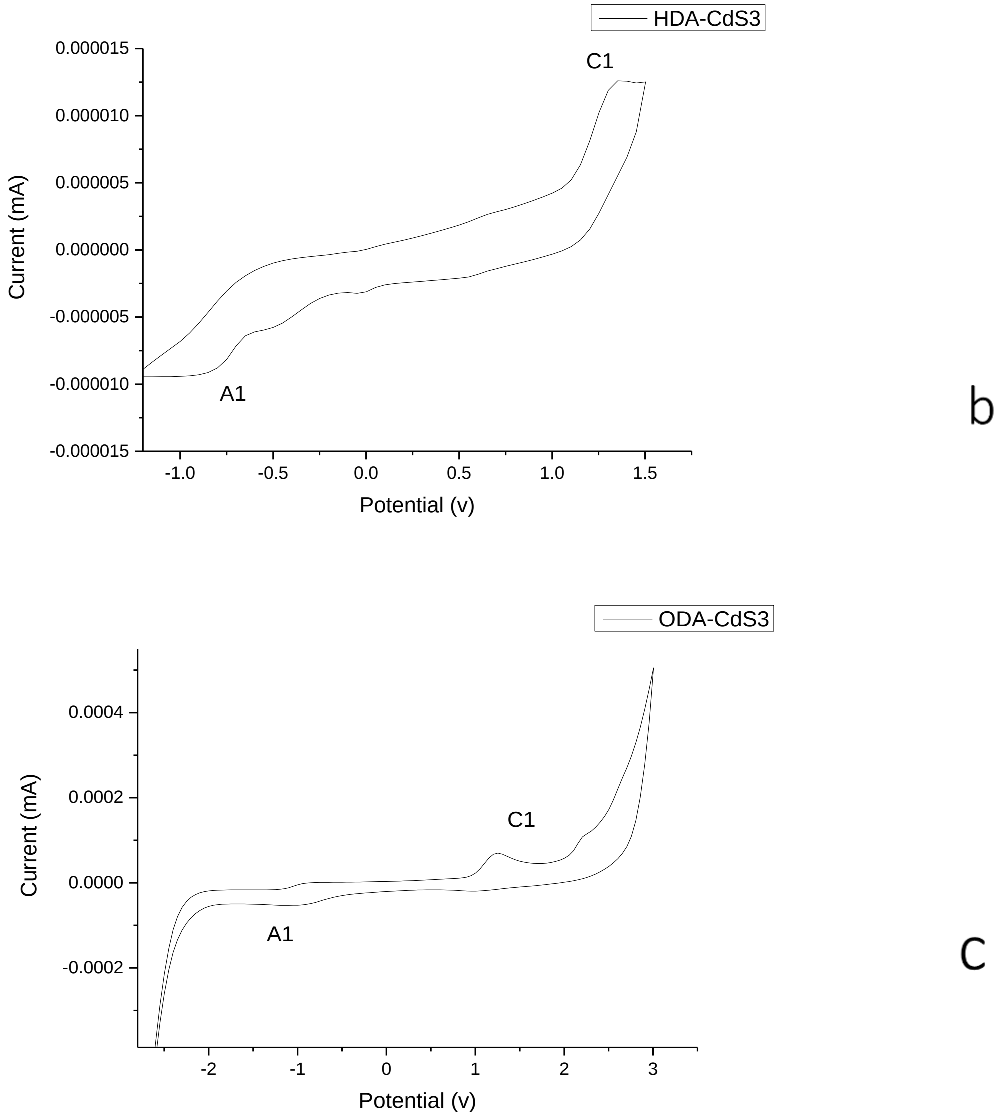
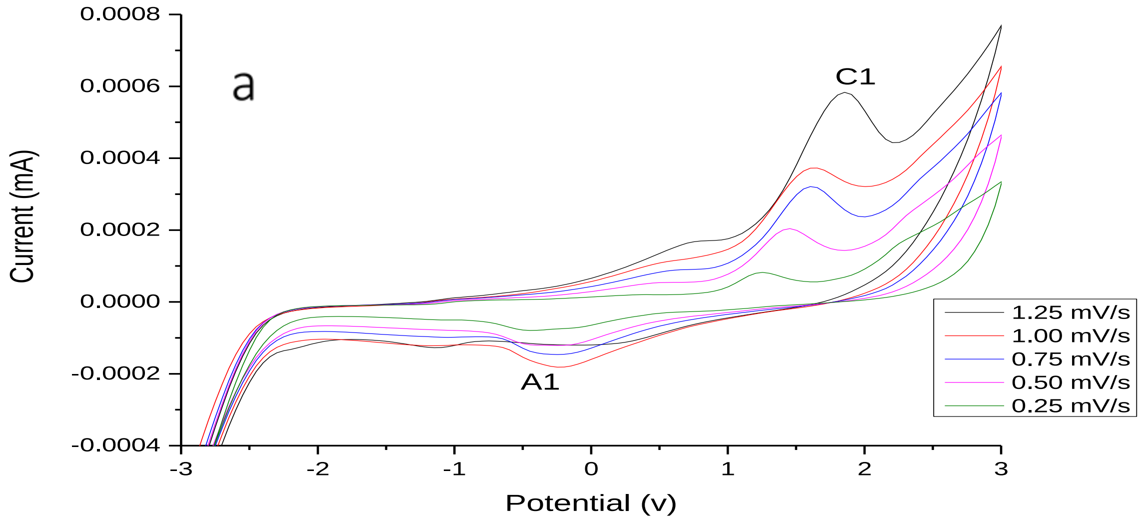


Figure 4. Cyclic voltammogram of OLM-CdS (a), HDA-CdS (b), and ODA-CdS (c) quantum dots at the scan rate of 1.25 mV/s at room temperature.



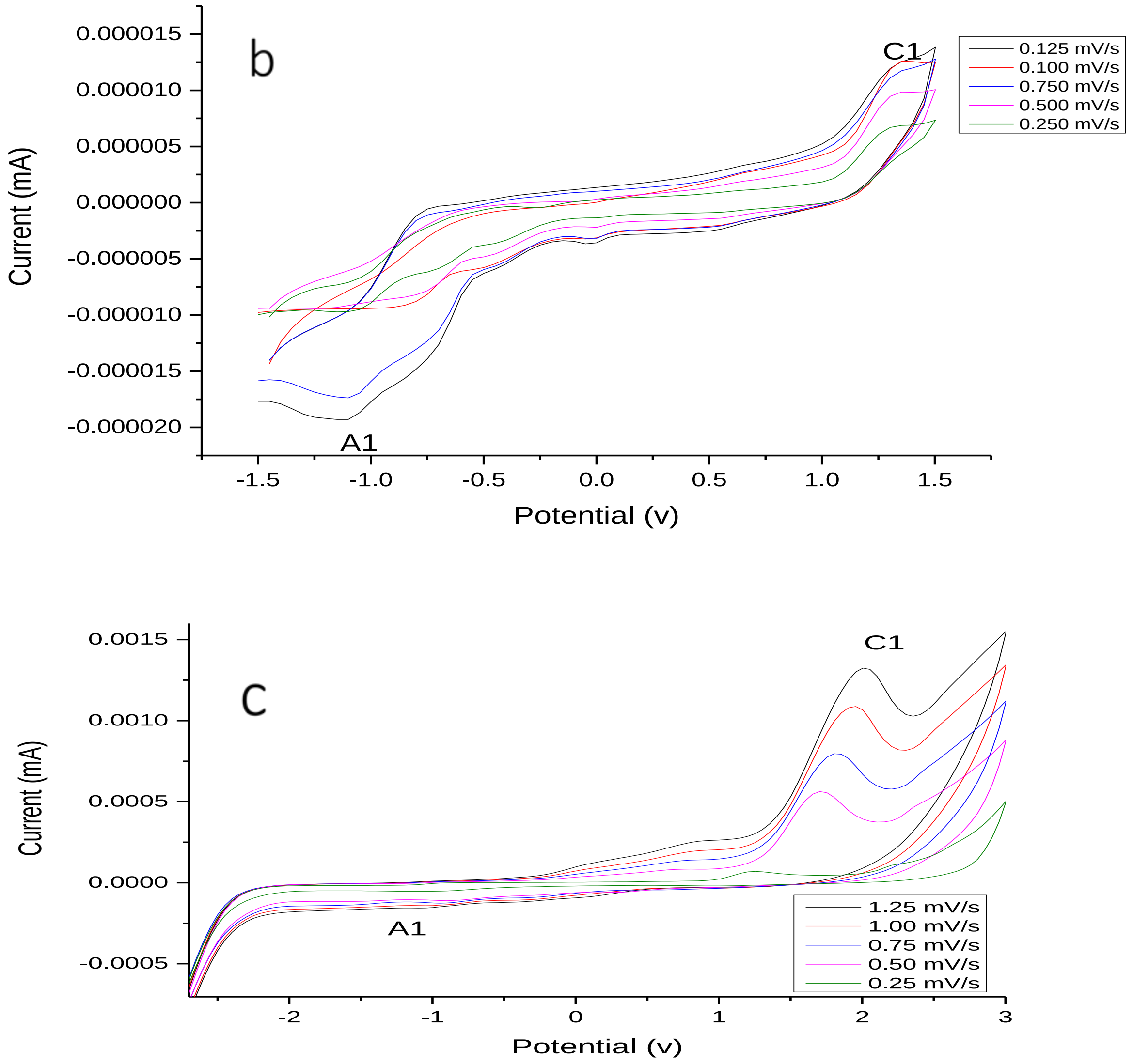


Figure 5. Cyclic voltammetry curves at various scan rate from 0.25-1.25 mV/s of OLM-CdS (a), HDA-CdS (b), and ODA-CdS (c) electrodes.

4. CONCLUSION

The photocatalytic degradation efficiency of methylene blue and methyl red was 93% and 83% for OLM-CdS, 75% and 48% for HDA-CdS and 70% and 52% for ODA-CdS respectively. From these results, we can conclude that the CdS quantum dots have high photocatalytic efficiency and the cationic dye, methylene blue is degraded better than anionic dye, methyl red by the CdS quantum dots. The predominant photocatalytic decomposition efficiency of the CdS quantum dots is ascribed to significant decrease in the recombination of electron-hole sets. The CdS quantum dots showed exceptional stability, reusability, and recyclability towards the photo decay of MB and MR. Electrochemical band energies were found to be 1.64 V for OLM-CdS, 1.92 V for HDA-CdS and 1.90 V. The band gaps are comparable, and this makes them more suitable for other applications such as fabrication of solar cells. The electrochemical properties of the CdS quantum dots display typical behavior expected with, oxidation peak of CdS anodic dissolution and a reduction peak showing the cathodic reduction of Cd^{2+}. However, the cyclic voltammograms indicated the capping agents influences the chemical reaction related to the charged CdS quantum dots. Fluctuation in the quantum dots not only influences the location of the HOMO and LUMO energy levels but also influences estimation of $E_{g.}$

ACKNOWLEDGEMENTS
Authors would like to thank Sasol and National Research Foundation for financial support.

CONFLICT OF INTEREST
There are no conflicts to declare.

References

1. A. Visheratina, A. Loudon, V. Kuznetsova, A. Orlova, Y.K. Gun'ko, A. Baranov and A. Fedorov, *Opt. Spectrosc.*, 125 (2018) 94.
2. M.M. Ghobashy, *Ionizing Radiation Effects and Applications*, (2018) 21. http://dx.doi.org/10.5772/intechopen.73234
3. M.L. Škorić, I. Terzić, N. Milosavljević, M. Radetić, Z. Šaponjić, M. Radoičić and M.K. Krušić, *Eur. Polym. J.*, 82 (2016) 57.
4. R.P. Souza, T.K. Freitas, F.S. Domingues, O. Pezoti, E. Ambrosio, A.M. Ferrari-Lima and J.C. Garcia, *J. Photochem. Photobiol., A*, 329 (2016) 9.
5. S. Anandan, Y. Ikuma and K. Niwa, *Sol. St. Phen.*,162 (2010), 239.
6. E.M. Saggioro, A.S. Oliveira and J.C. Moreira, in *Text. Wastewater Treat.* IntechOpen, (2016).
7. L. Li, M. Wang, in *Advanced catalytic materials-photocatalysis and other current trends*, IntechOpen., (2016).
8. X. Kang, S. Liu, Z. Dai, Y. He, X. Song and Z. Tan, *Catal.*, 9 (2019) 191.
9. J. Ge, Y. Zhang, Y.-J. Heo and S.-J. Park, *Catal.*, 9 (2019) 122.
10. M. Humayun, F. Raziq, A. Khan and W. Luo, *Green Chem. Lett. Rev.*, 11 (2018) 86.
11. O. Ola, M. M. Maroto-Valer, *J. Photochem. Photobiol., C*, 24 (2015) 16.
12. R. Leary, A. Westwood, *Carbon*, 49 (2011) 741.
13. N. Soltani, E. Saion, M. Z. Hussein, M. Erfani, A. Abedini, G. Bahmanrokh, M. Navasery and P. Vaziri, *Int. J. Mol. Sci.*, 13 (2012) 12242.
14. P.L. Cheton, F.S. Archibald, *Free Radical Biol. Med.*, 5 (1988) 325.
15. A. Samadi-Maybodi, H. Farzinia, *J. Photochem. Photobiol., A*, 357 (2018) 103.
16. T. Yao, X. An, H. Han, J.Q. Chen and C. Li, *Adv. Energy Mater.*, 8 (2018) 1800210.
17. P.P. Ingole, *Phys. Chem. Chem. Phys.*, 21 (2019) 4695.
18. M. Amelia, C. Lincheneau, S. Silvi and A. Credi, *Chem. Soc. Rev.*, 41 (2012) 5728.
19. Y. Zhu, N. Jain, M.K. Hudait, D. Maurya, R. Varghese and S. Priya, *J. Vac. Sci. Technol., B*, 32 (2014) 011217.
20. M. Morgenstern, A. Georgi, C. Straßer, C. Ast, S. Becker and M. Liebmann, *Physica E*, 44 (2012) 1795.
21. C. Schulte-Braucks, K. Narimani, S. Glass, N. Von Den Driesch, J. Hartmann, Z. Ikonic, V. Afanas' ev, Q. Zhao, S. Mantl and D. Buca, *ACS Appl. Mater. Inter.*, 9 (2017) 9102.
22. Y. Jang, A. Shapiro, M. Isarov, A. Rubin-Brusilovski, A. Safran, A.K. Budniak, F. Horani, J. Dehnel, A. Sashchiuk and E. Lifshitz, *Chem.Commun.*, 53 (2017) 1002.
23. B.-M. Bresolin, W.Z. Tang and M. Sillanpää, *Environ. Proc.*, 5 (2018) 879.
24. L.L. Mphahlele, P.A. Ajibade, *J. Sulfur Chem.*, 40 (2019) 648.

25. R. Rajendran, K. Varadharajan, V. Jayaraman, B. Singaram and J. Jeyaram, *Appl. Nanosci.*, 8 (2018) 61.
26. D. Ayodhya, M. Venkatesham, A.S. Kumari, G.B. Reddy, D. Ramakrishna and G. Veerabhadram, *J. Fluoresc.*, 25 (2015) 1481.
27. R. Akbarzadeh, S.S. Khalili and H. Dehghani, *New J. Chem.*, 40 (2016) 3528.
28. R.B. Anjaneyulu, B.S. Mohan, G.P. Naidu and R. Muralikrishna, *J. Asian Ceram. Soc.*, 6 (2018) 183.
29. S.A. Ansari, M. H. Cho, *Sci. Rep.*, 6 (2016) 25405.
30. M. Mahanthappa, N. Kottam and S. Yellappa, *Appl. Surf. Sci.*, 475 (2019) 828.
31. S.A. Bakar, C. Ribeiro, *RSC Advances*, 6 (2016) 36516.
32. R. Ullah and J. Dutta, *J. Hazard. Mater.*, 156 (2008) 194.
33. A. Gnanaprakasam, V. Sivakumar and M. Thirumarimurugan, *Indian J. Mater. Sci.*, 2015 (2015)
34. S.K. Haram, B.M. Quinn and A.J. Bard, *J. Am. Chem. Soc.*, 123 (2001) 8860.

© 2020 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).