ORIGINAL ARTICLE

Synthesis and characterization of CdS nanoparticle anchored Silica-Titania mixed Oxide mesoporous particles: Efficient photocatalyst for discoloration of textile effluent

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Abstract
An efficient photocatalyst consisting of CdS nanoparticle dispersed mesoporous silica-titania was prepared using amphiphilic triblock copolymer P123 as template and silica-titania sol–gel precursors. The CdS nanoparticle was incorporated into silica-titania mesoporous nanosturctures by post impregnation method. The synthesized catalyst has been characterized by FTIR, TEM, SEM, and EDAX analysis. The CdS nanoparticles incorporated silica-titania mesoporous particles exhibited an enhanced light harvesting, large surface area and excellent photocatalytic activity. Photocatalytic degradation experiments on methyleneblue solution at different pH of the medium revealed that, the catalyst ST0.5CdS0.2 is more effective in basic medium with a degradation efficiency of 98%. In addition, the catalyst is also tested for dye degradation against a raw textile dye effluent containing multiple dye molecules, and their results indicated that the raw effluent can be decolorized within 90min using ST0.5CdS0.2 catalyst.

Keywords: *Cadmium Sulfide; Mesoporous Material; Methylene Blue; Photocatalyst; Photodegradation; Silica-Titania; Textile Effluent.*

INTRODUCTION

The photocatalytic oxidation of organic pollutants in water is an advanced oxidation process has been proved to be an effective technique for environmental remediation [1-4]. Among a wide spectrum of semiconductors photocatalyst, TiO_2 has attracted significant attention over the past decades due to its unique physicochemical properties, such as stability, less toxic, insolubility, and high photoactivity, based on which widespread applications were accomplished [5-7]. The photocatalytic efficiency of titania is hampered by two main drawbacks which are the rapid recombination of photogenerated electron and hole pairs and wide band gap energy [8-9]. To overcome this limitation, doping transition elements / metal into titanium oxide improves its optical activity by narrowing the band gap energy level, aiding the absorption to visible region and prevent the electron–hole recombination [10-12]. Another alternative approach is to disperse TiO_2 into a nonreactive porous material such as silica, which will improve thermal, mechanical stability and photocatalytic activity by inhibiting crystal growth in addition to the formation of Ti–O–Si [13-16]. The physico-chemical properties of hybrid silica-titania are distinctly different from those of the

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individual components; thus demonstrating great promise for a range of potential applications [17-24]. In the present work, the above said approaches have been employed to harvest better efficiency from titania by synthesising intermixed mesoporous silica-titania with cadmium sulphide nanoparticle inclusion. Costa *et al.* studied the effect of CdS on the crystallinity of silica and titania composite nanoparticles [25], However, the present work is deals with preparation of ordered mesoporous structure using triblock copolymer (P123) self assembled micelles as structure directing agent and sol-gel method. In addition, the present research is focused on photocatalytic dye degradation on textile effluent.

Cadmium sulphide (CdS) has been one of the most widely exploited nanocrystalline semiconductor QDs in photosensitizer and photoelectrochemical cells due to its suitable band gap (2.4 eV) coupled with excellent optical properties [26-30]. CdS nanoparticle is also studied by precipitation method [31]. Depositing cadmium sulfide on titanium dioxide nanoparticles provides a composite nanosystem that is simultaneously sensitive to visible light and highly chemically stable. Core-shell nanoparticles having CdS core and titania as shell are proved to be especially promising for oxidative degradation of organic pollutants [32-34]. In the present research, it has been planned to harvest the synergistic properties resulting from the combination of CdS and titania hybrid system which can possibly be integrated by introducing into mesoporous siliceous framework. Further, we anticipate that the high specific surface area of mesoporous silica will protect cadmium sulfide from photocorrosion and will improve the adsorption properties of the photocatalyst. Herein, we report on the preparation and enhanced photocatalytic performance of well-ordered mesoporous particles consisting silica and titania with CdS nanocrystals. The synthesized photocatalysts were studied for the degradation of methylene blue as a test for the oxidation of organic pollutants in water as well as dye removal in a textile dye effluent.

EXPERIMENTAL SECTION
Chemicals and Reagents
Pluronic P123 (ethylene oxide (EO), Propylene oxide (PO)), triblock co-polymer composition as $EO_{20}PO_{70}EO_{20}$ was purchased from Sigma-Aldrich. The number average molecular weight of P123 is about 5300.Tetraethylorthosilicate (TEOS), Titanium tetraisopropoxide (TTIP), Methylene blue and Cadmium acetate were purchased from Aldrich. Analytical grade Hydrochloric acid was purchased from SRL, India. Doubled distilled water was used in all experiments. An untreated effluent is obtained from a textile dying industry situated in Tamil Nadu, India and its picture is shown in Fig. 1.

Preparation of Mesoporous silica-titania
Mesoporous silica-titania was prepared according to literature procedure, following the synthesis of SBA15 [17]. Typically, the mesoporous silica-titania with the mass ratio Ti/Si=0.1 was prepared as follows; 2.0g of pluronic P123 was dissolved in 60g of 2M HCl and 15g of distilled water. This mixture was stirred at room temperature. Then 3.1mL of TEOS and 1.3mL of TTIP was added. The mixture was kept under stirring at 313K for 24h and then heated at 373K temperature for another 24h under static conditions for ageing.
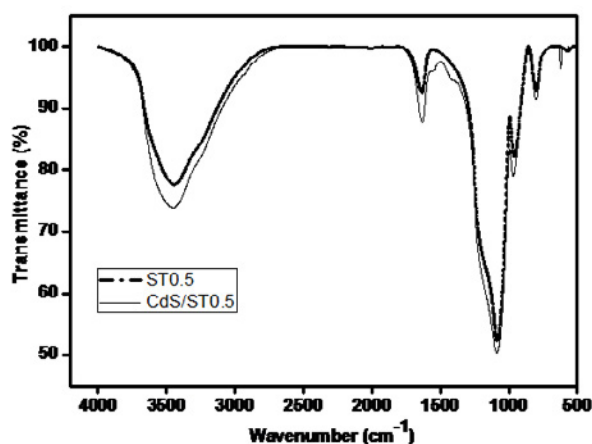

Fig. 1. FTIR spectrum of mesoporous silica-titania (ST0.5) and CdS embedded silica-titania(CdS/ST0.5).

The precipitate was filtered washed with water and air dried at room temperature. The resulting white powder was calcined at 500 °C for 5hrs in air. Mesoporous silica-titania with varying Ti/Si mass ratio was designated as TS0.1, TS0.3 and TS0.5 for Ti/Si=0.1, Ti/Si=0.3 and Ti/Si =0.5 respectively.

Deposition of CdS nanoparticles

Mesoporous silica-titania was dispersed in DD water and 5 w% of cadmium acetate dihydrate (Cd(OAC)$_2$.2H$_2$O) and equivalent weight sodium sulfide (Na$_2$S) was added and stirred for 30min. The light yellow precipitate was filtered washed with water air dried at room temperature. Mesoporous silica-titania having Ti/Si ratio is 0.5 with varying CdS concentration deposition was designated as ST0.5CdS 0.1, ST0.5CdS0.2 and ST0.5CdS0.5 for the CdS content 0.1 wt%, 0.2 wt% and 0.5 wt% respectively.

Characterization

Fourier Transform-Infrared spectra were recorded on a JASCO spectrometer with KBr as solvent. The absorption of mesoporous silica-titania with cadmium sulfide nanoparticle was monitored using a Shimadzu UV-2500 spectrophotometer. Wide-angle X-ray spectra were obtained using X-ray diffractometer with powder sample (with Cu Kα radiation) for the ground powder. The spectral window ranged from 2θ = 10 to 70. JEOL JEM-3010 analytical transmission electron microscope operating at 300 kV with a measured point-to-point resolution of 0.23 nm were used to record TEM images.

Photocatalytic Studies

Photocatalytic activity of the as-prepared nanostructured particles for the environmental application was evaluated by examining the photo degradation of methylene blue in water under UV-irradiation. The photocatalytic experiments were carried out as follows. 100mg of mesoporous nanostructures was dispersed in 100mL of 50 ppm aqueous solution of methylene blue and then irradiated with UV light of λ = 254 nm for a specified length of time. The effect of pH on the photocatalytic degradation reaction has been studied at representative acidic as well as basic pH such as 3 and 10.

RESULTS AND DISCUSSION

The mesoporous silica-titania mixed oxide particles having varying Ti/Si mass ratio such as Ti/Si = 0.1, 0.3 and 0.5 were synthesised and characterized by IR, XRD, TEM and EDAX analysis. The FTIR spectra of mesoporous silica-titania sol-gel precursors with atomic mass ratio Ti/Si = 0.5 is presented in Fig. 1. The characteristic bands of Si-O-Si vibrations dominate in the IR spectra. The ones around 1083 cm^{-1} and 793 cm^{-1} are attributed to the asymmetric and symmetric Si-O-Si stretching modes, respectively. The peak at 3640 cm^{-1} is due to the stretching vibration of OH group present at the surface of nanoparticle. The band around 1641 cm^{-1} is assigned to the Ti-O-Ti stretching mode, the absorption broad at 968 cm^{-1} region is related to Ti-O-Si bonds [17-18]. The CdS dispersion onto silica-titania does not change the pattern of IR absorption, however, there is slight increase in the intensity of absorption at 1641 cm^{-1} and a new peak is observed at 617cm^{-1} may be due to the presence of CdS nanoparticles.

Fig. 2a shows the low-angle XRD patterns of the mesoporous silica and the silica-titania composite. Diffraction pattern is for typical highly ordered
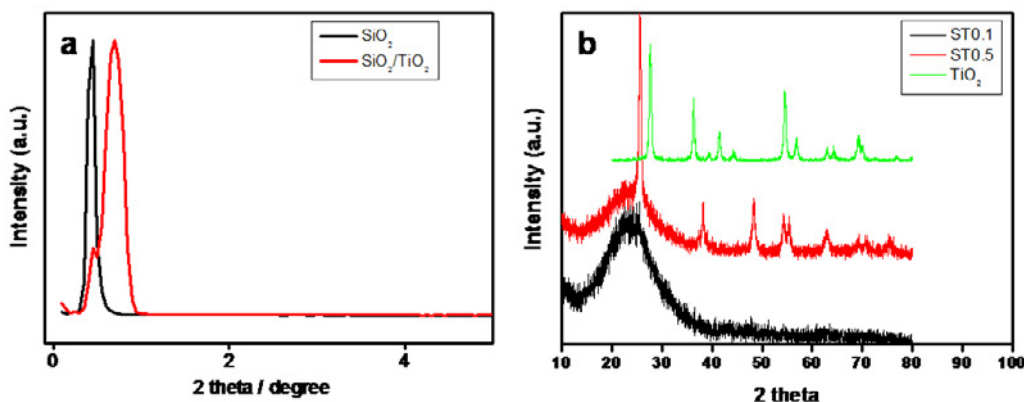

Fig. 2. XRD patterns of mesoporous silica-titania with CdS a) low angle and b) wide angle XRD.

mesoporous silica with a two-dimensional hexagonal symmetry (space group p6mm). In comparison to the SiO$_2$, the silica-titania show low angle XRD patterns similar to that of silica. Obviously, the hexagonal close packed ordered mesoporous structures was retained even after hybridizing with TiO$_2$ networks and calcination process, indicating that the introduction of TiO$_2$ into SiO$_2$ does not collapse the mesoscopic order. It is also noted that low-angle XRD peak of the mesoporous silica-titania composite system shift to high angles, when compared to the SiO$_2$. This may be due to the contraction of the silica frameworks by the presence of TiO$_2$ networks. Wide angle X-ray diffraction patterns of mesoporous silica-titania and titania nanoparticles is shown in Fig. 2b. The XRD peak positions of processed powders were well matched to the pure anatase phase of TiO$_2$ (JCPDS No.: 21-1272). Thus, two successive processes occurred simultaneously during aging process, i.e. hydrolysis-condensation of TTIP followed by crystallization to the more thermodynamically favoured anatase phase. The diffraction lines of titania is clearly seen in the higher concentration of Titania in silica (ST0.5). The XRD peaks corresponding to (110) and (101) planes indicate the high crystallinity. It is also noted that both lines (101) and (002) were significantly narrowed relative to the line (110), which indicate a preferential orientation of the primary particles.

Fig. 3a and 3b presents the HRTEM images of calcinated ST0.1 and ST0.3 in which a well ordered channels are illustrated and are characteristic of mesoporous materials. Fig. 3c depicts the HRTEM of ST0.5 where the highly ordered pore structure of SBA15 is still preserved. The mesopores for all the mixed oxide systems are regularly ordered is estimated to about 10 nm. The TEM images also show that both silica and titania networks are intermixed without showing any separate phase of silica or titania. The chemical identity of the mesoporous nanoparticles was also confirmed by EDS data, where the presence of Silicon, Titanium and Oxygen is evident (Fig. 3d).

Fig. 4a and 4b presents the HRSEM of CdS deposited ST0.5, the worm like structure indicates SBA15 type crystallite structure is preserved in ST0.5. The addition of CdS does not altered the structure of mesoporous silica-titania and very fine particle of CdS also seen in the image. From Fig. 4c the chemical identity of the mesoporous nanoparticle ST0.5CdS0.2 was confirmed, the EDAX data shows the presence of Silicon, Titanium, Cadmium, Oxygen and Sulphur. The Fig. 4d presents the bar diagram of elemental composition as calculate from Fig. 3c, clearly
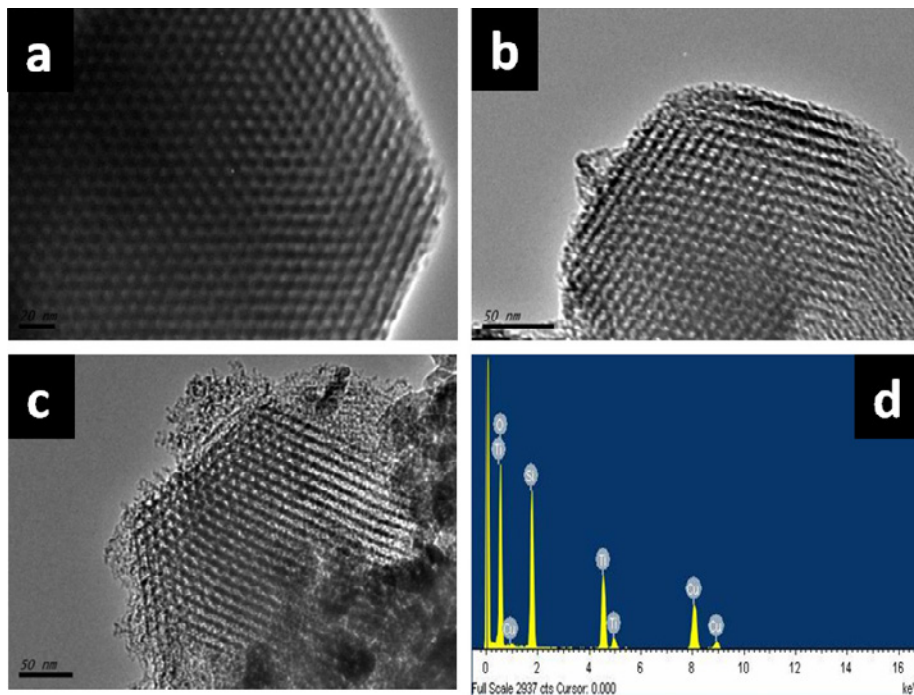

Fig. 3. TEM image of mesoporous silica-titania a) Ti/Si = 0.1, b) Ti/Si = 0.3 (c) Ti/Si = 0.5 (d) EDAX of (c).

dictates the composition of elements present in mesoporous ST0.5CdS0.2.

Photocatalytic studies

We evaluated the potential value of this system for photocatalytic applications and compared the catalytic efficiency of the mesoporous silica-titania with varying Ti/Si mass ratio that in terms of the degradation of methylene blue under UV light, the results of which are displayed in Fig. 5. It has been observed from Fig. 5a that the degradation of methylene blue on a mesoporous silica-titania was significantly enhanced by the increase in Ti/Si mass ratio. The mesoporous ST 0.5 shows superior photocatalytic activity towards the degradation of methylene blue dye in aqueous solution than ST 0.3 and ST 0.1.

Photocatalytic degradation of Silica-Titania and CdS-Silica-Titania

To enhance the photoactivity, we introduced CdS nanoparticles into mesoporous silica-titania by post synthetic incorporation method. Mesoporous silica-titania with Ti/Si mass ratio 0.5 (ST0.5) alone
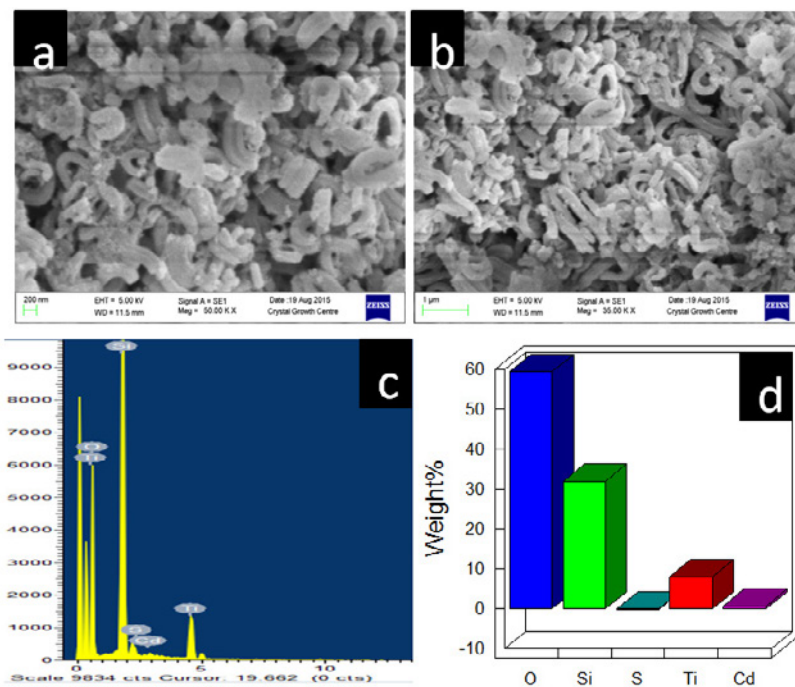

Fig. 4. (a) & (b) HRSEM image of mesoporous ST0.5CdS0.2 (c) EDAX of mesoporous ST0.5CdS0.2 and (d) bar diagram of elemental composition calculated from (c).
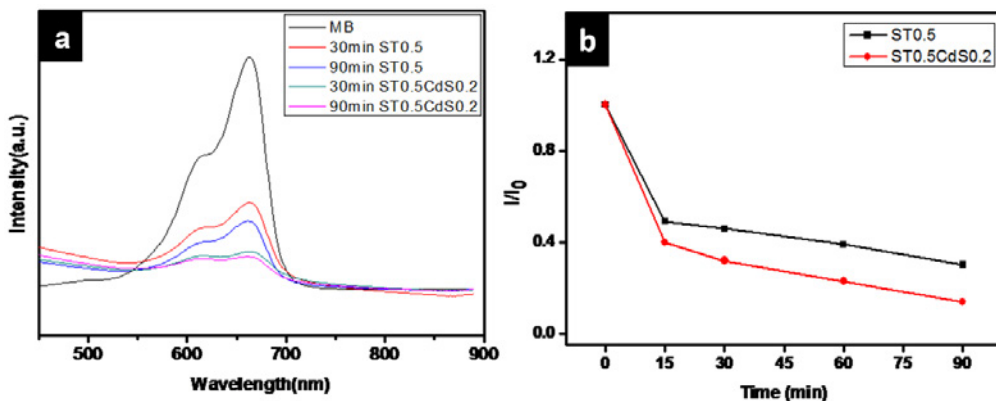

Fig. 5. photocatalytic degradation of methylene blue by silica-titania and silica-titania -CdS UV-vis absorption of methylene blue at various photo-irradiation duration. b) I/I_o Vs time curve for the photocatalytic degradation of methylene blue by ST0.5 and ST0.5CdS0.2.

was used for this study. The 0.1 and 0.2 wt% CdS deposited mesoporous ST0.5 and studied the photocatalytic activity. The photodegradation of methylene blue by mesoporous silica-titania-CdS is presented in Fig. 5a, the results demonstrates that the 0.2 wt% CdS deposited mesoporous silica-titania shows enhanced photoactivity. The ratio of the intensity of the absorbance peak at 664 nm, before and after irradiation (I/I_0), was correlated with time, as shown in Fig. 5b. The Fig. 5b clearly demonstrates that the CdS incorporation into the mesoporous silica-titania significantly increases the photocatalytic activity. Among the photocatalyst prepared the ST0.5CdS0.2 showed higher photocatalytic activity as seen from Fig. 5b that the quantity of methylene is decreased rapidly with time.

For comparison, mesoporous silica-titania with more amount of CdS (for instance, CdS 0.5 wt%) shows less photocatalytic activity, reflecting the fact that the enhanced photoactivity is not a consequence of simple superposing effect of the two components, but is due to the coupling between CdS and TiO_2. In addition the higher loading of CdS may block the mesoporous and thereby reduce surface area. To understand the change in surface area the CdS loaded ST0.5 was subjected to BET analysis. From the BET isotherm analysis (Fig. 6), it was observed that the CdS loaded ST0.5 showed surface area of 500.6540 m²/g, 512.8910 m²/g, 472.2856 m²/g for ST0.5CdS0.1, ST0.5CdS0.2, ST0.5CdS0.5 respectively, indicating a decrease in surface area with higher loading of CdS nanoparticle, which in turn reveals that the optimum quantity of CdS to be deposited on mesoporous silica-titania is 0.2 wt%.

The plausible mechanism for the photocatalytic activity can be understood through the energy band diagram of CdS and TiO_2 shown in Fig. 7. The transfer of the photo-excited electrons from the surface of CdS to TiO_2 occurs due to the small band gap of CdS and its higher conduction band potential compared to that of TiO_2. Thus, the recombination between photogenerated electrons
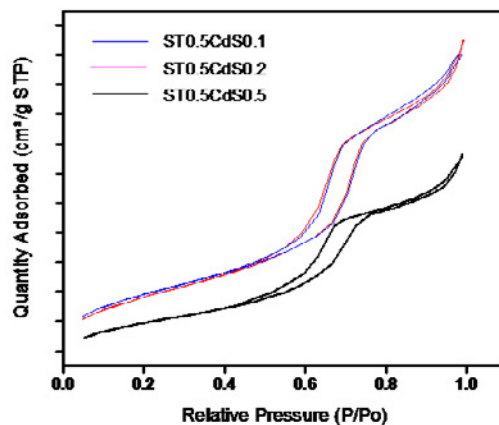

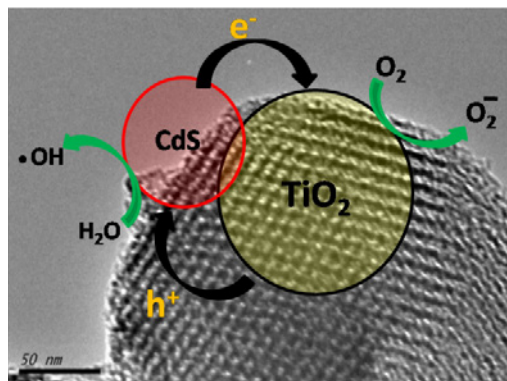Fig. 6. N$_2$ adsorption desorption isotherm of mesoporous silica-titania -CdS systems.

Fig. 7. Mechanism for the photocatalytic activity of CdS and Silica-TiO$_2$ catalyst.

and holes is subsequently reduced, allowing more opportunities for electrons to participate in the reduction reaction to form oxygen radicals, which are potential oxidants capable of effectively decomposing MB. The holes created by the UV light irradiation on TiO_2 can also migrate to the CdS surface and participate in the oxidation reaction to produce hydroxyl radicals, which simultaneously involve in the decomposition of organic substances.

Effect of pH

The pH of the solution has influential effect on the photocatalytic reaction particularly on the degradation rate. The photocatalytic degradation in different pH for specified period of UV irradiation time was carried out and the results are given in Fig. 8. From the figure the highest degradation was obtained in basic solution, indicating the catalyst ST0.5-CdS0.2 is more effective in basic

medium. The point of zero charge for titania is around 6 and for CdS nanoparticle it is 7.5, above this pH range the surface is negatively charged [35]. The presence of large quantities of OH^- ions on the mesoporous particle surface as well as in the reaction medium favors the formation of OH^- radical, which is reported as a major oxidizing species responsible for degradation process at basic pH [36-39]. In addition, at acidic pH, the H^+ ions react with the surface of the adsorbents, making it positively charged. At alkaline pH OH^- ions in solution interact with the adsorbents and making it as negatively charged. Since the methylene blue is positively charged it readily adsorb on the catalyst surface at basic pH.

Photocatalytic dye removal from textile effluent.

The activity of the catalyst towards untreated textile effluent was tested. The effluent was obtained from a dyeing industry situated in
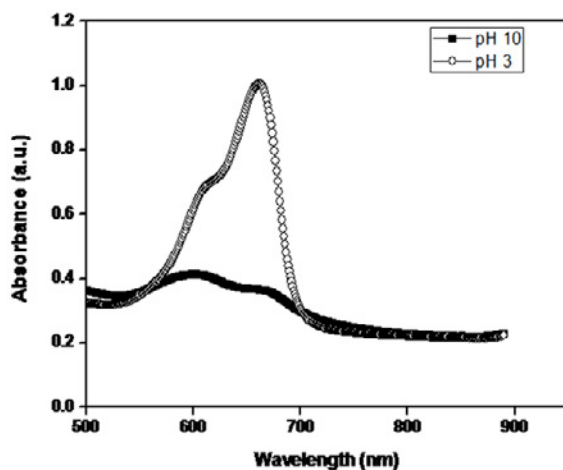

Fig. 8. Photocatalytic degradation of MB by ST0.5CdS0.2 at different pH after irradiating for 120min in UV source having a wavelength of 254nm.
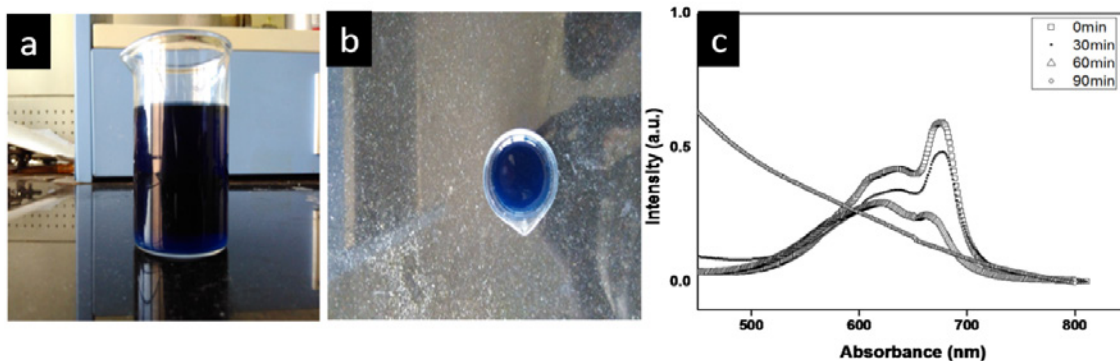

Fig. 9. (a) & (b) Photograph of textile dye effluent as received from industry (c) Photocatalytic degradation of textile dye effluent using ST0.5CdS0.2 for 90min in UV source having a wavelength of 254nm.

Tamil Nadu, India. The obtained effluent is dark blue in colour, shown in Fig. 9a and 9b. The UV-Vis absorption indicates the effluent contains mixtures of dyes with methylene blue may be in major proportion. The photo degradation studies indicated that the raw effluent can be decolorized within 90min using ST0.5CdS0.2 (Fig. 9c)

CONCLUSION

This study on the deposition of CdS nanoparticle on mesoporous silica-titania revealed an ordered mesoporous structure of silica-titania and both silica and titania networks are intermixed without showing any separate phase of silica or titania. The photocatalytic degradation studies using methylene blue dye show that the mesoporous ST0.5 has enhanced photocatalytic activity than ST0.3 and ST0.1. The photodegradation of MB with mesoporous ST0.5CdS demonstrated that the 0.2 wt% CdS deposited mesoporous ST0.5 shows enhanced photoactivity among CdS deposited silica-titania catalysts. The catalytic systems with more than 0.2 wt% showed less photocatalytic activity. This study recommends that incorporation of CdS into mesoporous silica-titania should be as low as 0.2wt%. Photocatalytic degradation experiments at different pH of the medium revealed that, the highest degradation was obtained in basic solution, the catalyst ST0.5CdS0.2 is more effective in basic medium. Further, the real-time textile dye effluent can very well be decolorized by the ST0.5CdS0.2 within a short duration.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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