



CdS-sensitized TiO₂ in phenazopyridine photo-degradation: Catalyst efficiency, stability and feasibility assessment

Ahed H. Zyoud^a, Nidal Zaatari^a, Iyad Saadeddin^a, Cheknane Ali^b, DaeHoon Park^c,
Guy Campet^c, Hikmat S. Hilal^{a,*}

^a Department of Chemistry, An-Najah N. University, PO Box 7, Nablus, West Bank, Palestine

^b Laboratoire d'Etude et Développement des matériaux Diélectriques et Semiconducteurs, Université Amar Telidji de Laghouat, Laghouat, Algeria

^c Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB), 87 Avenue du Dr. A Schweitzer, 33608 Pessac, France

ARTICLE INFO

Article history:

Received 3 March 2009

Received in revised form 17 August 2009

Accepted 19 August 2009

Available online 25 August 2009

Keywords:

Sand

TiO₂

CdS

Sensitization

Phenazopyridine

Photo-degradation

ABSTRACT

Mineralization of phenazopyridine, **1**, in water, under solar-simulator radiation was efficiently achieved using nanoparticle CdS-sensitized rutile TiO₂, TiO₂/CdS, **2**, as photo-catalysts. Despite that, **2** showed two main drawbacks. Firstly, the system was difficult to recover by simple filtration, and demanded centrifugation. Secondly, the sensitizer CdS showed relatively high tendency to leach out hazardous Cd²⁺ ions under photo-degradation reaction conditions. In an attempt to solve out such difficulties, **2** was supported onto sand surface. The sand/TiO₂/CdS system, **3**, was easier to recover but showed slightly lower catalytic activity compared to **2**. On the other hand, the support failed to prevent leaching of Cd²⁺. This indicates limited future applicability of CdS-sensitized TiO₂ photo-catalyst systems, in solar-based water purification strategies, unless leaching out tendency is completely prevented.

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1. Introduction

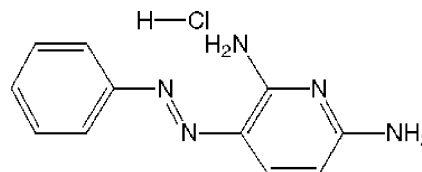
TiO₂ is an efficient catalyst for photo-degradation of organic contaminants in water using UV region. High oxidative power, high stability, low cost and environmental friendliness make TiO₂ a perfect photo-degradation catalyst for a wide range of contaminants [1–3]. However, its wide band gap (~3.0 eV) and its need for UV radiation limit its use to only small scale purifications. The solar energy cannot be efficiently used for such processes, because only a small fraction of UV reaches earth surface. Moreover, TiO₂ surface shows low absorptivity towards UV [4]. These factors inhibit using naked TiO₂ in solar-driven water purification at large scale.

To enable TiO₂ effectively function under visible solar light, dye sensitizers were suggested for solar cells [5] and water purification. CdS is widely described as possible sensitizer in water purification. TiO₂/CdS, **2**, was earlier studied from different angles, such as synthetic methods, characterization, photo-catalytic efficiency and kinetics [6–11]. Little effort is being made to assess feasibility of **2** in water purification and eliminate its hazards, despite the ten-

gency of CdS to degrade under light as known in solar cell research [12,13].

In a recent communication we reported on the activity of TiO₂/CdS systems in photo-degradation of methyl orange using UV and visible regions [14]. In the present work, we investigate photo-degradation of the medically active compound phenazopyridine, **1**, using solar simulator radiation. The major theme is to assess the future feasibility of CdS sensitizer for TiO₂ at large-scale photo-degradation processes, in terms of efficiency, recovery and environmental friendliness.

Photo-degradation of compound **1** has not been reported earlier. It was intentionally chosen here, due to its expected ease to degradation like other medically active compounds. Should **2** fail to survive under degradation conditions of **1**, it would not resist forcing degradation conditions of other more stable contaminants, and its hazard difficulties would appear.



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* Corresponding author. Tel.: +970 9 2945507; fax: +970 9 2387982.
E-mail address: hikmathilal@yahoo.com (H.S. Hilal).

2. Experimental

2.1. Materials

Commercial Rutile TiO₂ powder (less than 500 nm in diameter) was purchased from Aldrich. Rutile TiO₂ was intentionally used here due to its known lower catalytic activity compared to Anatase TiO₂ [15–17]. Thus it is desirable to enhance the activity of the less active Rutile system. The fact that Rutile is the cheapest form of TiO₂, gives further justification for choosing it here. Thiourea, CdCl₂ and organic solvents (analytical grade) were all purchased from either Aldrich–Sigma Co. or Frutarom Co. Contaminant **1** was kindly donated by Birzeit–Palestine Pharmaceutical Company in a pure form. The compound is widely used in urinary tract treatment and other medical prescriptions.

Preparation of system **2** was performed by deposition of CdS particles onto commercial TiO₂ powders as described in literature [6,14,17–22]. Supporting **2** onto insoluble sand particles to yield sand/TiO₂/CdS, **3**, was performed via two different approaches, as described in a preceding report [14]. In one technique, **2** was allowed to settle onto pre-cleaned sand particles by continuous mixing of sand with **2** in aqueous suspension. The alternative two-step technique, which was followed unless otherwise mentioned, involved chemical deposition of TiO₂ onto pre-cleaned sand particles. Based on literature, the deposited TiO₂ particles are of Rutile type. Calcination at 350 °C does not convert Rutile into the less stable Anatase [23–26]. Deposition of CdS onto sand/TiO₂ particles was then performed as described in literature [6,14,18–22]. Values TiO₂ and CdS uptakes in **3** were 5.0% and 0.41% by mass, respectively. For re-use experiments, special preparations were conducted with higher CdS uptake (1.9%). Details of preparation and annealing (at 350 °C for 3 h) were described earlier [14]. In this work, electronic absorption spectra, photoluminescence (PL) spectra, XRD and SEM techniques were used to shed more light on the nature of the **2**.

2.2. Equipment

Contaminant **1** concentrations were spectrophotometrically measured on a Shimadzu UV-1601 spectrophotometer, using the maximum absorption at 430 nm. Pre-constructed calibration curves were used. To analyze dissolved Cd²⁺ ions, anodic stripping differential pulse polarography (ADPP) was conducted using an MDE150 dropping mercury electrode on a PC-controlled POL150 Polarograph. The hanging mercury drop electrode (HMDE) method was followed. The analysis parameters were: initial potential –700 mV, final potential –400 mV, purging time 30 s, deposition time 20 s, scan rate 20 mV/s, pulse height 25 mV.

A PerkinElmer LS50 luminescence spectrophotometer was used to measure photoluminescence (PL) spectra of **2** particles suspended in ethanol. Solid state absorption spectra were measured for particles of **2** suspended in toluene, using the Shimadzu UV–vis 1601 spectrophotometer described above. Other measurements, performed on films of **2** deposited onto quartz substrates from ether suspensions by solvent evaporation, showed similar results. The PL and absorption spectra for **2** resembled earlier literature [23].

Powder X-ray diffraction (XRD) was recorded on a Philips XRD X'PERT PRO diffractometer with Cu K α ($\lambda = 1.5418 \text{ \AA}$) as a source. The XRD lines were identified by comparing the measured diffraction patterns to JCPDS data cards. Field emission scanning electron microscopic/energy dispersive spectroscopic (FE-SEM/EDS) studies were conducted on a Jeol microscope, model JSM-6700F.

Irradiation of reaction mixture was conducted using a model 45064 – 50 W Xe solar simulator lamp (Leybold Didactic Ltd.) equipped with a housing and a concentration lens. The Xe lamp has a high stability and an intense coverage of wide spectral range, from about 400 to 800 nm, with no much preference [27–33].

2.3. Catalytic experiments

Catalytic experiments were conducted in a magnetically stirred thermostated 100-ml beaker. The beaker out-side walls were covered with aluminum foil to reflect back astray radiations. Aqueous suspensions of known nominal concentrations of contaminant and catalyst were used under air. The pH was controlled by addition of NaOH or HCl dilute (0.05 M) solutions. Constant illumination intensity (0.0212 W/cm²) was achieved by directly exposing the reaction mixture to the Xe lamp that was vertically placed at constant distance from the surface.

Known amounts of water and **1**, together with added acid or base, were placed inside the reaction vessel. The catalyst was then added with continuous stirring in the dark. The reaction mixture was left for a few minutes before measuring the contaminant concentration. This was to check if contaminant loss occurred by adsorption onto solid systems. Reaction time was recorded the moment direct irradiation was started. The reaction progress was followed up by syringing out small aliquots, from the reaction mixture, at different time intervals. Each aliquot was then immediately centrifuged (5000 rounds/min for 5 min) in the dark, and the liquid phase was pipetted for spectral analysis of the remaining contaminant at 430 nm. The aqueous phase was also analyzed for dissolved Cd²⁺ ions, by polarography as described above. The reaction rate was measured based on analyzing remaining contaminant concentration with time. Turnover number (contaminant reacted moles per nominal TiO₂ mole after 60 min) and quantum yield (contaminant reacted molecules per incident photon) were also calculated and used for efficiency comparison. Complete mineralization of organic contaminants into carbon dioxide, and other compounds, under solar simulator light, is assumed based on earlier reports [34]. Disappearance of phenazopyridine was confirmed here by the absence of its 430 nm absorption band after reaction cessation. Complete mineralization was also evident from the absence of any benzene derivatives, in both **2** and **3** catalyst systems. This was confirmed by absence of any absorption bands characteristic for phenyl groups at 200 nm or longer, as observed from absorption spectra for solutions. Literature shows that azo groups of organic dyes, which have similar structure to phenazopyridine, are converted into nitrogen gas [2]. Other nitrogen atoms are commonly converted into nitrate ions and/or ammonium, which is in turn converted into nitrate ion as a final product [2]. Polarographic analysis of remaining reaction mixture indicated conversion of amine groups and hetero-nitrogen atom of phenazopyridine into NO₃⁻.

Reuse experiments were conducted using recovered catalysts **2** or **3** by centrifugation or filtration, respectively, after reaction cessation. The recovered catalyst system was re-used in a similar manner to the fresh catalyst samples, as described above.

3. Results and discussions

3.1. Characterization of **2**

The TiO₂/CdS system was characterized using different techniques. Gravimetric analysis showed that the CdS uptake in **2** was 3.15% by mass. Solid state electronic absorption spectra for annealed and non-annealed TiO₂/CdS are shown in Fig. 1. The annealed TiO₂/CdS showed a band at 540 nm for CdS, compared to the non-annealed counterpart which showed a band at 520 nm. The slight red shift in CdS absorption band, after annealing, is due to slight increase in particle size due to annealing, *vide infra*. Each system showed a strong band starting at 400 nm for the TiO₂ particles. The CdS electronic absorption spectra resembled earlier reports [23] in terms of band positions.

PL spectra measured for annealed and non-annealed **2** are shown in Fig. 2. Fig. 2(a) shows a maximum emission at 570 nm

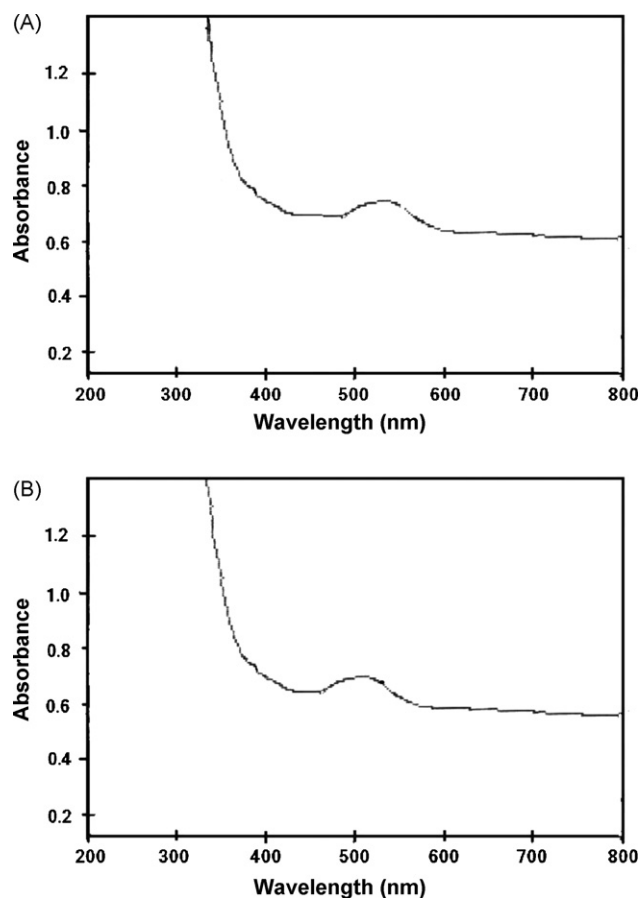


Fig. 1. Solid state electronic absorption spectra measured for TiO_2/CdS particles, dispersed in toluene (a) pre-annealed and (b) non-annealed.

for the pre-annealed system, whereas Fig. 2(b) shows a maximum emission at 540 nm for the non-annealed counterpart. The observed red shift is due to slight increase in particle size by annealing, as discussed below.

The CdS particles in **2** are in the nano-size scale. Fig. 3 shows the SEM micrographs for pre-annealed and non-annealed **2** particles. Each TiO_2 particle is covered with sub-monolayer of CdS particles of comparable sizes. Fig. 3 indicates that the sizes for TiO_2 are in the

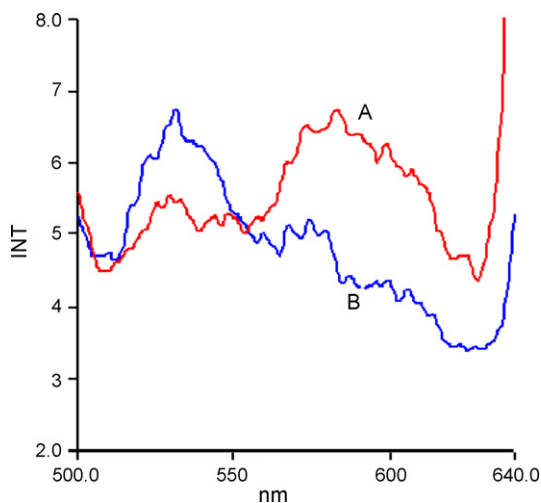


Fig. 2. Emission PL spectra measured at room temperature for TiO_2/CdS particles suspended in ethanol (a) pre-annealed and (b) non-annealed. Excitation frequency was 220 nm.

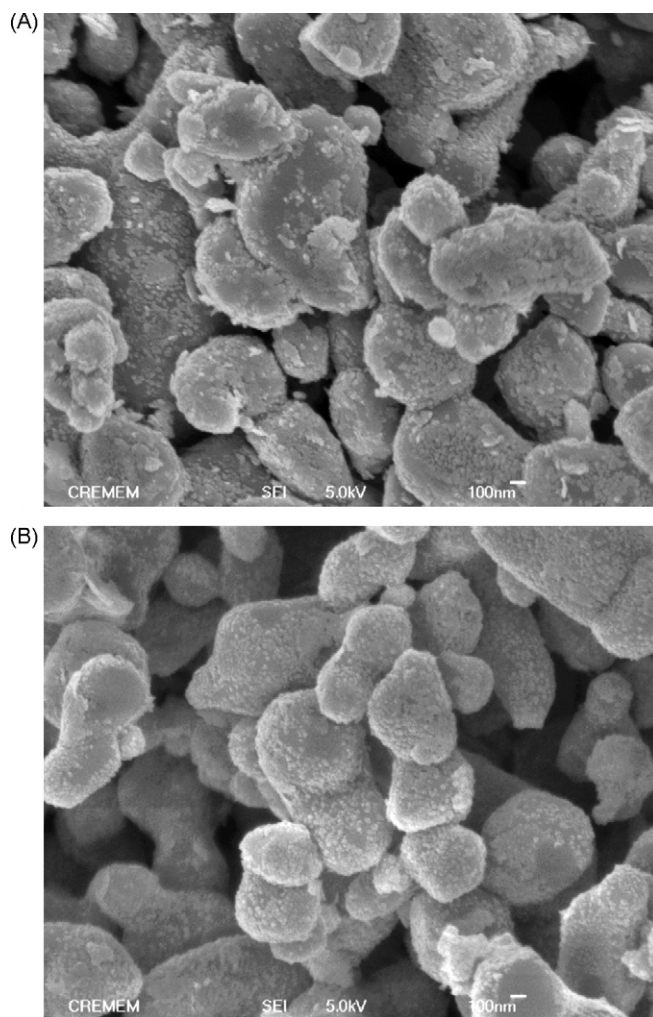


Fig. 3. SEM micrograph for TiO_2/CdS powder (a) pre-annealed and (b) non-annealed. The micrographs show larger particles of TiO_2 covered with mono-layers of nano-sized CdS particles.

range 400–500 nm, while the size for CdS particle is about 20 nm in diameter. In the non-annealed **2**, the CdS exists as nearly spherical particles, Fig. 3(b). Annealing caused agglomeration and sintering between flaky CdS particles, as shown in Fig. 3(a).

X-ray diffraction patterns were measured for CdS powder and TiO_2/CdS system. Despite the relatively low uptake of CdS onto TiO_2 in **2**, and thin sub-monolayer coverage level, the X-ray diffraction pattern showed noticeable peaks for the supported CdS system at 2θ values of 26.7° , 44.07° and 52.5° , Fig. 4(a). Due to small intensity of the CdS peaks, compared to those of TiO_2 , no conclusive calculation of particle size for the supported CdS could be made. Therefore, CdS particle sizes were calculated from XRD diffraction patterns measured for CdS powders prepared in a similar manner to supported CdS particles, Fig. 4(b). Particle size was calculated using the Scherrer formula [35]. The calculated CdS particle diameters for non-annealed and annealed CdS powders were 17 and 20 nm, respectively. The data are consistent with literature values [36]. Little crystallite growth by annealing at 350°C is observed from measured particle sizes. The X-ray diffraction patterns show a cubic crystal type for CdS with (lattice parameters $a=b=c=5.83040\text{ \AA}$) and ($\alpha=\beta=\gamma=90^\circ$). The distinguished peaks of powder CdS were at 2θ values of 26.7° , 32.14° , 44.07° and 54.9° . Peaks for hexagonal closely packed CdS are also observed.

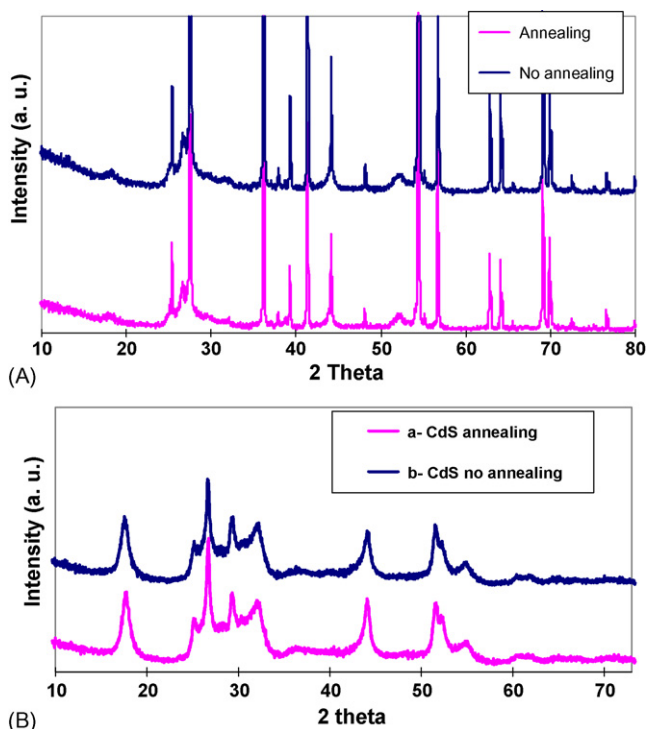


Fig. 4. X-ray diffraction patterns for (a) TiO₂/CdS and (b) CdS powder.

3.2. Photo-catalytic degradation of phenazopyridine

The three systems naked TiO₂, **2** and **3**, were used as catalysts in photo-degradation of **1**, under solar simulator radiation. To assess sensitizing ability of CdS, a comparative study between the three catalyst systems was performed. The catalyst efficiency was studied in terms of initial reaction rates, values of turnover number and values of quantum yield. The relatively low turnover number values are due to small fractions of surface active sites (atoms) that are accessible to reactants. Since the TiO₂ particles are relatively large (in the order of 500 nm radius), the relative surface-area-to-size ratio is small. Thus a big proportion of the atoms is buried in bulk of the particles, and is not accessible to reactants.

Control experiments, conducted under illumination in the absence of catalyst systems, showed no loss of contaminant concentration. Experiments conducted using different catalyst systems in the dark showed no significant contaminant loss due to contaminant adsorption, on different catalyst surfaces. In photo-catalytic experiments, the decrease in contaminant amount paralleled the increase in NO₃⁻ concentration. Thus the decrease in contaminant concentration is an indication of photo-degradation rather than merely adsorption. Unless otherwise stated, catalytic measurements were conducted using pre-annealed samples of **2** and **3**.

3.2.1. Sensitizing effect of CdS

When a cut-off filter (removing 400 nm and shorter wavelengths) was placed between the solar simulator and the reaction mixture, the naked TiO₂ showed no catalytic activities. Both **2** and **3** functioned with the cut-off filter. This is direct evidence in favor of CdS sensitization.

Fig. 5 shows reaction profiles of phenazopyridine consumption with time in the presence of different catalyst systems using solar simulator radiations. The slight loss of **1** using naked TiO₂ and sand/TiO₂, with no CdS in Fig. 5, is due to small UV fraction in the solar simulator spectrum. This was confirmed using a cut-off filter, *vide supra*. The sensitized system **2** efficiently catalyzed the photo-degradation of **1**, as shown in Fig. 5.

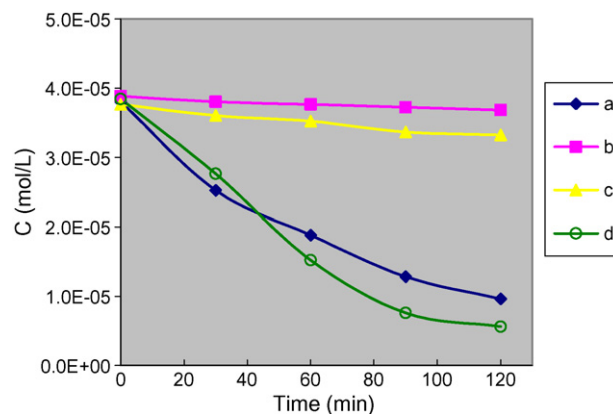
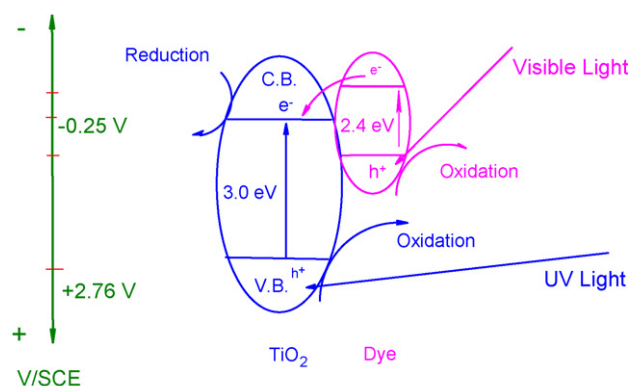


Fig. 5. Reaction profiles of photo-degradation of phenazopyridine (neutral aqueous 50.0 ml suspension, 10.0 ppm, $\sim 4.0 \times 10^{-5}$ M) under solar simulator radiation (0.0212 W/cm^2) at room temperature, using different catalyst systems (a) 2.0 g sand/TiO₂/CdS (~ 0.1 g TiO₂/CdS), (b) 2.0 g sand/TiO₂ (~ 0.1 g TiO₂), (c) 0.1 g TiO₂ and (d) 0.1 g TiO₂/CdS. Turnover number (and quantum yield) values are: 0.00077 (2.55×10^{-4}); 0.000048 (1.59×10^{-5}); 0.0000944 (3.13×10^{-5}) and 0.000929 (3.08×10^{-4}) respectively.

Excitation of naked TiO₂ occurs in the UV region, whereas CdS (band gap ~ 2.4 eV) is excited readily in the visible. Visible excitation creates electron-hole pairs in the CdS particle. The electron travels across the CdS conduction band to the TiO₂ conduction band. It then moves across the TiO₂ particle conduction band where it reduces a species such as an oxygen molecule. The hole, formed in the CdS valence band undertakes oxidation of the contaminant molecule (or possibly OH⁻ to a strongly oxidizing radical OH^{*} as discussed below). The mechanism is schematically summarized in Scheme 1 [14,15].

Supporting naked TiO₂ onto sand did not enhance its efficiency, as shown in Fig. 5. Catalyst **3** showed sound activity, despite the known tendency of support to screen active sites away from incident light. Although **2** showed slightly higher efficiency than **3**, the latter has an edge over the former in being easier to recover.

Kinetic study on system **2** was conducted. The results resembled earlier reports of solar-driven degradation processes [3,14]. Based on initial rate calculations, Fig. 6 indicates that the order of the reaction rate was 0.5 with respect to nominal concentration of **2**. The non-linear dependence of rate on nominal catalyst concentration is presumably due to the tendency of solid catalyst particles to screen incident light. Similar observations are reported [3,14]. Turnover number values, measured after 60 min, showed systematic decrease as catalyst concentration was increased, within the experimental conditions. This is another evidence of light screening



Scheme 1.

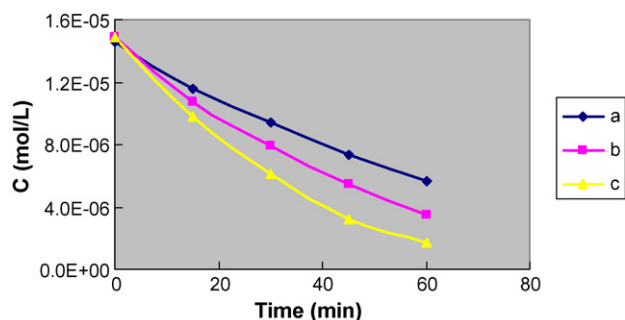


Fig. 6. Effect of TiO_2/CdS nominal amount on photo-degradation reaction of phenazopyridine (neutral aqueous 50 ml suspension, 5 ppm phenazopyridine, $\sim 2 \times 10^{-5}$ M), under solar simulator (0.0212 W/cm^2) at room temperature (a) 0.05 g, (b) 0.1 g and (c) 0.15 g. Turnover number (and quantum yield) values are: 0.000711 (11.74×10^{-5}), 0.000456 (15.11×10^{-5}) and 0.000353 (17.54×10^{-5}) respectively.

effect. Quantum yield values, measured after 60 min, only slightly increased with higher concentrations. When quantum yields are calculated per mole catalyst, the values decrease with increasing catalyst concentration. These data support the screening effect associated with higher catalyst concentrations.

Effect of contaminant concentration or reaction rate was studied, as shown in Fig. 7. At lower contaminant concentrations (7.5 ppm or lower), the turnover number values did not change with concentration. The turnover number value decreased with higher contaminant concentration. The quantum yield values followed a similar trend to changing contaminant concentration. Values of turnover numbers and quantum yields are calculated from reaction profiles shown in Fig. 7. These behaviors are expected. Literature showed that photo-degradation is independent of contaminant concentration, and in some cases, the rate is lowered with increased initial concentration [3]. Different explanations are proposed, all of which rely on the adsorption of contaminant molecules on the solid surface in a Langmuire Hinshelwood model [37]. One acceptable explanation is the fact that at higher contaminant concentration, the contaminant molecules may compete with oxygen or the adsorbed intermediates and inhibit degradation [3,15].

The reaction rate was not affected by temperature, as shown in Fig. 8. The activation energy was lower than 4 kJ/mol. This behavior resembles earlier results for different contaminant photo-degradation systems [14]. The independence of reaction rate of temperature is justified in literature [3,15,32,33].

Effect of pH on reaction rate was investigated. Fig. 9 shows that the activity was relatively higher in basic media. This could partly be explained by lower leaching tendency of CdS from 2, as will be

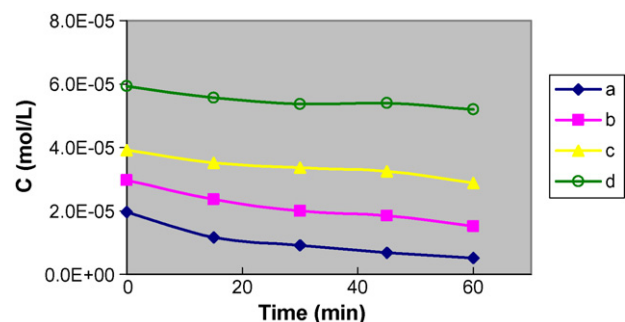


Fig. 7. Effect of phenazopyridine concentration on degradation reaction using TiO_2/CdS (0.1 g) in 50 ml neutral suspension at room temperature under solar simulator (0.0212 W/cm^2). Phenazopyridine concentrations are: (a) 5 ppm (2.0×10^{-5} M) (b) 7.5 ppm (3.0×10^{-5} M) (c) 10 ppm (4.0×10^{-5} M) and (d) 15 ppm (6.0×10^{-5} M). Turnover number (and quantum yield) values are: 0.000577 (0.000191), 0.000577 (0.000191), 0.000418 (0.000138) and 0.0002884 (0.0000956) respectively.

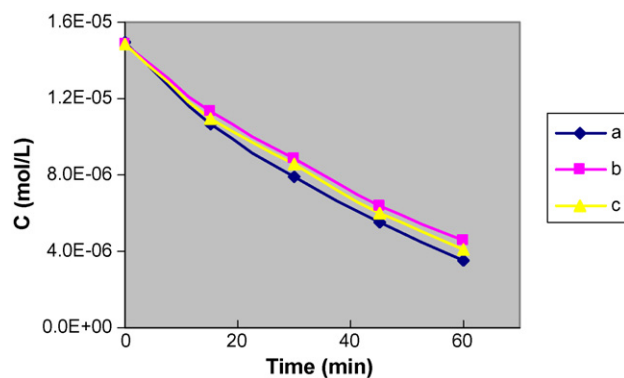


Fig. 8. Temperature effect on photo-degradation reaction of phenazopyridine (neutral suspension, 50 ml, 5 ppm, 2.0×10^{-5} M) under solar simulator (0.0212 W/cm^2) using TiO_2/CdS (0.1 g). (a) 30 °C, (b) 45 °C and (c) 60 °C.

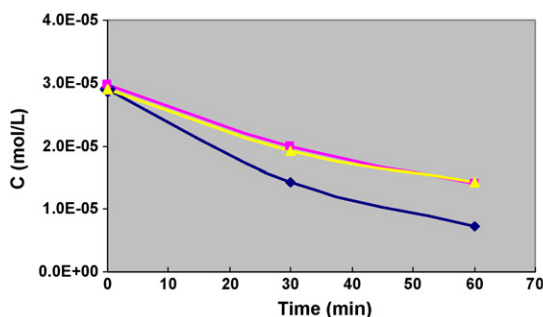


Fig. 9. Effect of pH on photodegradation reaction of phenazopyridine (50 ml, 10 ppm, 4.0×10^{-5} M) using Sand/ TiO_2/CdS (2.0 g) at room temperature. Values of pH are: (a) 9.5, (b) 4 and (c) 7.8. Turnover number (and quantum yield) values are: 0.000868 (0.000287), 0.000623 (0.0002066) and 0.0005865 (0.0001945) respectively.

discussed later. Moreover, the presence of OH^- is a source of OH^\bullet formation which could be a photo-degradation route.

3.2.2. Leaching out studies

The tendency of system 2 to leach out Cd^{2+} ions under photo-degradation of 1 in the visible region was studied at different pH values. Fig. 10 shows that Cd^{2+} continued to leach out from compound 2, with time. Such results were confirmed by polarography. Leaching out occurred at different pH values, but slightly lower

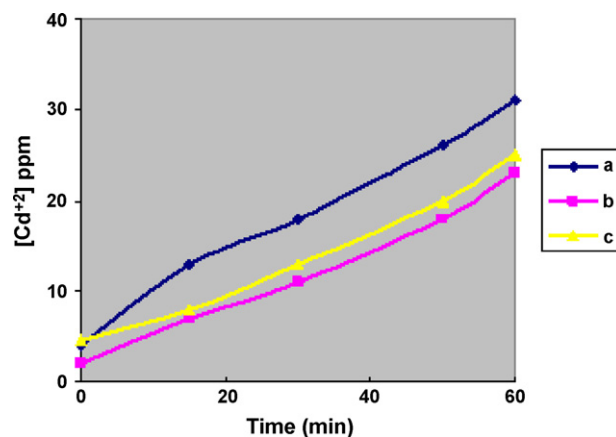


Fig. 10. Reaction profiles showing concentrations (ppm) of Cd^{2+} ions leaching out of non-annealed TiO_2/CdS (0.1 g) under phenazopyridine degradation conditions (solar simulator 0.0212 W/cm^2 , room temperature, in 70 ml suspension, containing 5 ppm contaminant) at different pH values: (a) 3.5, (b) 9 and (c) neutral. Percentage values of Cd^{2+} leaching out after 60 min are: 63%, 56% and 60%, respectively.

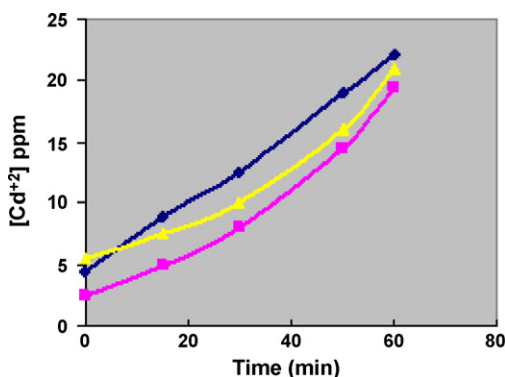


Fig. 11. Reaction profiles showing concentrations (ppm) of Cd^{2+} ions leaching out of pre-annealed TiO_2/CdS (0.1 g) under phenazopyridine degradation conditions (solar simulator 0.0212 W/cm^2 , room temperature, in 70 ml suspension, containing 5 ppm phenazopyridine) at different pH values: (a) 3.5 (b) 9 (c) neutral. Percentage values of Cd^{2+} leaching out after 60 min are: 63%, 56% and 60%, respectively.

at higher pH. It is known that lower pH values encourage more dissociation of CdS by taking more H_2S away from CdS , leaving higher concentrations of Cd^{2+} ions in solution [38,39]. This behavior is known even with no irradiation. Under PEC conditions, such dissolution is presumably more pronounced [12,13], and acidic conditions induce more leaching of Cd^{2+} ions. In addition to radical effect discussed above, this explains the higher catalyst efficiency at higher pH.

CdS leaching out is a serious concern. Firstly, because catalytic activity is lowered, viz. the CdS is removed and less TiO_2 sensitization occurs. Secondly, the Cd^{2+} ions are hazardous to health. Therefore, the wisdom behind using CdS sensitizers for water purification is questionable. Work is still being conducted on CdS -sensitized TiO_2 for water purification [4,6–12,33,34,40–44]. It should be noted here that unless such leaching out is completely prevented; the whole TiO_2/CdS based water purification processes should be questioned. Unfortunately, very little efforts, if any, have been made to prevent such leaching tendency.

Pre-annealing of **2** did not prevent leaching out. Fig. 11 shows that Cd^{2+} ions continued to leach out from pre-annealed **2** under photo-degradation conditions of **1**, at different pH values. This indicates that pre-annealing, which is commonly practiced in CdS -sensitization strategies, is not a solution for Cd^{2+} leaching out.

In an attempt to prevent Cd^{2+} ion leaching, the system **2** was supported onto stable solid sand support, to yield **3**. The Cd^{2+} ions continued to leach out from **3** under photo-degradation conditions at different pH values, as shown in Fig. 12. Annealing the system **3** did not make a significant difference and the Cd^{2+} ions continued to leach out, as shown in Fig. 13.

3.2.3. Catalyst recovery and reuse

The results indicate that sand support is not able to prevent Cd^{2+} ion leaching, Figs. 12 and 13. However, the sand support made it easier to isolate the catalyst system, by simple filtration. Such a process is not feasible for the unsupported system **2**, which demanded more complicated centrifugation processes. Supporting naked TiO_2 particles onto insoluble supports has been widely reported for UV photo-degradations [3,8,14,15,45–68]. However, only a few reports are known for supporting the combined TiO_2/Dye degradation catalysts onto insoluble supports [14,15] (Fig. 14).

While keeping an eye on leaching out tendency, special samples of **3**, with high CdS content were prepared. The samples were used in photo-degradation of **1** under visible light using neutral solutions. After reaction cessation, the catalyst system was recovered easily by simple filtration. Fig. 10 shows that the system loses its efficiency on reuse. Despite the high concentrations of CdS used, its

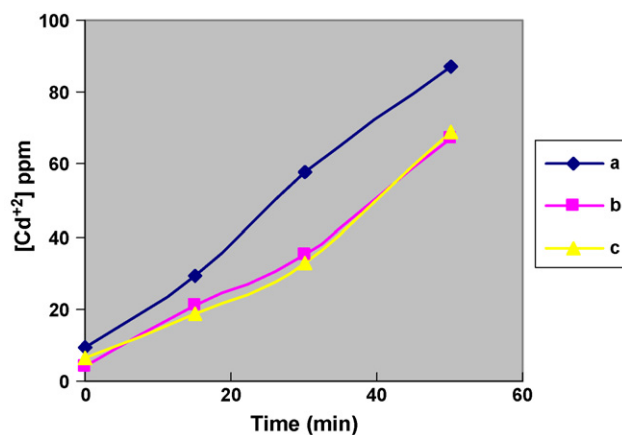


Fig. 12. Reaction profiles showing concentrations (ppm) of Cd^{2+} ions leaching out of non-annealed sand/ TiO_2/CdS (1.0 g) under phenazopyridine degradation conditions (solar simulator 0.0212 W/cm^2 , room temperature, in 70 ml suspension, containing 5 ppm phenazopyridine) at different pH values: (a) 3.5, (b) 9 and (c) neutral. Values of leaching out percentage after 60 min for Cd^{2+} are: 97%, and 74% and 77%, respectively.

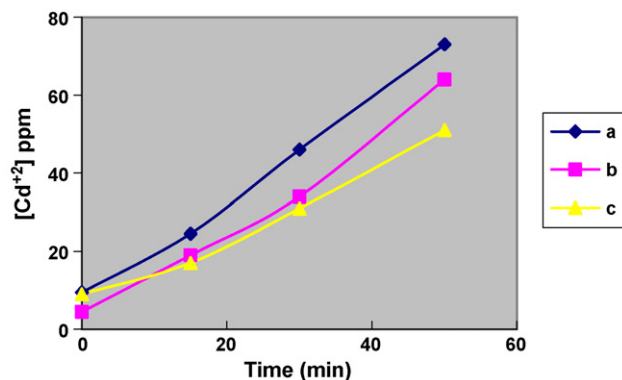


Fig. 13. Reaction profiles showing concentrations (ppm) of Cd^{2+} ions leaching out of pre-annealed sand/ TiO_2/CdS (1.0 g) under phenazopyridine degradation conditions (solar simulator 0.0212 W/cm^2 , room temperature, in 70 ml suspension, containing 5 ppm phenazopyridine) at different pH values: (a) 3.5, (b) 9 and (c) neutral. Values of leaching out percentage after 60 min for Cd^{2+} are: (a) 81%, (b) 71% and (c) 57%, respectively.

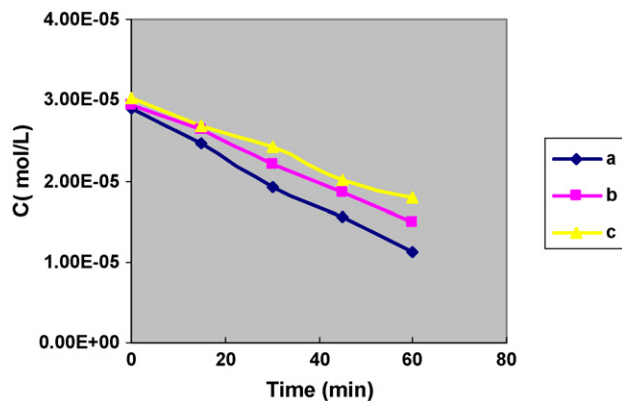


Fig. 14. Reaction profiles of phenazopyridine photodegradation by fresh and recovered catalyst sand/ TiO_2/CdS (1.0 g, containing 5% TiO_2 and 1.9% CdS by mass). (a) Fresh sample, (b) 2nd use and (c) 3rd use. All reactions were conducted at room temperature using neutral 50 ml suspensions of contaminant (10 ppm, $4.0 \times 10^{-5} \text{ M}$).

high tendency to leach out causes efficiency lowering on re-use.

The tendency of CdS to leach out under photo-degradation of **1** sheds light on the feasibility of using it in degrading other more stable contaminants. Typically, medically active compounds are not highly stable and degrade readily [69–72]. The tendency of CdS to leach out, under the conditions described here, indicates the low value of using it under degradation of other more stable contaminants.

4. Conclusion

CdS sensitized TiO₂ efficiently in phenazopyridine degradation under visible light, but decomposed and leached out hazardous Cd²⁺ ions in water. Annealing the TiO₂/CdS system did not prevent leaching out. Supporting TiO₂/CdS onto sand particles yielded a catalyst system that is easy to isolate by simple filtration. The support failed to completely prevent Cd²⁺ ion leaching out. Unless the tendency of CdS to leach out Cd²⁺ ions is completely prevented, its application as sensitizer should be avoided.

Acknowledgements

Help from technical staff at ANU is acknowledged. The authors wish to thank the French-Palestine University Program (Al-Maqdisi) for financial support of this project. Gift of chemicals from Birzeit-Palestine Pharmaceutical Co. is also acknowledged. The authors acknowledge help from technical staff at ICMCB, University of Bordeaux in XRD, SEM and FT-IR spectral measurements.

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