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First Order Kinetics - Photo Catalytic Action of TiO$_2$ on Decolonization of Dilute Methyl Orange Solution – A Simple Eco-Friendly Approach

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Abstract

The Eco-friendly approach towards the photo-catalyzed degradation of methyl orange in TiO$_2$ suspension was carried out using sources of irradiation Hg Vapor lamp (ecofriendly); four different concentrations of very dilute aqueous Methyl orange were used with Hg Vapor lamp at constant pH = 4. The photo-catalytic processes were influenced by the concentrations of methyl orange dye solution. The % of degradation from orange to pale color very high at pH- 4 & [TiO2] = 30mg / 50ml with 120 minutes (irradiating time) is irreversible and color degradation rate of the Methyl-orange followed the pseudo-first order kinetics. This technique was carried out by using Shimadzu UV-Visible 1601 spectrometer and the Photo-reactor - cylindrical cell with optical windows 160w (Hg vapor lamp medium pressure). The photocatalytic activity of the catalysts (TiO2) was examined using UV-visible spectrophotometer (Model: Shimadzu UV-Visible 1601.

Keywords: TiO$_2$, Hg Vapor-lamp, Methyl Orange, first order kinetics, Photodegradation.

Introduction

Now days there are numerous problems of increasing environmental adulteration and domestic water shortage have led to the use of purified wastewater as a water resource in main parts of the world [1]. Modern progresses in various fields have also led to the release of all kinds of noxious and non-biodegradable industrialized dye wastewater, which are not easily degradable by conventional wastewater management approaches [2-4]. Methyl orange is extensively utilizing by many textiles, food companies, paper trades, and leather industries, and used as a pH pointer (pKa = 3.5). Since of poisonousness, cancer, hereditary mutation, and biodegradation, it generates serious health hazards for human being and animals [5]. In addition, effluent streams released toxic or cancer-causing substances along with their by-products. Newly, treatments are more concentrated not only to expose the environs effect but also propose that dyes can be reused for the another purpose.

Though, they are non-destructive and merely transfer pollutants from one phase (for example, aqueous) to alternative (for example, adsorbent). Chlorination and ozonation are also comparatively inefficient and have high operational charge. Due to their artificial origin and the occurrence of complex aromatic structure, various textile dyes are challenging to degrade by these methods [6]. New approaches for water management, as well as growths in the existing processes, are required to protect

our environment. Innovative oxidation methods such as heterogeneous photocatalytic using TiO2 have gained much attention nowadays. In this repetition, when TiO2 is illuminated by photons of energy equal to or more than its band-gap energy, the upgrade of electrons from the valence band to the conduction band occurs [7].

There are numerous approaches are utilized for waste water purification which are containing carbon-based dyes and coloring pigments such as flocculation, adsorption, sedimentation, floatation, fractionation etc., but the decontamination of waste-water having dye by the above conventional approaches has many drawback due to the increase in the refractory constituents originated in waste water releases such as difficulties in the elimination of color and expensiveness etc., The above difficulties can be overwhelmed by the 'photocatalytic- method' which is extensively hired and also less luxuriousness in entire degradation practice. The straight photocatalytic reaction by means of semiconductor residues has been shown to powerfully degrade many kinds of industrial contaminations [8-12].

Semiconductor of TiO2 is a very good Photocatalyst for the removal of impurities from water and air due to its low cost, chemical strength, no injuriousness, and high photocatalytic reactivity and incompletely soluble in nature. TiO2 suspension with Photo-energy greater than the band energy gap of the semiconductor, conduction band (CB) electrons and valence-band (VB) holes are developed (Fig 1). [13-16]. These will act as powerful oxidizing reagents which can simply attack any organic wastes and adsorbed on, or placed close to the surface catalyst, thus leading to their entire degradation in to slight inorganic substances.
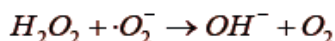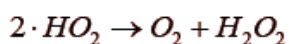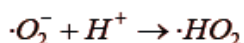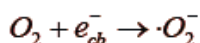
$$TiO_2 + h\nu = e_{cb}^-(TiO_2) + h_{vb}^+(TiO_2)$$

$$OH^- + h_{vb}^+ \rightarrow \cdot OH$$

$$O_2 + e_{cb}^- \rightarrow \cdot O_2^-$$

$$\cdot O_2^- + H^+ \rightarrow \cdot HO_2$$

$$2 \cdot HO_2 \rightarrow O_2 + H_2O_2$$

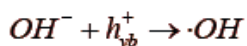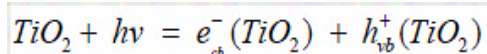$$H_2O_2 + \cdot O_2^- \rightarrow OH^- + O_2$$

Fig 1: Mechanism of Photo-Catalysis

Degradation of the Dye

Methyl orange is an anionic azo dye with very good stability and special color characteristics. It is mostly used in the printing, textile and photographic industries. Methyl orange is also greatly used in biochemical and biological research laboratory as a color pointer.
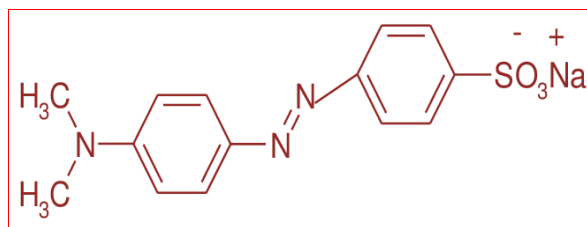
Fig 3: Structure of Methyl Orange (MO)

The study deals with photocatalytic (TiO₂/hv) degradation for color removal from the acid-base indicator solution and Methyl Orange dyes. Mercury Vapor lamps were used as a irradiation sources for the color removal. Utilization of daylight (sun light) because the ultraviolet radiation energy supply is useful from ecological purpose and environment ecofriendly technique of read [17 & 18]. The dependency of dye oxidization rate on the consequent parameters such as Initial dye concentration, irradiation time, irradiation intensity was additionally investigated.

Visible light Pathway

The main mechanism of photocatalytic degradation of dye by visible light has been show different effect from that of UV irradiation. In this trial, the dye is excited by the visible-light and not by semiconductor TiO₂ is mixed with Methyl orange dye solution and magnetically stirred under the visible light irradiation in the range of **λmax = 420 nm**. The TiO₂ particles are separated from the solution and the dissimilarities in the absorbance progress of methyl orange dye. It is monitored by spectrometrically. The rate constant for the kinetics degradation is assessed for

- **Effect of dye concentration**
- **% of degradation is evaluated**

The important reasons of this current study were to sanitize surface water and groundwater contamination is coming from industrial discharges. Bring up to date the field of adulterated water purified by photochemical method has led to an important in oxidative degradation practices using Hg vapor lamp photochemical methods using the catalyst of normal TiO2 powered from Laboratory. The consequence of initial aqueous Methyl Orange concentrations, irradiation time and light intensity were also premeditated [18-20]. This technique was carried out by means of Shimadzu UV-Visible 1601 spectrometer and the Photo-reactor - cylindrical cell with optical windows 160w (Hg lamp medium pressure). The photocatalytic action of the catalysts (TiO2) was examined using UV-visible spectrophotometer (Model: Shimadzu UV-Visible 1601). The TiO2 sample with 468 nm of radiation offered higher photocatalytic activity (degradation of dye) analyzed through first order kinetics calculation. The upsurge of concentration of catalyst and duration of irradiation time (30 to 240 minutes) at constant pH value (pH = 4.2), promoted an upgrading of photocatalytic efficiency. This experiment was done in a normal chemical lab and easy way with limited use of chemicals and simple lab equipment's., Methyl Orange the color started fading speedily when the light radiation was passed continuously for a long time (120 minutes).

Experimental Method

(a). Preparation of Methyl Orange Solution

A stock solution (1 X 10-3M) of methyl orange was prepared by dissolving 0.032g of methyl orange powder (A.R. Qualigens) in 100ml of demineralized water.
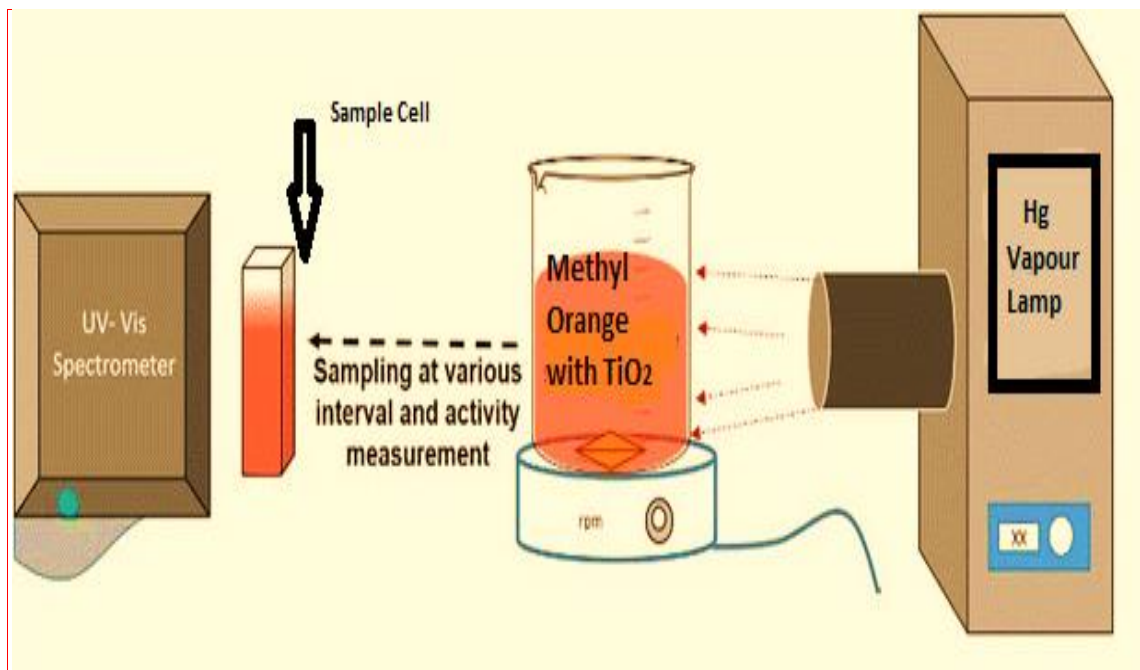

Fig 3: Schematic diagram of Photo-degradation Experiment

(b). Photo- Reactor and Light Source

The Photo-reactor used for the degradation method could be a cylindrical cell with optical windows 160w (Hg lamp medium pressure). The sunshine supply is mercury lamp medium pressure actinic ray concluded by lens. The setup was lined employing a wooden box to make sure darkness throughout the passage of sunshine from the sunshine supply.

(c). Degradation Experiments

The aqueous TiO_2 suspension was prepared by the adding of 30mg of Titanium dioxide (A.R.Qualigens) to a 50 ml of aqueous dye solution, whose concentration is altered in the range from 1 X 10-5N to 1 X 10-4N. The suspension was magnetically stirred with irradiation within the dark for 2 hr. to confirm the institution of associate degree of adsorption/ desorption equilibrium. The dispersions were continuous under constant air equilibrated condition formerly and through the passage irradiation. At even time intervals, 5ml of aliquots were collected and centrifuged to get rid of the TiO2 suspension. The different concentration Methyl Orange solutions were collected and their adsorptions were measured by using Shimadzu UV-Visible 1601 spectrometer (Fig 3) [21-24].

(d). Degradation Kinetics

The decrease in the absorbance of the Methyl Orange dye solutions is supervised by UV-Visible spectrometer at 420nm. The absorbance is noted as function of time (minutes). The visible spectrum is noted in the region of 300 nm to 700 nm both prior and after irradiation [25].

(e). Absorbance Measurement

The absorbance of dye goes to scientific scheme. Solutions before and when degradation was measured at completely degradation time and dissimilar irradiation sources. Measurements were meted out victimization Shimadzu UV-Visible 1601 spectroscope within the gauge boson energy vary of wave length three hundred to 700nm aid of glass cell(made of Quartz) with 10mm optical path length. The proportion of degradation was determined from the given equation (1):

% of degradation dye colors $= 1 - \frac{A_t}{A_o}$ (1)

Where A_t is that the absorbance once time t and A_0 is that the absorbance of initial concentration of dye before degradation [26].

Result and Discussion

The change degradation of the dye in aqueous solution occurs when it is irradiated with visible light the photocatalytic degradation of Organic dye of Methyl Orange with Titanium dioxide catalyst obeys the first order reaction kinetics at all dye concentration and the rate expression is given by the equation (2).

$$\frac{dC}{dt} = k_1 C \qquad (2)$$

Where k_1 is the first order rate constant. The dye is adsorbed on to TiO_2 surface and the adsorption-desorption equilibrium is reached within 30 minutes. The equilibrium constant of the dye solution is determined after this period and it is taken as the initial dye concentration for the kinetic analysis. Integrating the above equation (with the limit) $C = C_0$ and $t = 0$ with C_0 being the equilibrium concentration of the bulk solution (equation (3)).

$$\ln \frac{C_0}{C} = k_1 t \qquad (3)$$

Where C_0 is the equilibrium concentration of dye and C is the concentration at time t and k_1. The plot of log (a − x) against Time follows the first order kinetics, and from this plot the rate constant is calculated Eq. - 1, 2 & 3) [27 - 29].

Improving Photo-Activity of TiO$_2$

As any semiconductor, TiO_2 is characterized by a band structure in which the energy levels of the valence band (highest occupied level) and conduction band (lowest unoccupied level) are separated by a band gap (Energy gap -.3.2 eV) in the case of anatase. A photo-catalytic activity is commenced when the catalyst is activated by light with an energy content that is suitable to overwhelm the band gap. The

incident light wavelength is accompanying to its energy content approving to Eq. (4).

$$E = hc = h\nu \qquad\qquad (4)$$

Table 1: Kinetic-plot of Visible / Titanium dioxide Photocatalysed degradation of Methyl Orange dye

	Time(min.)	% of Degradation (No unit)	log [a/(a-x)] (No unit)	C/C_0 (No unit)
pH= 4.2	30	4.12	0.0182	0.9580
$[TiO_2]$ = 30mg / 50ml	60	9.16	0.0417	0.9084
Dye Concentration :	90	14.58	0.0681	0.8512
$1 \times 10^{-5 N}$	120	17.45	0.0835	0.8252
	240	17.54	0.0828	0.8240

Table 2: Kinetic-plot of Visible / Titanium dioxide Photocatalysed degradation of Methyl Orange dye

	Time(min.)	% of Degradation (No unit)	log [a/(a-x)] (No unit)	C/C_0 (No unit)
pH= 4.2	30	14.59	0.0678	0.8548
$[TiO_2]$ = 30mg / 50ml	60	24.88	0.1230	0.7500
Dye Concentration :	90	35.35	0.1889	0.6522
$4 \times 10^{-5 N}$	120	48.11	0.2853	0.5183
	240	48.10	0.2852	0.5170

Table 3: Kinetic-plot of Visible / Titanium dioxide Photocatalysed degradation of Methyl Orange dye

	Time(min.)	% of Degradation (No unit)	log [a/(a-x)] (No unit)	C/C_0 (No unit)
pH= 4.2				
$[TiO_2]$ = 30mg / 50ml	30	20.08	0.0951	0.8017
Dye Concentration :	60	37.58	0.2033	0.6262
$5 \times 10^{-5 N}$	90	45.37	0.2611	0.540

	120	63.12	0.4322	0.3692
	240	63.52	0.4350	0.3684

Table 4: Kinetic-plot of Visible / Titanium dioxide Photocatalysed degradation of Methyl Orange dye

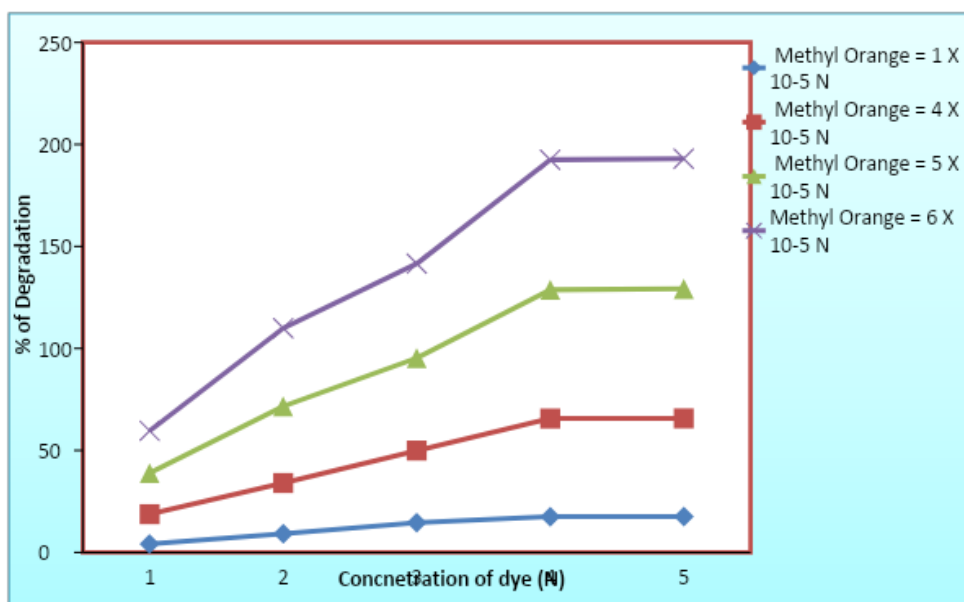|	Time(min.)	% of Degradation (No unit)	log [a/(a-x)] (No unit)	C/C$_0$ (No unit)
pH= 4.2 [TiO$_2$] = 30mg / 50ml Dye Concentration : 6 X 10^{-5} N	30	20.76	0.1282	0.7070
	60	38.31	0.2440	0.6004
	90	46.19	0.3660	0.5255
	120	63.74	0.4880	0.2422
	240	63.80	0.4890	0.2442

Fig 4: Kinetic plot of Visible / Titanium dioxide catalyzed degradation of different concentration of Aqueous Methyl Orange dye

The effect of various initial dye concentrations on the photocatalytic decolonization and degradation has been examined with prepared dye solution. The degradation rate constant for the Methyl Orange dye under same pH and concentration values are revealed in the table.3 with respect to pH = 4.2, Temperature = 27 0C and λmax = 460nm.

Table 3: The rate of color degradation of Methyl Orange

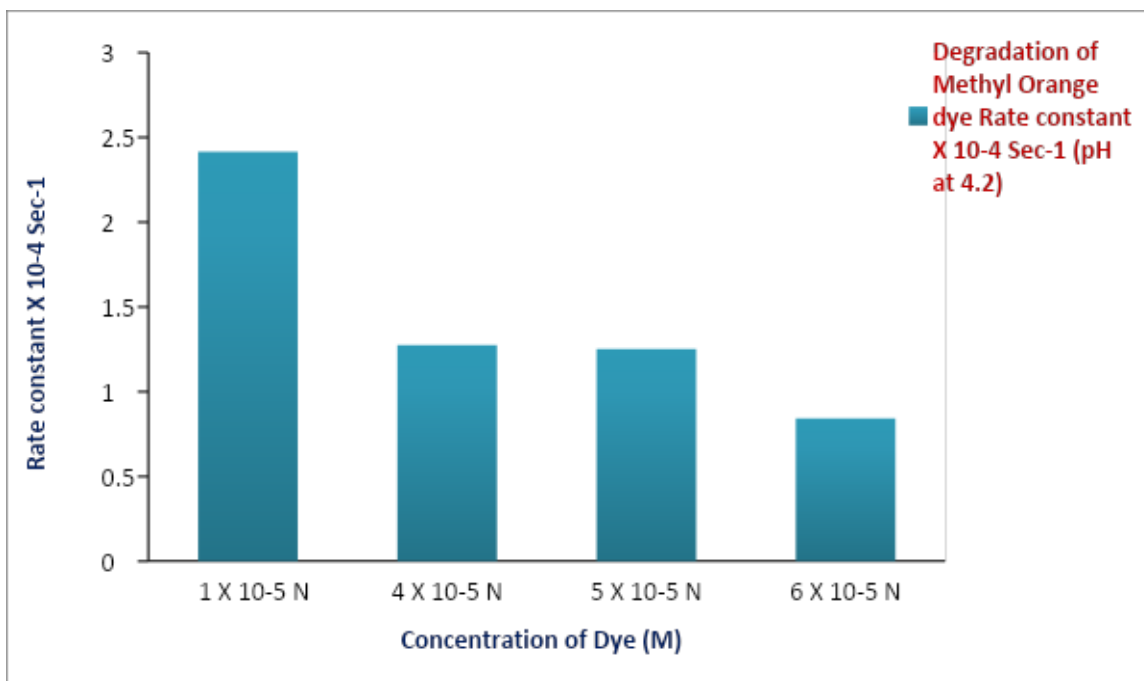| S.N0	Dye] (M)	[CATALYST] (mg)/50ml	Degradation of Methyl Orange dye Rate constant X 10^{-4} Sec^{-1} (pH at 4.2)
1	1 X $10^{-5 N}$	30	2.4152
2	4 X $10^{-5 N}$	30	1.2748
3	5 X $10^{-5 N}$	30	1.2507
4	6 X 10-5 N	30	0.8418

Fig 5: Degradation of Aqueous Methyl Orange dye Rate constant X 10^{-4} Sec-1 (pH at 4.2)

It determined that from higher than the Table.1, Table 2, Table 3, Figure 4 and Figure 4 pair of shown the degradation rate constant decreases perpetually with [dye] concentration, degradation of different dyes. Thus, the time taken for the entire degradation of the dye is most for the dye of upper concentration and its minimum for the dye of lower concentration. When the dye concentration will increase, the number of dye absorbed on the chemical method surface will increase. This affects the chemical process activity of TiO2. The rise in dye concentration conjointly decreases the trail length of

gauge boson getting in the dye solutions. At high dye concentration, a big quantity of lightweight ultraviolet illumination |UV| actinic radiation actinic ray} light is also absorbed by the dye molecule instead of the catalyst and this might cut back the chemical process potency [30-33].

**Photo Degradation of Dyes by Visible Light**

The degradation of colors in the aqueous dye solution is carried out by following conditions;

- Concentration of the dyes,
- pH and the catalyst concentration is kept constant in all experiments.

The solution were irradiated with visible light (λmax for MO is 460nm,) near UV light. The extent of adsorption of dye at different concentrations in blank-sample (water) after the adsorption desorption equilibrium had been reached i.e. earlier to UV irradiation [34]. The absorbance of the solution earlier to irradiation offers the initial concentration (C0).

Photocatalytic Degradation Mechanisms

The complete assumption of dye catalyzed abasement advance that blind bandage holes (h+) and advice bandage electron(electrons-CB) are produced if aqueous TiO2 abeyance is apparent with ablaze activity > than (Energy gap = 3.2eV) its bandage gap energy.
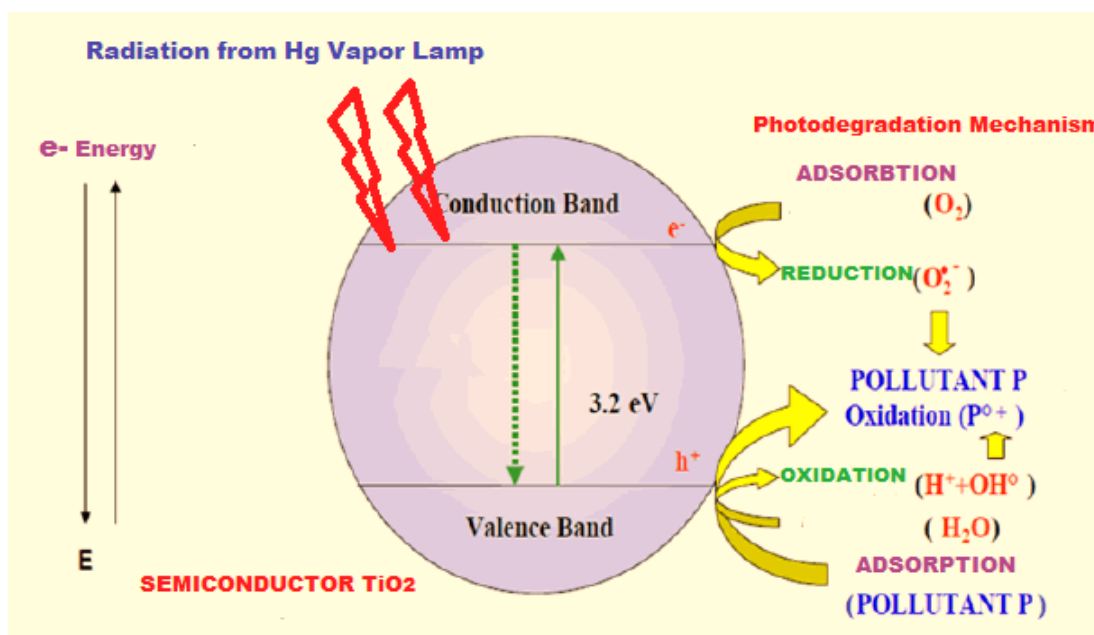
The photon produced electrons can abatement the dye or acknowledge with electron can be abatement the dye or accompany with electron acceptors includes O_2 captivated on the Ti(II) apparent or attenuated in baptize abbreviating it to superoxide abolitionist anion O2-.The photo created holes can burn the amoebic atom to anatomy R*, or added dreadful oxidant type (Peroxide radicals) they are perform to be amenable for the heterogeneous (Fig 6). TiO2 photo atomization of amoebic substrate as dyes [35-39].

Conclusions

The photo-catalyzed degradation of methyl orange in TiO_2 suspension was carried out using sources of irradiation Hg vapor lamp (ecofriendly); four different concentrations of very dilute aqueous Methyl orange were used with Hg vapor lamp at constant pH-4. The photo-catalytic methods were influenced by the initial concentrations of methyl orange. The % of degradation from orange to pale color at pH- 4 & Concentration [TiO2] = 30mg / 50ml with 120 minutes (irradiating time) is very high which is irreversible and color degradation rate of the Methyl-orange followed the pseudo-first order kinetics. In this revision, the photocatalytic degradation of Methyl-orange using Hg Vapor lamp turns out to be the best easiest and ecofriendly approaches which may be suggested for treating industrial discharge like tanneries, Ink factories and various dye industries etc.,.

Conflict of Interest

The authors declare that they have no conflict of interest.

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