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Enhancement of Photodegradation of Picric Acid (2,4,6-Trinitrophenol) by Fabrication of Visible-Light-Active SnO_2 Quantum Dots/TiO_2 Nanospheres Composite

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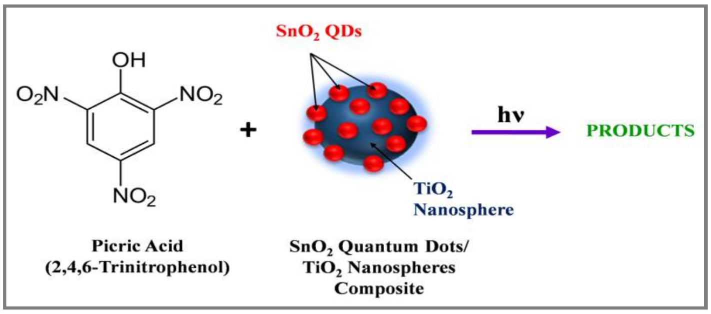
ABSTRACT

Environmental pollution and energy crisis have become recent worldwide concerns. Currently water pollution is presenting the most serious global concerns. Huge amounts of organic wastes are discharged into water bodies, causing serious environmental pollution. SnO_2 quantum dots/TiO_2 nanospheres composite frameworks are excellent candidates as photocatalyst due to their strong visible-light absorbing ability, high tunability, high specific surface areas and semiconductive properties. Herein, a visible-light driven SnO_2 quantum dots/TiO_2 nanospheres composite has been prepared by bottom-up approach. The effect of various parameters such as pH, concentration of dye, amount of semiconductor and light intensity on rate of degradation was observed. The photocatalytic behavior of as-synthesized samples shows better activity than pure TiO_2 nanospheres. This study presents a choice for potential applications of quantum dots (QDs) in treatment of wastewater containing organic contaminants.

Graphical Abstract



Keywords: Quantum Dots, Endocrine Disrupting Chemicals (EDCs), Picric Acid, 2,4,6-Nitrophenol Degradation, Nanoparticles, Photocatalyst, Waste water treatment

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INTRODUCTION

Environmental pollution is a formidable challenge that the world is currently facing. This may become even worse, if no proper and effective solutions are provided. Especially, the fast economic growth, rapid urbanization and industrialization in recent decades have resulted in huge amount of organic wastes like dyes, aromatic hydrocarbons, pharmaceuticals, and other persistent organic compounds like endocrine disrupting chemicals (EDC) etc., that are discharged into water bodies with negligible or no treatment at all. This not only causes serious aquatic pollution, but also increases energy consumption for decontamination of polluted waters. Conventional water and wastewater treatment technologies are ineffective or less effective towards removal and/or degradation of a number of contaminants. Existing treatment process such as reverse osmosis (RO) is typically energy intensive. One feasible solution to this challenging issue is to add an additional advanced oxidation processes (AOPs) treatment unit to current water treatment facilities. Various AOPs are capable of degrading a wide range of organic compounds by generation of highly reactive radicals like hydroxyl radicals, ($^{\bullet}OH$), holes, (h^+), and other reactive oxygen species, etc. Among them, semiconductor-based photocatalytic technologies are gaining growing acceptance as an effective and promising choice, because of some desirable features such as low cost, high efficiency, low toxicity, etc.

A novel g-C_3N_4/PDI@MOF heterojunction was synthesized by Li *et al.,* [1], via the *in situ* growth of NH_2-MIL-53(Fe) onto the g-C_3N_4/PDI layer. This heterojunction was applied as a photocatalyst for the removal of pharmaceutical and phenolic micropollutants in the presence of H_2O_2 and visible LED light ($420 < \lambda < 800$ nm). The photocatalytic performance for the removal of with a maximum efficiency of up to 90% tetracycline for 1 h, 78% carbamazepine (2.5 h), 100% for bisphenol A (10 min) and 100% for p-nitrophenol (30 min) was observed respectively. It was revealed that photocatalyst has good stability and reusability.

A series of ZrO_2-Cr_2O_3 nanoparticles, were synthesized by Norrozi *et al.,* [2] and used to efficiently remove the organic dye of p-nitrophenol in aqueous media.

Padervand *et al.,* [3] prepared sheet-like BiOCl/AgCl-BiOI/AgI quaternary nanocomposites by a facile single-step co-precipitation method using 1-methyl-3-(oxiran-2ylmethyl)-1H-imidazolium-3-chloride ([MOYI]Cl) ionic liquid (IL) and tetrabuthyl ammonium iodide (TBAI) as Cl and I sources and also template agents. Photoactivity of this sample was evaluated by photodegradation of Acid blue 92 and 3-methyl-4-nitrophenol aqueous solutions. This nanocomposite was found to be efficient for the removal of the contaminants within 120 min. It was revealed that as-prepared nanostructure had high capacity to decrease the concentration of both types of pathogenic bacteria in 5 h i.e. gram-negative (*E. coli*) and gram-positive (*S. aureus*).

Darabdhara and Das [4] carried out photocatalytic degradation of toxic phenolic compounds using Au@Ni loaded reduced graphene oxide (rGO) nanostructures. Core-shell nanoparticles of Au and Ni were successfully designed on rGO with size less than 8 nm via a solvothermal method This Au@Ni/rGO nanocomposite exhibited excellent photoresponsive behaviour towards degradation of phenol, 2-chlorophenol and 2-nitrophenol under natural sunlight irradiation having more than 87% degradation.

Padervand *et al.,* [5] also synthesized of Nd_2CuO_4-Nd_2O_3 photosensitive nanocomposites by a combined electrochemical deposition-pyrolysis method. This photocatalyst has a band gap of 3.3 eV. Its catalytic activity was evaluated by photodegradation of two semivolatile organic compounds, 4-methoxy-2-nitrophenol and 3-methyl-4-nitrophenol , which are known as important pollutants. It was indicated that as-prepared photocatalysts can be recycled and used again.

Magnetically $ZnFe_2O_4$/ZnO/perlite nanocomposites (with different molar ratios) were synthesized by Bayat *et at.,* [6] As-prepared nanocomposites were used for photocatalytic degradation of methylene blue (MB) and 4-nitrophenol (4-NP) under visible LED light radiation. Highest photocatalytic activity was found in nanocomposite with a molar ratio of 2:1, which showed the dergradation of 97 and 67% of MB (20 mg L^{-1}) and 4-NP (10 mg L^{-1}) aqueous solutions within 150 min, respectively.

An eco-friendly and bio-surfactant assisted room temperature synthesis has been proposed by Mansingh *et al.,* [7] for preparing magnetic retrievable Fe_3O_4@rGO nanocomposite using *Averrhoa carambola* leaf extract. It was later used for 2-nitrophenol reduction and TCH (Tetracycline hydrochloride) degradation under visible light illumination. The role of bio-molecules present in leaf extract is quite crucial in the process of tuning morphology and opto-electronic features of Fe_3O_4 nanoparticles. Out of nanocomposites prepared 3 wt% loaded rGO (FG-3) showed the best results with 95.85% of 2-Nitrophenol reductions (20 ppm) and 94.09% TCH (10 ppm) degradation on exposure to visible light irradiation for 30 and 60 mins respectively.

A visible-light responsive Cu-Fe bimetallic amidoxime-modified polyacrylonitrile (denoted by Cu/Fe-AO-PAN) fiber was prepared by Wang *et al.,* [8] via a facile and rapid microwave-assisted synthesis method. P-nitrophenol (PNP) was used as a model system to evaluate the photocatalytic performance of the Cu/Fe-AO-PAN fiber in a photo-Fenton conditions Various parameters like microwave heating temperature, irradiation time, Cu/Fe molar ratio, photo-Fenton reaction conditions, (pH, H_2O_2 concentration) and fiber dosage were optimized. PNP removal rate of approximately almost 100% was achieved within 150 min under visible light irradiation under these conditions. Bimetallic Cu/Fe-AO-PAN exhibited improved pH tolerance, photocatalytic performance and stability as compared to the monometallic Fe-AO-PAN fiber.

Mohan *et al.,* [9] prepared synthesized Fe_2O_3/RGO nanocomposite (NC) via a simple and green hydrothermal method. As-synthesized NC was tested for its photocatalytic activity for degradation of model organic pollutant, 4-nitrophenol (4-NP) under visible light irradiation. This NC was proposed as benign photocatalyst for degrading 4-NP in 50 min. H_2O_2 acts as a promising oxidant because of its high efficiency, low cost and produces harmless co-additives.

A series of copper chromite samples with different Cu/Cr molar ratios (0.5-2.0) were synthesized by Hosseini *et al.,* [10] using the citric acid complexation sol–gel method from $Cu(NO_3)_2 \cdot 3H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ precursor salts (copper and chromium nitrates). The photocatalytic activity of the as-prepared samples was tested for degradation of p-nitrophenol from aqueous solutions. It was revealed that the sample with Cu/Cr = 0.6 exhibited the highest photodegradation and degradation rate in 100 min of exposure.

Paliwal *et al.,* [11] observed degradation of non-biodegradable methylene blue using undoped and Co-doped bismuth ferrite as photocatalysts. The effect of various parameters such as pH, concentration of dye, amount of photocatalyst and light intensity on the reaction rate has been evaluated. The rate of photodegradation of dye was monitored spectrophotometrically. It was indicated that doping of bismuth ferrite by cobalt increases the rate of photocatalytic degradation may be due to narrowing of band gap.

Photocatalytic performance of rGO/CuS composite, rGO and CuS was evaluated by Ruchi *et al.,* [12] using a model system azure B. Optimum conditions obtained for photocatalytic degradation of azure B were: pH = 8.5, [Azure B] = 2.80×10^{-5} M, amount of composite = 0.10 g and light intensity = 50.0 mW cm^{-2}. They concluded that composite showed good photocatalytic activity as compared to individual CuS and rGO.

Jat *et al.* [13] studied photocatalytic degradation of fast green under visible light using SnO_2-TiO_2. This composite was synthesized by hydrothermal method using stannic chloride (hydrate) as precursor for SnO_2 quantum dots. It was observed that photocatalytic activity of composite was more than titania nanopowder for degradation of fast green.

MATERIALS AND METHODS

Preparation of composite: The composite of SnO_2 and TiO_2 was fabricated by a simple hydrothermal method via bottom-up approach as reported earlier [14]. Size of SnO_2 QDs and TiO_2 Nanospheres was found to be about 5 nm and 29 nm respectively.

Degradation Process: The photocatalytic activity of the catalyst was evaluated by measuring the rate of degradation of 2,4,6-trinitrophenol (2,4,6-TNP). A stock solution of (1.0×10^{-3} M) was prepared by dissolving 0.0229 g of 2,4,6-TNP in 100 mL doubly distilled water. Further working solutions were prepared from this stock solution as and when required. The absorbance of experimental solution was determined at $\lambda_{max} = 360$ nm. The desired pH of 2,4,6-TNP solution was adjusted by the addition of standard 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. Experimental solutions were irradiated with a 200 W tungsten lamp and about 3 mL aliquot was taken out every 30 min. The intensity of light was varied by changing the distance between the light source and reaction mixture. The absorbance of the solution at various time intervals was measured with the help of a UV-Vis spectrophotometer (Model UV-1700 Pharmaspec). A decrease was observed in the absorbance of 2,4,6-TNP solution with increasing time of exposure. A plot of 1 + log A versus time was found to be linear, which indicates that the photocatalytic degradation of 2,4,6-TNP followed pseudo-first order kinetic.

RESULTS AND DISCUSSION

The rate constant was calculated using the expression:

$$k = 2.303 \times \text{slope} \qquad \dots (1)$$

A Typical runs have been given in Table 1 and graphically represented in figure 1.

Typical Run: pH = 8.0, [2,4,6-TNP] = 8.0×10^{-5} M, Semiconductor = 0.10 g, Light intensity = 50.0 $mWcm^{-2}$

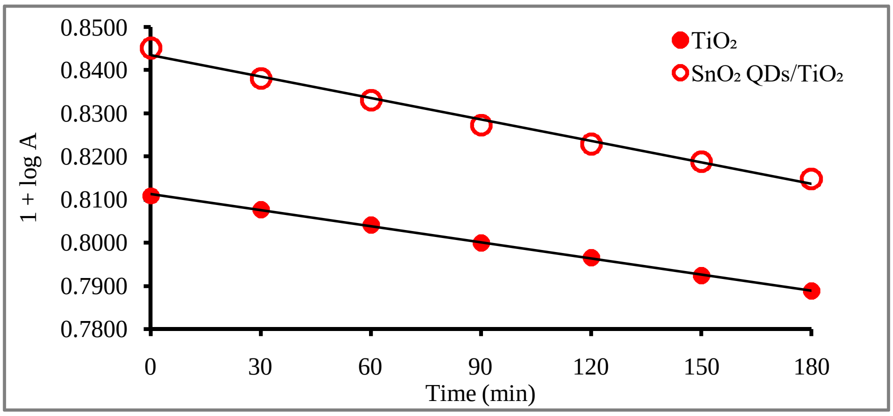

Figure 1. Typical runs.

The rate constant calculated in presence of TiO_2 was found to be 4.70×10^{-6} sec^{-1} whereas rate constant in presence of TiO_2/SnO_2 was 6.4×10^{-6} sec^{-1}, which is almost 37.02 %higher. It may be concluded that SnO_2 decoration of nano-TiO_2 increases its photocatalytic efficiency in visible range for degradation of 2,4,6-trinitrophenol.

Effect of parameters:

pH variation: The effect of variation of pH was studied in the range 5.0–9.5 and reported in figure 2. It was observed that the rate increases with an increase in pH up to 8.0,but the rate of degradation decreases with a further increase in pH. An electron from conduction band is abstracted by dissolved oxygen to generate $O_2^{\cdot -}$ and remaining hole in valance band abstracts electron form OH ions to generate$^{\bullet}$OH radicals. An increase in the rate of photocatalytic degradation of 2,4,6-TNP with the increase in pH may be due to the availability of more $^{\bullet}$OH radicals. A decrease in the rate of photocatalytic degradation of 2,4,6-TNP may be due to the fact that 2,4,6-TNP is present in its anionic form, which will experience a force of repulsion with the negatively charged surface of the semiconductor due to absorption of more OH^- ions on the surface of the photocatalyst. [2,4,6-TNP] = 8.0×10^{-5} M, Semiconductor = 0.10 g Light intensity = 50.0 $mWcm^{-2}$.

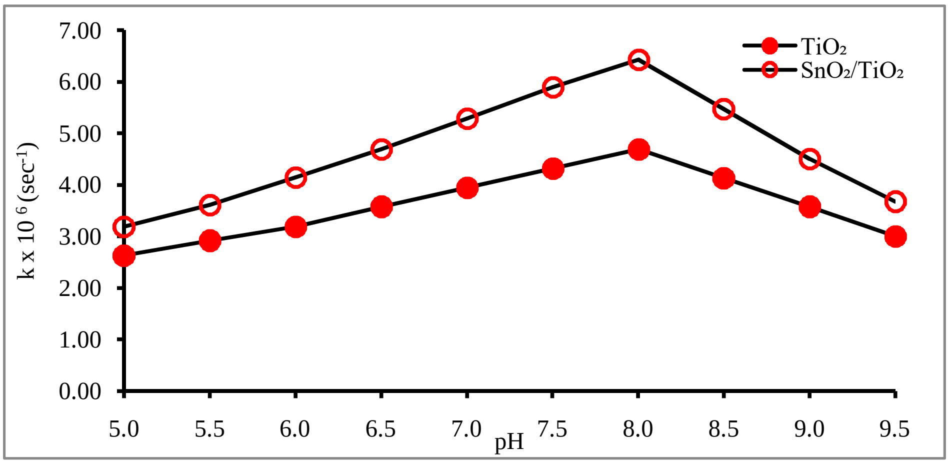

Figure 2. Variation of rate constant with pH.

2,4,6-Trinitrophenol concentration variation: The effect of 2,4,6-trinitrophenol concentration on its photocatalytic degradation was observed in the range of 2.0×10^{-5} to 1.40×10^{-4} M. The results are reported in figure 3. As the concentration of the 2,4,6-trinitrophenol was increased, it was observed that the its degradation increases due to more availability of 2,4,6-TNP molecules for excitation but after 8.0×10^{-5} M (optimum condition), the efficiency of the photocatalytic degradation showed a declining behavior. Here, 2,4,6-TNP will start acting as an internal filter and it will not allow the desired light intensity to reach the surface of the semiconductor present at the bottom of the reaction vessel. pH = 8.0, Semiconductor = 0.10 g, Light intensity = 50.0 $mWcm^{-2}$

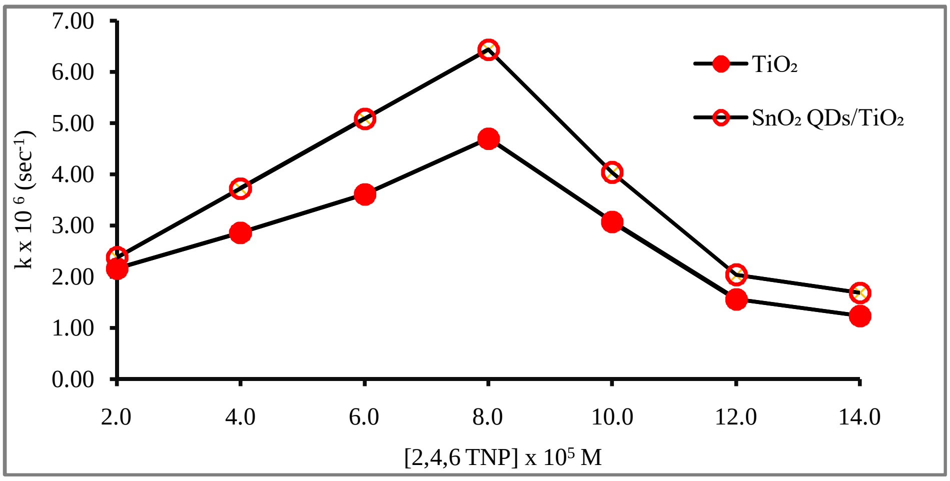

Figure 3. Variation of rate constant with concentration of 2,4,6-TNP.

Amount of composite variation: The amount of composite may also affect the degradation of dye and hence, different amounts of TiO_2/SnO_2 composite were used. Their results are graphically represented in figure 4. It was observed that the rate of photocatalytic degradation increases with increase in amount of composite up to a certain value (0.10 g), but on further increasing the amount of composite, the rate of the reaction gradually declined. pH= 8.0, [2,4,6-TNP]=8.0×10^{-5} M, Light intensity=50.0 $mWcm^{-2}$.

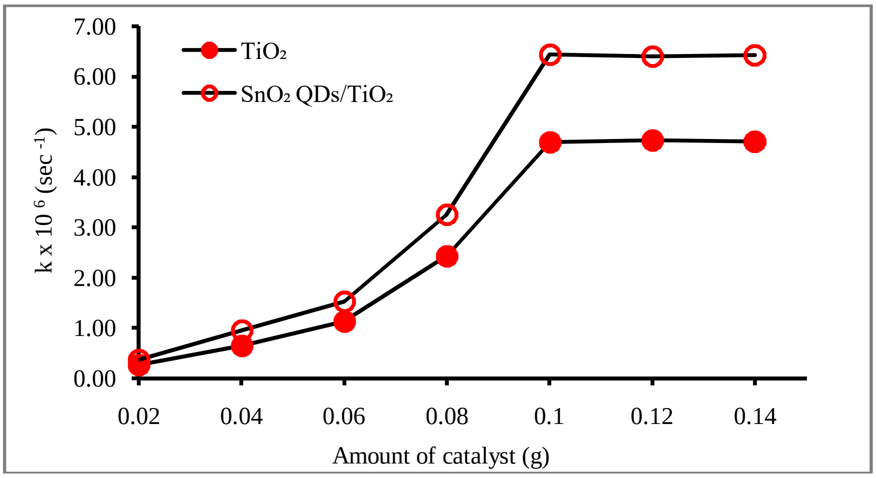

Figure 4. Variation of rate constant with amount on photocatalyst.

As the amount of composite was increased, the exposed surface area of the composite increases but above 0.10 g an increase in the amount of composite will only increase the thickness of layer of the composite and not its exposed surface area. As a result, the rate of degradation became virtually constant and shows a plateau like behavior.

Light intensity variation: The effect of light intensity on the photocatalytic degradation of 2,4,6-trinitrophenol was also investigated by changing the distance between the light source and the exposed surface area of composite. The distance between the light source and exposed surface area of photocatalyst was varied from 20.0 to 70.0 $mWcm^{-2}$.The variation of results is graphically presented in figure 5. It was observed that as the light intensity was increased, the rate of photodegradation increases upto a certain value. Further increase in light intensity results in a decrease in the rate of photodegradation. The maximum rate was observed at 50.0 mW cm^{-2} for degradation of 2,4,6-trinitrophenol.

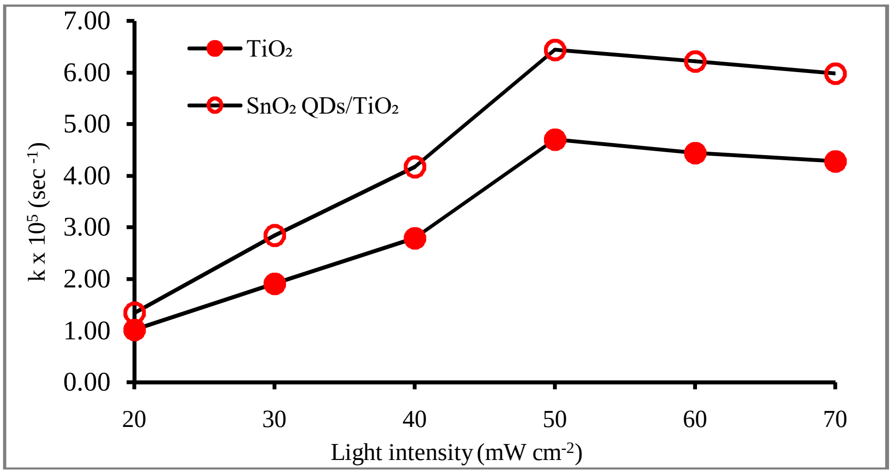

Figure 5. Variation of rate constant with light intensity.

Rate constants with different light intensities are represented in figure 5. It was observed that photocatalytic degradation of 2,4,6-trinitrophenol was more on increasing the intensity of light as this increases the number of photons striking per unit area of photocatalyst surface per unit time. On further increasing the intensity above 50.0 $mWcm^{-2}$, there was a slight decrease in the rate of photodegradation. This may be due to some thermal effects or side reactions. pH=8.0, [2,4,6-TNP]= 8.0×10^{-5} M, Semiconductor = 0.10 g.

Mechanism: Mechanism of photocatalytic degradation of 2,4,6-TNP in presence of the as-prepared composite TiO_2/SnO_2 photocatalyst has been proposed. Electrons in TiO_2 are excited to its conduction band on light irradiation. When two semiconductors are closely coupled in the nanocomposite, conduction and valence bands of SnO_2 act as sink for the photogenerated electrons.

This minimizes the recombination of the photogenerated electron-hole pairs in TiO_2 and gives sufficient time for these electrons and holes to migrate across the surface of the coupled nanocomposite photocatalysts, where these pairs participate in redox reactions with 2,4,6-TNP that are adsorbed on the surfaces of the photocatalysts. The holes can react with surface-bound H_2O (or) OH^- to produce the hydroxyl radical and the electrons can reduce surface adsorbed O_2 to generate superoxide anion radical ($O_2^{\bullet-}$). The participation of ${}^{\bullet}OH$ radical as an active oxidizing species was confirmed by using its scavenger, where the rate of degradation was significantly reduced. The mechanism is as follows:

$TiO_2/SnO_2 \rightarrow e^- + h^+$ ... (2)

(1) $h^+ + OH^- \rightarrow {}^{\bullet}OH$ (Oxidation) ... (3)

$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+$ ... (4)

(2) $O_2 + e^- \rightarrow O_2^{\bullet-}$ (Reduction) ... (5)

$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet}$ ... (6)

$O_2^{\bullet-} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$ ... (7)

$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$. ... (8)

(3) ${}^{\bullet}OH$ + 2,4,6-TNP $\rightarrow$ Products ... (9)

APPLICATION

Quantum dots are having numerous applications like light emitting diodes (LEDs), solar cells, sensors, imaging, quantum computation, etc. Coupling of a semiconducting photocatalysts with quantum dots (QDs) has been found effective in enhancing the photocatalytic conversion performances of the composites.

CONCLUSION

The TiO_2/SnO_2 QDs composites have been prepared successfully. Then the samples were employed in photodegradation of 2,4,6-TNP. Properties of as-obtained photocatalysts were investigated. TiO_2/SnO_2 composites exhibited a broad absorption and excellent photocatalytic activity. The observation of present work explores the possibility of using TiO_2/SnO_2 composites as a potential candidate for better photocatalytic performance in treatment of polluted water.

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