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Adsorption and photocatalytic degradation of an industrial azo dye using colloidal semiconductor nanocrystals

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Abstract:

In this study, mercaptosuccinic acid capped CdSe nanocrystals was successfully synthesized by in-situ medium colloid and used as photocatalyst for the effective photodegradation of methylene blue from aqueous solution under visible light and sunlight irradiations. The particle size and the crystal structure of these nanocrystals were analyzed by different analytical techniques. Dye adsorption prior to photocatalysis using these nanomaterials was studied via the experimental quantification of kinetics and isotherms. These experimental data were modeled including the application of statistical physics theory to analyze the corresponding adsorption mechanism. A maximum adsorption capacity of 27.1 mg/g (80% dye removal) was observed in 10 min using an initial concentration of 30 mg/L.

Statistical physics calculations indicated that the adsorption energy was lower than 40 kJ/mol. It was also established that the dye adsorption was associated to the electrostatic interactions and hydrogen bonding. Overall, the dye removal was a spontaneous, feasible process and exothermic. Adsorption properties of CdSe-MSA nanocrystals improved the dye photodegradation efficiency under visible light thus achieving up to 80% degradation in 60 min. The synergic effect of adsorption and photocatalytic degradation performance was mainly due to the surface area, small size (3.7 nm) and structural defects (selenium vacancies $\text{Se}_\bullet$, interstitial of cadmium I_{Cd}), which enhanced the response of these nanomaterials inside the visible range for the photocatalytic activity. In summary, these nanocrystals are promising materials to be used in wastewater treatment under sun light for the removal of organic compounds like dyes.

Keywords: Functional organic nanocrystals, Methylene blue, Adsorption, Photocatalysis, Statistical physics modeling, Sunlight, Wastewater treatment.

1. Introduction:

The increasing consumption of fossil fuels and environmental pollution are major world challenges that require extensive research on different areas including the use of sustainable solar energy (Meinardi et al. 2017; Sauvé and Desrosiers 2014). Various industries (e.g., paper industry, textile industry, cosmetics, paper, clothing and hair coloring) use synthetic organic dyes and, consequently, generate environmental impacts and human health risks upon consumption directly or indirectly. Large-scale production associated to these industries generates polluted effluents that can alter significantly the aquatic environment due to the hazardous toxicological profile of dyes (Sousa et al. 2018). On the other hand, the optical and optoelectronic applications such as photocatalysts and solar cells based on semiconductors taking advantage of solar energy have emerged as one of the most promising strategies to resolve energy problems and to meet the fundamental challenge of environmental protection (Belver et al. 2020).

To date, there are several consolidated technologies for wastewater treatment such as adsorption (Azha et al. 2019), membrane-based processes, ultrafiltration (Liu et al. 2017), solvent extraction (Hu et al. 2005), reverse osmosis (Nataraj et al. 2009) and electrochemical treatment. In particular, advanced oxidation processes (AOPs) are a wide range of technologies applied to degrade the wastewater pollutants based on the generation of reactive oxidant species like hydroxyl radical ($\cdot\text{HO}$) or superoxide radical ($\cdot\text{O}_2^-$) with high oxidant

capacity(Deng and Zhao 2015)During the course of a photocatalytic process, electron-hole pairs are formed in the semiconductor material by irradiation of visible/UV light with energy more than or equal to its bandgap, which can further generate free radicals on the material surface. The resulting free radicals are efficient oxidizers of organic compounds degradation. At the present time, the advanced oxidation processes based on semiconductor photocatalysts have extended their applications including the goal of an effective and eco-friendly wastewater purification(Guo et al. 2013; Jaseela et al. 2019; Bel Haj Mohamed et al. 2021).Photocatalysis is a low-cost and convenient approach to degrade/remove dyes and other organic pollutants from wastewaters by light radiation(Jabeen et al. 2017).During last decades, the nanomaterials have been recognized as excellent catalyst in various fields. The chemical and physical properties of semiconductor nanoparticles can be significantly enhanced in comparison to the bulk counterpart due to their high surface-to-volume ratio; therefore, these nanomaterials have been successfully applied in different branches of science and technology(Peng et al. 2005).Semiconductors in the form of colloidal nanocrystals have a large number of surface atoms and are generally capped with organic ligands, which ensure a surface passivation and prevent their aggregation. Also, these materials are dispersible in solvents allowing their easy processing and they can provide surface functionality adapted to the desired applications. Several studies have been focused on photocatalytic activity for the degradation and removal of different pollutants using distinct semiconductor materials likeTiO₂(Hashimoto et al. 2005) , ZnO (Raskar et al. 2019) ,ZnS(Raskar et al. 2019) ,CdS (Zhao et al. 2007) , SnO₂(Cheng et al. 2018) and GO-based composites (Han et al. 2018).CdSe is a n-type semiconductor with a band gap in the visible range (1.65-1.8 eV) (Lo et al. 2004; Kotkata et al. 2009)and it has received numerous applications in labeling(Wang et al. 2011) , sensors(Huang et al. 2008), optometric devices(Jung et al. 2008) , solar cells(Yang et al. 2011; Im et al. 2010) and photocatalysis (Lo et al. 2004).Although it has been widely used for biological applications, its immobilization on a solid support for photocatalytic applications has not been explored extensively.

As stated, there are physical, chemical and biological techniques used to remove dyes from an aqueous solution. Nevertheless, these methods may show disadvantages such as energy intensiveness, long processing time, high cost and generation of toxic wastes(Sajab et al. 2013).To the best of author knowledge, several researchers have indicated that the adsorption process is considered as one of the most promising technologies to treat dye-containing wastewaters because of its simplicity of design,ease of operation, cost-effective, wide source of adsorbents and it does not produce harmful substances and wastes(Ilgin et al.

2019; Yazidi et al. 2019; Atrous et al. 2019). Inorganic and organic adsorbents have been applied to remove dyes from an aqueous solution. However, some of these adsorbents may suffer from problems in the separation from the treated fluid and their performance can be affected by the presence of co-adsorbates in wastewaters. It is important to indicate that the adsorption phenomenon is also present in the photodegradation of organic pollutants from water. It has been demonstrated that the photocatalytic degradation rate depends significantly on the adsorption properties of the photocatalyst for the target pollutant molecules. Note that the adsorption of pollutant molecules on catalyst surface can significantly improve the degradation efficiency. In this regard, the semiconductor nanocrystals can be used as an effective adsorbent due to their good chemical and thermal stability, solubility in a wide range of operating conditions, surface area, morphology, low cost and feasible synthesis method (Bel Haj Mohamed et al. 2014, 2018)]. Therefore, this paper has focused on the preparation of semiconductor nanocrystals with tailorable surface area and high adsorption properties to be used as model photocatalysts for exploring the adsorption-photocatalysis synergy in the degradation of organic pollutants. Furthermore, the combination of adsorption and photocatalytic degradation has been analyzed to determine its potential application to treat wastewaters polluted by organic molecules.

Based on this background, the synthesis of CdSe-mercaptop succinic acid (CdSe-MSA) colloidal nanocrystals and their application in the adsorption/photodegradation of a dye molecule are reported in this paper. Methylene blue (MB) is a cationic thiazine dye that was used as a model dye molecule to evaluate the photocatalytic activity of NCs. The adsorption of MB on CdSe-MSA was performed at different operating conditions to determine kinetics and isotherms where the effect of temperature was analyzed on the adsorption-photodegradation process. Statistical physics and thermodynamic calculations were carried out to interpret this system. Overall, the kinetics analysis and modeling results indicated that a synergistic effect between adsorption and photocatalysis was present for MB removal with colloidal nanocrystals, which improved the photocatalytic performance. A possible mechanism for the MB degradation was also proposed using these results.

2. Materials and Methods

2.1. Materials

Analytical grade chemicals were used without further purification. They included cadmium (II) acetate dehydrate (Sigma-Aldrich, $C_4H_6CdO_4 \cdot 2H_2O$, $\geq 98\%$), selenium dioxide (Sigma-

Aldrich, SeO_2 , $\geq 98\%$), sodium borohydride (Sigma-Aldrich, NaBH_4 , 98%), mercaptosuccinic acid (Sigma-Aldrich, $\text{C}_4\text{H}_6\text{O}_4\text{S}$, 97%) and sodium hydroxide (KOH, 99%). All aqueous solutions were prepared with ultra-pure water. MB dye ($\lambda_{\text{max}} = 665 \text{ nm}$, Merck Ltd, India) was used as received without further purification (Asfaram et al. 2015; Safardoust-Hojaghan and Salavati-Niasari 2017) and its molecular structure is described in Table 1.

2.2. Preparing of MSA-capped CdSe nanocrystals

In this work, CdSe nanocrystals were prepared by an aqueous method in the presence of organic capping molecule mercaptosuccinic acid (MSA). The method applied for the preparation of nanocrystals was based on a previous study of nanocrystals of II–VI semiconductors (Ben Brahim et al. 2017; Ouni et al. 2021). In particular, $\text{Cd}(\text{CH}_3\text{OO})_2\text{H}_2\text{O}$ and MSA were mixed in deionized water by stirring in a three-necked flask at room temperature. The solution was then degassed by bubbling nitrogen for 30 min. The pH of the resulting mixture was adjusted to 11 by drop wise addition of NaOH (1M) and the solution became transparent and clear. An aqueous solution of Na_2SeO_3 was prepared using selenium dioxide (SeO_2), NaOH solution and a quantity of the reductant sodium borohydride (NaBH_4) to obtain the Se^{2-} precursor. Then, this solution was quickly injected with a syringe into the flask containing the stock solution and the mixture was heated at 100°C under the presence of N_2 with continuous refluxing. After 2h, the color of this solution changed from colorless to yellow. This color change was related to the formation of CdSe-MSA nanocrystals. Finally, as soon as the desired temperature was reached, the flask was cooled to stop the growth of these nanocrystals. The nanocrystals powders precipitated by centrifugation and washed three times with water, ethanol and 2-propanol. Note that the nanocrystals colloidal dispersion was stable, homogeneous and light yellow. They were stored at room temperature until their further use in photocatalytic studies.

2.3. Photocatalyst characterization

Several analytical techniques were used to investigate CdSe nanocrystals. XRD measurements were performed using a Philips X'Pert PRO MPD diffractometer equipped with a $\text{CuK}\alpha$ radiation source ($\lambda = 1.542 \text{ \AA}$). The diffraction patterns were recorded in the range of 2θ from 20 to 70° using a step size of 0.02 . TEM images were obtained with a JEOL 2010 microscope operated at 200 kV . Nanocrystals were dropped on carbon-coated copper grids to obtain TEM samples where the excess solvent was evaporated. The nanocrystals size and size-distribution data were obtained based on the TEM images by measuring at least 100

randomly selected nanocrystals using image processing program (ImageJ, version 1.50). A multichannel Raman spectrometer T64000 Jobin-Yvon-Horiba equipped with an Olympus BX40 confocal microscope system was used to record the Raman spectra. An argon krypton laser operated at 488 nm with approximately 50 mW of radiation power was used to analyze the sample. FTIR spectra were recorded using a Perkin Elmer (version 5.3) spectrophotometer at room temperature in the spectral range of 400-4000 cm⁻¹ using KBr pellet disks. The absorption spectra were recorded in the wavelength range of 200-800 nm at room temperature using a SPECORD 210 Plus spectrophotometer with a quartz cuvette. Photoluminescence (PL) spectroscopy was applied to analyze the defects and emission properties of the CdSe using the exciting source of a 325 nm-line helium-cadmium laser. Photocatalytic experiments were carried out under irradiation using UV light source (Arc Lamp 50-500W, 66901, Newport) and sunlight.

2.4. Kinetics and isotherms of MB adsorption

These experiments were used to analyze the impact of temperature and dye concentration on the MB adsorption. For the adsorption kinetic experiments, 30 mg of CdSe nanocrystals powder was added to 30 mL of MB aqueous solution at the initial concentrations of 10, 15, 20, 25 and 30 mg/L. All concentrations of dye solutions were prepared by diluting the stock solution (100mg/L). The solution pH was adjusted at 7 and controlled by adding NaOH into the solution during the experiment. This pH value was chosen as optimum value for obtaining the maximum adsorption (Kaur et al. 2019). As a result, the efficiency of MB photodegradation was expected to increase with pH owing to the electrostatic interactions between the negative photocatalyst surface and MB cations. The adsorption isotherms of MB dye on CdSe nanocrystals were determined at three temperatures from 300 to 320 K. After the corresponding adsorption experiment, the supernatant fraction was used to determine the adsorption capacities via the quantification of dye concentration with UV-Vis spectroscopy recording the MB characteristic absorption band at 665 nm. The equilibrium MB adsorption capacity Q_e was calculated with the following equation (R. et al. 2018; Li et al. 2020)

$$Q_e(\text{mg/g}) = \frac{V(C_0 - C_e)}{m} \quad (1)$$

while the dye removal (%) of nanocrystals was obtained via the next equation:

$$\text{Dye removal} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

where C_0 (mg/L) is the initial concentration, C_e (mg/L) is the equilibrium concentration in the solution, C_t (mg/L) is the dye concentration at time t , V is the volume of the solution (L) and m is the mass of the CdSe-MSA catalyst (g). Each adsorption experiment was performed for 2h with magnetic stirring in the dark.

2.5. Photocatalytic degradation of MB

A comparative study of the photocatalytic degradation of MB dye in aqueous solution was performed using two types of irradiation: a mercury lamp and sunlight. For this photocatalytic process, 30 mg of CdSe-MSA nanocrystals were mixed with a 30 mL of a MB solution with initial concentration of 10mg/L in 100mL cylindrical Pyrex reactor under continuous stirring. First, the suspension was magnetically stirred in absence of light exposure to reach the adsorption-desorption equilibrium between MB dye and photocatalyst surface. After that, the photocatalysis reaction was started when the suspension was exposed to sunlight or visible light. In successive sampling times, 2 mL of the solution were taken and precipitated by absolute ethanol to separate the supernatant (dye solution) from the catalyst where the final concentration was determined by UV-Visible spectroscopy. According to the Beer–Lambert law, the degradation efficiency (%D) of MB was calculated with the next equation (Kaur et al. 2019):

$$\%D = \frac{C_0 - C}{C_0} \times 100 = \frac{A_0 - A}{A_0} \times 100 \quad (3)$$

where A , A_0 , C_0 and C were the absorbance and concentration of MB dye solution (mg/L) before and after irradiation, respectively, at different times using CdSe-MSA nanocrystals. The photocatalytic degradation of MB with this catalyst followed a pseudo first-order kinetics model, also known as Langmuir-Hinshelwood model. This model is given by (Ouni et al. 2021; Lakshmipathy et al. 2017):

$$-\frac{dC}{dt} = k_{app}C \quad (4)$$

Integrating the last equation and using the boundary condition of $C = C_0$ at $t = 0$, the next expression is obtained:

$$C = C_0 e^{-k_{app}t} \leftrightarrow \ln \frac{C}{C_0} = -k_{app}t \quad (5)$$

where k_{app} (min^{-1}) is the apparent reaction rate constant and t is the irradiation time. Note that k_{app} was calculated from the slope of $\ln (C/C_0)$ versus t .

3. Results and discussion

3.1. Photocatalyst characterization

XRD pattern of CdSe-MSA is shown in Figure 1.a and was compared to that of the JCPDS card No. 019-0191. The diffraction peaks were very broad thus indicating a very small crystal size. The high-intensity diffraction peaks at $2\theta^\circ = 28.33, 44.41$ and 51.34° matched with the (111), (220) and (311) crystalline planes of the cubic phase of CdSe-MSA. However, it is convenient to note that the high intensity of the (111) peak suggested that this direction was the most preferred. A shift in the peak positions corresponding to the nanocrystals sample compared to those of the CdSe bulk crystal was identified according to the JCPDS data cards. This shift was originated from the relaxation at the surface often observed in crystals of very low dimension, which altered the inter-plan distances that became small (Wang et al. 2017). From the (111) plane, the crystallite size of the nanocrystals was calculated to be 1.7 ± 0.1 nm using the Debye Scherrer formula:

$$D = \frac{0.9\lambda}{\beta_{hkl}\cos\theta} \quad (6)$$

where D is the average crystal size in nm, $K = 0.9$ is the shape factor, $\lambda = 0.15406$ nm is the wavelength of X-ray, β_{hkl} is the full width at half maximum and θ is the reflection angle of Bragg. For the cubic crystal structure of CdSe, the lattice parameter was calculated from the (111) plane and was $5.74 \text{ \AA}$, which was considerably lower than its corresponding bulk value ($6.05 \text{ \AA}$). Note that Scherrer's formula only takes into account the effects of the crystallite size that come from the XRD peak broadening, but the possible presence of intrinsic strain within the crystal (i.e., grain boundary, stacking faults, dislocations) are not considered. Therefore, it then provided an overestimation of the nanocrystal size for the compressive strain and underestimation for the size for the extensive strain (Nath et al. 2020). Therefore, the method proposed by Williamson and Hall allowed deconvoluting the two effects: size and micro-strain (Nath et al. 2020; Williamson and Hall 1953). This method considers that all the peaks are purely Lorentzian. Indeed, the integral width β_{total} of the convolution of a Gaussian of the nanocrystals is the integral width β_{size} due to the size effect and the integral width β_{strain} due to micro-stress from the physical line broadening of X-ray diffraction peak:

$$\beta_{hkl} = \beta_{size} + \beta_{strain} \quad (7)$$

The micro-strain ϵ and broadening β_{strain} are related by the following relation (Stokes and Wilson 1944):

$$\beta_{strain} = 4\epsilon \tan\theta \quad (8)$$

So, the total broadening due to strain and size, in a particular peak having the hkl value, can be expressed as:

$$\beta_{hkl} = \frac{0.9\lambda}{D \cos\theta} + 4\epsilon \tan\theta \quad (9)$$

The last equation can be re-arranged to get:

$$\beta_{hkl} \cos\theta = \frac{0.9\lambda}{D} + 4\epsilon \sin\theta \quad (10)$$

Plotting the value of $\beta_{hkl} \cos\theta$ as a function of $4\sin\theta$ (see Figure 1.b) can be used to estimate the micro-strain where ϵ can be estimated from the line slope and the crystallite size from the intersection with the vertical axis. This linear regression showed a determination coefficient $R^2 = 0.99$. Therefore, the intrinsic strain and particle size were 0.166 and 0.41 nm, respectively. This compressive strain was a result of the reduced lattice parameter of the crystals. This result confirmed that the compressive strain of surface generated by organic ligands, during the growth of CdSe-MSA nanocrystals, resulting in the crystallinity imperfection and distortion through the relaxation of atomic positions (Wu et al. 2007; Thandavan et al. 2015). High Resolution Transmission Electron Microscopy (HRTEM) images of CdSe nanocrystals are shown in Figure 2.a. These images demonstrated the formation of monodisperse nanocrystals with reasonable spherical shape. The histogram of nanocrystals size distribution indicated a mean value of 3.7 ± 0.1 nm, see Figure 2.b, which was nearly the same value as that obtained from XRD data analysis. The clear continuous lattice fringes obtained by HRTEM images were associated to the single-crystalline property of CdSe-MSA. The observed interplanar spacing of 0.34-0.37 nm corresponded to the (111) crystalline planes of cubic phase thus showing that the nanocrystals grown along (111) plane.

FTIR spectroscopy was used to identify the surface modification of CdSe nanocrystals by grafting an organic ligand with the thiol group (S-H) to allow their binding to cadmium. A typical FT-IR spectrum is shown in Figure 3. The total disappearance of the characteristic band of the thiol group (S-H), which is generally observed between $2560-2660 \text{ cm}^{-1}$, indicated the cleavage of the S-H bond and the fixation of the sulfur atom and cadmium atoms on the nanocrystals surface (Bel Haj Mohamed et al. 2021; Arivarasan et al. 2019; Abd El-sadek and Babu 2011). Furthermore, MSA capped CdSe nanocrystals showed a broad absorption band at around 3280 cm^{-1} due to the presence of OH stretching vibration of water molecules. The band located at 2982 cm^{-1} corresponded to the vibration mode by asymmetric stretching bond

of-CH₂. The C=O vibrational band of MSA molecules at 1697 cm⁻¹ was shifted to a lower frequency at about 1560 cm⁻¹. The bands located at 1380 cm⁻¹ corresponded to symmetric vibration of the (COO-) group. The band at 918 cm⁻¹ could be caused by C-H bending. These results clearly indicated that the MSA molecules were well attached to the surface of CdSe nanocrystals.

Raman spectroscopy was employed to investigate the resonances and to estimate if they were due to the size, lattice parameter or surface strain of the CdSe nanocrystals. Also, the magnitude order of these modes of lattice vibrations was determined and the crystalline quality of synthesized nanocrystals was evaluated. Figure 4 shows the Raman spectrum of CdSe-MSA nanocrystals. Raman spectrum contained two principal peaks at 194.3 and 295.7 cm⁻¹. The first was attributed to the first order of longitudinal optical (1LO) phonons of CdSe with a low wavenumber shift of 17 cm⁻¹ compared to the 1LO mode of bulk CdSe (LO CdSe = 212 cm⁻¹) (Todescato et al. 2013; Neto et al. 2010). This shift was due to the reduction in size of the CdSe nanocrystals. At the same time, the 1LO peak of CdSe had a low intensity band between 150-180 cm⁻¹ corresponding to the surface optical (SO) phonons due to the large specific surface area and LO phonons of the CdSeS alloy at the interface of nanocrystals-ligand (Chaparro et al. 2000; Tschirner et al. 2012).

In terms of intensity, this 1LO phonon band of CdSe was weaker. This finding was related to the less ordered in the nanocrystals structure. This behavior was observed with the broader band in the (111) plane in the XRD analysis and the compressive strain calculated by the Williamson-Hall method. The second band was also associated with the longitudinal optical (1LO) phonons of CdSeS alloy and CdS nanocrystals, which was in agreement with those measured experimentally (Tschirner et al. 2012). The absence of impurity and defect-related vibrational modes suggested the occurrence of only a single phase of the synthesized nanocrystals. This result showed that ligand coating had occurred on the CdSe nanocrystals involving the sulfur atom of the ligand with Cd atoms at their surface.

To determine the size, absorption range and band gap energy, UV-Vis spectra were recorded, as presented in Figure 5.a. CdSe-MSA nanocrystals had a large absorption starting from 580 nm, which became strong near 380 nm thus indicating that MSA capped CdSe nanocrystals can absorb a significant portion of visible light. Band gap energy E_g values for these nanocrystals can be estimated from the UV-vis spectrum using the Tauc model (Soltani et al. 2013):

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (11)$$

Where α is the absorption coefficient, $h\nu$ is the photon energy, A is a constant and $n=1/2$ is a transition-dependent factor. The absorption coefficient (α) was determined from Beer–Lambert’s relation (Soltani et al. 2013, p.):

$$A = \frac{I}{I_0} = e^{(-\alpha d)} \quad \text{or} \quad \alpha = 2.303 \frac{A}{d} \quad (12)$$

Where d is the path length of the quartz cuvette and A is the absorbance determined from the UV–Visible spectrum. The band gap energy values can be determined by extrapolation of the linear part of $(\alpha h\nu)^2$ versus $h\nu$, see Figure 5.b. The line intersection with the x-axis corresponded to the value of the optical gap energy. The estimated band-gap energy of CdSe-MSA nanocrystals increased from 1.74 to 2.4 eV, which was due to the quantum confinement effects induced by the nanosized crystallites in CdSe semiconductors, subsequent in more discrete energy spectra (Smida et al. 2018). This result indicated that the CdSe-MSA had a suitable band gap for photocatalytic decomposition of organic contaminants under visible-light irradiation.

The exciton peak position can be converted into the corresponding particle size of nanocrystals using the next empirical expressions (Bacherikov et al. 2006):

$$D = 0.344 \exp \left(\frac{\lambda_{\max} - 252.7}{129.3} \right) \quad (13)$$

In the case of these nanocrystals, $\lambda_{\max}$ was 480 nm and the corresponding D value was 2 nm, which was slightly greater than the sizes obtained from XRD and TEM results. CdSe nanocrystals have $\lambda > 400$ nm indicating that they were suitable for the solar spectrum. Therefore, there was an enhancement in photocatalytic efficiency under solar light because the samples were capable to absorb more amount of solar energy for the degradation of organic molecules like dyes (Dake et al. 2020).

The PL spectrum of purified CdSe-MSA nanocrystals was obtained using a photoluminescence spectrophotometer with an excitation wavelength $\lambda_{\text{exc}} = 325$ nm at room temperature. Figure 6 shows PL spectrum of CdSe nanocrystals redispersed in water. PL spectrum showed a broad emission band around 532 nm with a FWHM of 126 nm. Since the absorption maximum was located at approximately 391 nm, a Stokes shift of approximately 141 nm was identified between the absorption threshold and the emission maximum at 532 nm (Figure 5.a). Due to the large surface-to-volume ratio of the small size and incomplete surface

passivation, these surface atoms can represent some localizing defect sites owing to unsaturated dangling bonds, which behaved as carrier trapping sites thus resulting in non-radiative recombination and led to a large emission spectrum shift with an FWHM increase. Moreover, this shift resulted from the global response of the nanocrystals sizes distribution because the transition energies collected on these populations were integrating all the transition energies of all the nanocrystals.

A Gaussian fitting allowed to decompose the emission spectrum into 3 intense and broad bands in the visible range located at 458 nm (2.71 eV), 525 nm (2.32 eV) and 592 nm (2.09 eV). The first blue emission located at 458 nm was strongly correlated to the nanocrystals size and was attributed to the direct recombination of excitons between the band edges (the fundamental exciton recombination). It was attributed to radiative recombination of an electron from the conduction band (BC) to the valence band or from the conduction band with a thiol group energy level ($R-S^-$) from organic ligands localized on the surface of CdSe nanocrystals (Bel Haj Mohamed et al. 2021; Soheyli et al. 2017). The presence of MSA can also provide carrier (hole) trapping sites and leads to quenching of radiative excitonic recombination. As suggested by Klimov et al. (Klimov et al. 1999), the hole trapping sites were not related defects, but rather arisen from intrinsic nanocrystal states or surface states that remained unchanged even after surface treatment (Klimov et al. 1999). Due to surface states of Cd^{2+} or Se^{2-} ions, it twisted energy states within the band gap in the nanocrystals. The band located at 525 nm may be due to the contribution of an electron localized on a selenium vacancy (V_{Se}) with a hole in the valence band (BV) (Klimov et al. 1999). Note that the last band located at 592 nm was attributed to the transition from cadmium interstitial of (I_{Cd}) to the valence band (BV) (Bel Haj Mohamed et al. 2021; Gaponenko 1998). Finally, the large emission could be accredited to the selenium vacancy and interstitial of cadmium generated in the CdSe nanocrystals, which played a vital role in the photocatalytic activity.

3.2. Adsorption and photocatalytic degradation of MB dye

3.2.1. Adsorption kinetics

Kinetics studies on the MB adsorption were conducted at 28 °C. Figure 7 shows the pseudo-first- and second-order kinetic models used to correlate the MB adsorption on CdSe-MSA nanocrystals. Note that the pseudo-first-order kinetic model has been widely used to predict the dye adsorption kinetics, which is given by (S 1898; Ho and McKay 1999; Pan et al. 2010; Ghasemi et al. 2014):

$$q(t) = q_e(1 - \exp(-K_1 t)) \quad (14)$$

Where $q(t)$ and q_e represent the amount of dye adsorbed (mg/g) at any time t and equilibrium, respectively, and K_1 is the corresponding adsorption rate constant (min^{-1}). The pseudo-second-order kinetic rate equation [2-4] is defined as:

$$q(t) = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \quad (15)$$

Where K_2 (mg/g min) is the pseudo-second-order rate adsorption constant. Results of adsorption kinetic modeling are reported in Tables 2 and 3. The pseudo-first-order model showed higher R^2 than the pseudo-second-order kinetic model thus concluding that this model was the best to correlate the MB adsorption kinetics using CdSe-MSA nanocrystals. The adsorption rate constant K_1 increased as a function of initial MB concentration thus suggesting that the adsorption relaxation time ($\tau = 1/K_1$) was of the order of a few minutes. Also, it was identified that there were two phases of the adsorption process. The first phase was associated to the diffusion of dye molecules on the nanocrystals surface, while the second one corresponded to the adsorption equilibrium. The adsorption capacity and the adsorption relaxation time varied from 8.87 to 23.9 mg/g and from 8.13 to 0.107 min, respectively, when the MB concentration increased from 10 to 30 mg/L. These results were related to a high number of adsorption sites available on the nanocrystals surface, which allowed a fast and high mass transfer gradient for the MB diffusion to CdSe-MSA surface. The amount of adsorbed dye increased with the stirring time to reach a plateau after 10 minutes thus indicating the adsorption equilibrium, which was caused by a limited number of MB molecules that diffused to the CdSe-MSA surface sites. Note that more than 90% of the maximum catalyst adsorption capacity was reached after 10 min of stirring. Then, the remaining 10% was reached after 120 min. Therefore, 120 min of stirring were required before proceeding with the photocatalytic activity. Finally, the equilibrium quantity increased with the initial concentration.

3.2.2. Adsorption isotherms

Figure 8 and Table 4 show the results of dye adsorption isotherm where the Langmuir, Freundlich isotherm, Langmuir-Freundlich and Redlich-Peterson equations were used to correlate these equilibrium experimental data. In particular, the Langmuir model assumes that the adsorption occurs with the monolayer formation of adsorbate molecules on a

homogeneous adsorbent surface with uniform energies of adsorption(Langmuir 1918).This model is represented by the following equation(Takeda et al. 1995; Nayak et al. 2017):

$$q_e = q_{max} \frac{K_e C_e}{1 + K_e C_e} \quad (16)$$

Where C_e (mg/L) is the dye concentration in solution at adsorption equilibrium, q_e is the equilibrium adsorption capacity (mg/mg), K_e (L/mg) is the equilibrium constant and q_{max} (mg/g)is the monolayer adsorption capacity of tested nanocatalyst. The calculated values of the Langmuir parameters were $q_{max} = 31.1$ mg/g and $K_e = 0.386$ L/mg with $R^2 = 0.96$. K_e value indicated a significant affinity of the adsorbent for the favorable adsorption of MB dye molecules.

On the other hand, the Freundlich model assumes a heterogeneous adsorption surface having sites with different adsorption energies. It is described as(Freundlich 1907):

$$q_e = k_f C_e^{1/n_F} \quad (17)$$

Where K_f (mg/g) is the Freundlich adsorption constant and n_F is the degree of nonlinearity between solution concentration and adsorption where $1/n_F \in (0.1, 1)$ indicates a favorable adsorption. The calculated value of $1/n_F$ was ~ 0.33 thus confirming the favorable MB adsorption by CdSe-MSA nanocrystals.

Redlich–Peterson is expressed by the following equation(Redlich and Peterson 1959):

$$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta} \quad (18)$$

where K_R (L/g), a_R (L/mg $^{1-1/\beta}$) and β are the corresponding isotherm parameters. Note that if $\beta \rightarrow 1$ the adsorption follows the Langmuir model and if $\beta \rightarrow 0$ the adsorption fits the Freundlich model. Data fitting indicated that $R^2 = 0.97$ and $\beta = 1$ for the Redlich–Peterson isotherm thus confirming the best correlation with a Langmuir-type isotherm model.

Finally, the Langmuir -Freundlich ($L-F$) isotherm model was also used to describe the adsorption equilibrium data(Abu-Alsoud et al. 2020):

$$q_e = \frac{q_{max}(K_{LF} C_e)^{n_{LF}}}{1 + (K_{LF} C_e)^{n_{LF}}} \quad (19)$$

where K_{LF} is the adsorption affinity constant and n_{LF} is the heterogeneity index.

The calculated L-F parameters were $Q_{max} = 27.07$ mg/g and $K_{LF} = 0.47$ L/mg with $R^2 = 0.98$.

Data fitting using this isotherm outperformed the results from Langmuir, Freundlich and

Redlich–Peterson models. The maximum adsorption capacity calculated with the Langmuir-Freundlich model was 27.1 mg/g, which agreed with the experimental data of 28.5 mg/g.

3.2.3. Statistical physics modeling

Statistical physics models were used to complement the analysis of MB adsorption via the calculation of the next physicochemical parameters: the number of adsorbed dye molecules per adsorption site (n), the density of adsorption sites (D_M) and the corresponding adsorption energies. In particular, the Hill model was used assuming that the adsorption was a monolayer process where the adsorption sites of CdSe-MSA nanocrystals can bind a fraction, one or more dye molecules (Bouزيد et al. 2016). Also, other statistical physics models were considered assuming that the MB dye molecules were adsorbed via the formation of two layers with one and two different adsorption energies (Bouزيد et al. 2016). The mathematical equations of these models are given below (Bouزيد et al. 2016; Mohamed et al. 2018; Bouزيد et al. 2016; Pang et al. 2020):

Monolayer process:

$$q_e = \frac{n \cdot D_M}{1 + \left(\frac{C_{1/2}}{C_e} \right)^n} \quad (20)$$

Double layer process with one adsorption energy:

$$Q_e = n \cdot D_M \frac{\left(\frac{C_e}{C_1} \right)^n + 2 \left(\frac{C_e}{C_1} \right)^{2n}}{1 + \left(\frac{C_e}{C_1} \right)^n + \left(\frac{C_e}{C_1} \right)^{2n}} \quad (21)$$

Double layer process with two adsorption energies:

$$Q_e = n \cdot D_M \frac{\left(\frac{C_e}{C_1} \right)^n + 2 \left(\frac{C_e}{C_2} \right)^{2n}}{1 + \left(\frac{C_e}{C_1} \right)^n + \left(\frac{C_e}{C_2} \right)^{2n}} \quad (22)$$

Where $C_{1/2}$, C_1 and C_2 are the corresponding concentrations at half saturation, respectively. These three models were applied to correlate the MB adsorption data of CdSe-MSA nanocrystals and the fitting results suggested that the monolayer adsorption model ($R^2 = 0.98 - 0.99$ and $RMSE = 1.84 - 3.49$) was the best to interpret the adsorption mechanism of MB dye, see Figure 9 and Table 5. Note that the calculation of adsorption energy via this model was performed with the next equation (Atrous et al. 2019; Bouzid et al. 2016; Mohamed et al. 2018; Bouzid et al. 2019; Pang et al. 2020).

$$(Bouzid et al. 2019b) \Delta E_1^a = R.T.\ln\left(\frac{C_s}{C_{1/2}}\right) \quad (23)$$

where C_s is the dye molecule solubility (g/L), R is the universal ideal gas constant ($8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$) and T is the absolute value of adsorption temperature. The fitted parameters of this statistical physics model are given in Table 6.

Overall, the number of adsorbed dye molecules per adsorption site of CdSe-MSA nanocrystals increased with temperature. This result indicated that there was an aggregation process where the formation of MB dimmers in the solution and a multi-molecular adsorption process ($n > 1$) could be expected. Therefore, a non-parallel adsorption orientation prevailed for the removal of this dye molecule. The density of adsorption sites D_m decreased with temperature. Note that if the number of adsorbed MB dye molecules per adsorption site increased, the space in the CdSe-MSA nanocrystals surface reduced and, consequently, the number of adsorption sites available for dye removal became limited. The adsorption capacities at saturation (q_{sat}) decreased as a function of aqueous solution temperature thus indicating an exothermic adsorption process. The maximum adsorption capacity at saturation was 27.1 mg/g at 298 K and the adsorption energy was 24.39 kJ/mol corresponding to physical interactions for MB dye adsorption. It could be expected weak electrostatic forces and hydrogen-bond interactions between MB molecules and the functional groups of CdSe-MSA nanocrystals.

Thermodynamic functions of this adsorption process were calculated with the statistical physics model: the configurational entropy (S_a), Gibbs free energy (G_a) and the internal energy (E_{int}). Specifically, the configurational entropy is given by the following equation (Mohamed et al. 2018; Bouzid et al. 2016):

$$\frac{S_a}{K_B} = D_m \left(\ln \left(1 + \left(\frac{C_e}{C_{1/2}} \right)^{n_1} \right) - \frac{\left(\frac{C_e}{C_{1/2}} \right)^{n_1} \cdot \ln \left(\left(\frac{C_e}{C_{1/2}} \right)^{n_1} \right)}{\left(1 + \left(\frac{C_e}{C_{1/2}} \right)^{n_1} \right)} \right) \quad (24)$$

480

481 The Gibbs free energy (G_a) is defined by (Mohamed et al. 2018; Bouzid et al. 2016):

$$\frac{G_a}{K_B \cdot T} = \log \left(\frac{C_e}{Z_v} \right) \left(\frac{n_1 \cdot D_m}{\left(1 + \left(\frac{C_{1/2}}{C_e} \right)^{n_1} \right)} \right) \quad (25)$$

483 Where Z_v represents the translation partition function per unit of volume (Bouzid et al. 2016;
484 Mohamed et al. 2018; Bouzid et al. 2016; Pang et al. 2020). Finally, the
485 adsorption enthalpy H_a is given by (Bouzid et al. 2016; Mohamed et al. 2018; Bouzid et al.
486 2016; Pang et al. 2020):

$$\frac{H_a}{K_B \cdot T} = \log \left(\frac{C_e}{Z_v} \right) \left(\frac{D_m \left(\frac{C_e}{C_{1/2}} \right)^{n_1}}{\left(1 + \left(\frac{C_e}{C_{1/2}} \right)^{n_1} \right)} \right) - D_m \cdot \ln \left(1 + \left(\frac{C_e}{C_{1/2}} \right)^{n_1} \right) \cdot \frac{\left(\frac{C_e}{C_{1/2}} \right)^{n_1}}{\left(1 + \left(\frac{C_e}{C_{1/2}} \right)^{n_1} \right)} + \frac{D_m \left(\frac{C_e}{C_{1/2}} \right)^{n_1}}{\left(1 + \left(\frac{C_e}{C_{1/2}} \right)^{n_1} \right)} \quad (26)$$

488 The variation of these thermodynamic functions with respect to the equilibrium MB
489 concentration at different temperatures is illustrated in Figure 10.

490 The evolution of configurational entropy (S_a) showed one stationary point corresponding to
491 $C_{1/2}$ where the disorder is maximum when half of the density of adsorption sites (D_M) of CdSe-
492 MSA nanocrystals surface were occupied. Note that if $C_e < C_{1/2}$, the disorder increased and MB
493 molecules had several adsorption sites to interact during the adsorption process on CdSe-MSA
494 nanocrystals. This entropy decreased until all the adsorption sites of CdSe-MSA nanocrystals
495 were fully occupied. The adsorption temperature reduced the configurational entropy.

496 For the case of Gibbs free enthalpy, $\Delta G_a < 0$ indicating that the adsorption of MB molecules on
497 CdSe-MSA nanocrystals was a thermodynamic spontaneous process. G_a decreased with the
498 MB concentration and solution temperature thus confirming that the adsorption feasibility of
499 MB on CdSe-MSA nanocrystals was affected by the thermal agitation effect. Finally, Figure
500 10 shows that all calculated values of the adsorption enthalpy were negative, which confirmed
501 the thermodynamic nature of an exothermic process (Sghaier et al. 2021). The adsorption
502 enthalpy increased as a function of the solution temperature where this behavior could be due

to increment of the thermal collisions produced by the MB adsorption on the surface of CdSe-MSA nanocrystals. The adsorption enthalpy values (H_a) were lower than 40 kJ/mol. As stated, the hydrogen bond could be the main interaction during MB adsorption.

3.3. Photocatalytic degradation of MB dye using solar and UV irradiations

As stated, the photocatalytic activity of CdSe-MSA nanocrystals was evaluated in MB degradation using a contact time of 10 min, 30 mL of solution at pH 7 and 298 K. These photocatalytic degradation studies were performed using visible light and sunlight. It is important to recall that the CdSe-MSA nanocrystals showed an adsorption capacity up to 23.9 mg/g within 10 min of contact time to reach the adsorption-desorption equilibrium phase. Figure 11 displays the absorption spectra of MB without nanocatalyst versus time under visible-light irradiation. The blank test showed a slight dye degradation of 20% after 2 h of irradiation thus confirming that the removal of this organic molecule by direct photolysis was not effective. Note that only a very small decrement of dye concentration was observed when the solution was exposed to sunlight under the same conditions but in the absence of nanocatalyst. Therefore, there was no significant dye degradation by photolysis during the whole test period.

Figures 12 and 13 report the evolution of the absorption spectra and MB photodegradation versus time under visible light with the CdSe-MSA nanocatalysts. As soon as the solution was exposed to visible light with the presence of nanocatalyst, the color of MB dye became faint and the maximum peak at 664 nm observed in the absorption spectra decreased quickly with respect to the irradiation time. MB concentration in the solution reached to its half after only 60 min (i.e., the half-life degradation time). The degradation efficiencies for CdSe-MSA nanocrystals were 60% after 10 min and the degradation rate increased rapidly up to 97% after 120 min. According to different studies (Sui Abideen and Teng 2018; Gómez-Avilés et al. 2019), the impact of the initial concentration on the photocatalytic photodegradation rate of organic compounds can be described by a pseudo-first-order kinetic. Figure 14 shows the linear plots of $\ln(C/C_0)$ versus time for the MB photodegradation with CdSe-MSA nanocrystals under visible light after 120 min. Results of data fitting ($R^2 = 0.97$) confirmed that this photodegradation followed a pseudo-first-order kinetics. The apparent photodegradation rate (k_{app}) was calculated from the slope of $\ln(C_0/C)$ versus t and was 0.01 min⁻¹.

Herein, it is important to remark that the solar photocatalytic treatment is an attractive method for the wastewater depollution because it is an effective, simple and economical system using renewable energy (Belver et al. 2020; Borges et al. 2016). Therefore, the photodegradation experiment with sun light was similar to that performed under UV irradiation. When the adsorption equilibrium was reached, the dye solution was submitted directly under solar illumination on a sunny day between 11am and 3pm. Figures 15 and 16 report the evolution of the absorption spectra and MB photodegradation versus time under visible light with the CdSe-MSA nanocatalyst. MB spectrum showed that the main absorption band responsible for the blue color disappeared completely after 240 min with an almost total degradation rate of 99%. This degradation efficiency was almost five times greater than that obtained in the case of blank tests. The apparent degradation rate constant was illustrated, see Figure 17.

Note that sunlight required 240 min to reach 99% MB photodegradation, while UV irradiation required 120 min to obtain a 97% MB photodegradation, see Figure 18. Under sunlight irradiation, this nanocatalyst absorbed the totality of the solar spectrum in the visible range because of its gap energy, which allowed their activation only with the available visible irradiation thus representing nearly 40% of the solar resource (400 W/m). In contrast, UV radiation represented only 5% (50 W/m²) of the total available solar flux received at the surface of the earth in the most favorable sunlight conditions (Kopp and Lean 2011). This high efficiency may be due to the high absorption of nanocrystals in the visible range in addition to their specific surface area and crystallinity, which contributed to the availability of adsorption sites (Dake et al. 2020). The band gap of CdSe-MSA nanocrystals favored the absorption of visible light. These results showed that these nanocrystals could be promising candidates for photocatalytic applications under solar light.

The processes involved in the photocatalytic degradation of this organic dye can be understood as follows. The electrons were excited by visible light irradiation and generation of hole (h⁺) in the valence band to conduction band, see Equation (27). Both electrons and h⁺ transferred to the crystals surface and reacted with molecular oxygen (O₂) and H₂O molecules to produce free hydroxyl radical (•OH) and superoxide radical anion (•O₂⁻), Equations (29)-(30). These free radicals worked as strong oxidizing agent as well as active site for photocatalytic degradation of organic pollutants. These phenomena can be summarized in the following equations (Ramki et al. 2020):

The scheme for MB removal by the synergistic effect of adsorption and photodegradation is presented in Figure 19. As indicated, the highly reactive hydroxyl radicals (*OH) and superoxide radicals (${}^*O_2^-$) reacted with MB dye adsorbed on CdSe nanocrystals and led to its degradation/decoloration resulting in its colorless form by converting it into CO_2 , H_2O and other degradation products, see Equation (31). The dye degradation rate depended on the morphology and crystallinity of the photocatalysts. Nanomaterials with large surface area and high crystallinity can increase the number of active sites and promote the separation efficiency of the electron-hole pairs in the photocatalytic reactions (Dake et al. 2020; Kuriakose et al. 2014). The emission of blue-green (400–550 nm) indicates the density of selenium vacancies (S_e) and interstitial of cadmium (I_{cd}) to tune the luminescent properties at visible light emission region. Consequently, the ions defects of crystal lattice can absorb light at visible region to create electron-hole pairs responsible for photodegradation process of dyes in nanocrystals catalyst active surface. This interstitial defect can introduce different energy levels within the forbidden gap of CdSe-MSA catalyst. The excited electrons trapped and slowed down the recombination by vacancies and interstitial of which energy levels can involve in the valence and conduction bands of CdSe-MSA, acting as trap centers of the photogenerated charges. The trap of charge carriers can decrease the recombination rate of electron-hole pairs and increase the lifetime of charge carriers. Consequently, the photocatalytic activity of nanocrystals was increased by these defects, which could facilitate the transfer of the photogenerated carriers by trapping the excited electrons and restrain the electron-hole recombination. During this process, the photogenerated charges participated in the production of active hydroxyl radicals and superoxide anion radicals and, consequently, these radicals could convert MB into less harmful degraded products.

4. Conclusions

CdSe-MSA nanocrystals were successfully synthesized via the colloidal method and the contribution of adsorption and photocatalytic of MB dye molecule from aqueous solution was

investigated. Kinetics and isotherms were quantified to determine the impact of adsorption of MB on tested nanocrystals. Results showed spontaneous exothermic adsorption thus obtaining adsorption capacities up to 23.9 mg/g. Statistical physics calculations were used to analyze the steric and energetic parameters associated to the MB adsorption on the nanocrystals surface. It was found that this adsorption process was governed mainly by electrostatic interactions and hydrogen bonding where a non-parallel adsorption geometry occurred. The adsorption capacity of CdSe-MSA nanocrystals favored the direct interaction of photo-generated electrons with adsorbed MB molecules and, hence, facilitated a fast photodegradation. CdSe-MSA nanocrystals showed a remarkable UV-light photocatalytic activity for MB dye with a conversion rate of 80% in 60 min. Results of this study indicated that these semiconductor nanocrystals can be used as an effective material for dye removal from wastewaters with effective photodegradation activity under sunlight. This approach could be a sustainable and cost-effective treatment system for the remediation of water polluted by organic compounds like dye.

Author's contribution:

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Sabri Ouni: Writing - original draft, Visualization, Conceptualization, Methodology

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Mohamed Haouari: Writing - Reviewing and Editing, Visualization, Supervision

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851

Figures

Figure 1

a: XRD patterns of CdSe-MSA nanocrystals b: Uniform deformation model plot for CdSe-MSA nanocrystals

Figure 2

(a) TEM and HRTEM images (the lattice fringes with interplanar spacing of 3.5 Å are clearly seen) and (b) histogram of size distribution of CdSe-MSA nanocrystals

Figure 3

FT-IR spectrum of CdSe-MSA nanocrystals

Figure 4

Raman spectrum of CdSe-MSA nanocrystals

Figure 5

(a) UV-vis and PL spectrum and (b) Tauc plot of CdSe-MSA nanocrystals

Figure 6

PL spectrum of CdSe-MSA nanocrystals

Figure 7

Kinetics for the MB adsorption on CdSe-MSA nanocrystals and its modeling with the pseudo-first-order equation.

Figure 8

Adsorption isotherm of MB dye on CdSe-MSA nanocrystals at pH = 7 and 300 K.

Figure 9

Adsorption isotherms of MB dye on CdSe-MSA nanocrystals at 298-318 K and pH = 7 and their statistical physics modeling

a)

b)

c)

Figure 10

a) Configurational entropy, b) Gibbs free energy and c) adsorption enthalpy as function of equilibrium concentration of MB onto CdSe-MSA nanocrystals

Figure 11

The absorption spectrum of MB photodegradation without nanocrystals in visible-light irradiation

Figure 12

The absorption spectra of MB photodegradation in the presence of CdSe-MSA nanocrystals under UV light irradiation

Figure 13

Photodegradation efficiency of MB dye by CdSe-MSA nanocrystals under UV light irradiation

Figure 14

Linear plot of $\ln(C_0/C)$ versus time of MB degradation in the presence of CdSe-MSA nanocrystals under UV light irradiation

Figure 15

The absorption spectra of MB degradation in the presence of CdSe-MSA nanocrystals under solar light irradiation.

Figure 16

Photodegradation efficiency of MB dye by CdSe-MSA nanocrystals under solar light irradiation.

Figure 17

Linear plot of $\ln(C_0/C)$ versus time of MB degradation in the presence of CdSe-MSA nanocrystals under solar light irradiation.

Figure 18

Apparent first order rate constant of MB degradation in the presence of CdSe-MSA nanocrystals under UV and solar light irradiations

Figure 19

Proposal of degradation mechanism of MB dye using CdSe-MSA nanocrystals under sunlight irradiation