COD Reduction in Common Effluent from Industrial Area Using TiO₂

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Abstract— *Advanced Oxidation Process can mineralize a wide range of organic compounds. Photo-catalysis of wastewater using Titanium Dioxide is an advanced oxidation process (AOP). For the purpose of decontamination of waste water, titanium dioxide is used frequently in laboratory scale experiments. The study on TiO₂ catalysis as discussed here forms the basis of a simple and cost effective method to treat mixed waste from textile and chemical zone of MIDC having a wide variation in its characteristics.*

Keywords— ***COD reduction, effluent treatment, wastewater treatment, TiO₂ catalysis, Titanium dioxide***

I. INTRODUCTION

Photo-catalysis is a phenomenon where an electron-hole pair is generated on exposing semiconducting materials to light of suitable energy. Thus, the chemical reactions that occur in the presence of a semiconductor and light are collectively termed as photocatalytic reactions [3]. Organic contaminants can be completely mineralized by irradiation in presence of semiconductor, TiO₂ [1], [23], [28], [32], [61].

Photocatalytic detoxification has been focused as an alternative method to clean up polluted water. This technique adopts the possibility of combining the heterogeneous catalysis with solar/UV light to achieve mineralization of toxic pollutants present in effluents. This technique appears to offer a great deal of hope in handling hazardous and toxic chemical wastes into harmless end products at ambient temperature. Many catalysts like TiO₂, ZnO, WO₃, SnO₂, ZrO₂, CeO₂ and CdS have been put into use for photocatalytic oxidation of water borne environmental contaminants. However, Degussa P25 TiO₂ has proven to be an excellent catalyst for photo oxidation of many organic pollutants [37].

Heterogeneous photo-catalysis is a promising new technique which has been successfully used to eliminate toxic and bio-resistant organic and inorganic compounds from aqueous-solution through their transformation into benign compounds. Many researchers have been attempting photocatalytic liberalization of water borne environmental contaminants with different semiconductors employing solar/UV light. TiO₂ is found to exhibit excellent photocatalytic activity in breaking down organic compounds. Extensive research has been carried out on the ability of photo-catalysts to promote degradation and total mineralization of various pollutants [12], [13], [24], [29] [33], [34], [59]. It is relatively inexpensive, chemically stable and not photo corrosive. The photo-generated holes are highly oxidizing and photo-generated electrons are reducing enough to produce super oxide from oxygen.

1.1. Mechanism of Photo-catalysis

The primary photochemical processes occurring upon irradiation of a semiconductor are now well established [7], [8], [18]. By definition, a semiconductor has band structure, roughly characterized as a series of energetically closed spaced energy levels associated with covalent bonding between atoms comprising the crystallite (the valence band) and a second series of spatially diffuse, energetically similar levels lying at higher energy and associated with conduction in the macromolecular crystallite (the conduction band) [13]. The magnitude of the fixed energy gap between the electronically populated valence band and the largely vacant conduction band governs the extent of thermal population of the conduction band (and hence the magnitude of the electrical conductivity of the particle) in its intrinsic (undoped) state [41]. The band gap also defines the wavelength sensitivity of the semiconductor to irradiation.

Photo-excitation with light of energy greater than the band gap promotes an electron from the valence band to the conduction band, creating an electronic vacancy or "Hole" (h⁺) at the valence band edge. The classical picture of a hole is that of a highly localized electron vacancy in the lattice of the irradiated semiconductor particle. This hole can also be identified as a chemical entity: for example, a bound O⁻ lattice radical or a surface associated OH radical in a metal oxide or an S⁻ or SH radical in the substrate or surface of metal chalcogenide. This hole can initiate further interfacial

electron transfer or other chemical reactions to an adsorbate, or with the surface bound OH radical, can itself diffuse into the solvent bulk.

The photo-generated electron (e) usually relaxes thermally to the conduction band edge (and the hole to the valence band edge), but further deactivation is more difficult because of energetic mismatching of the energies of the electron and hole. Only in special cases can non-thermalized "hot electrons" be transferred across the semiconductor interface at a rate competitive with internal relaxation [44].

As stated earlier, absorption of a photon with energy greater than the band gap energy leads to the formation of an electron/hole pair. In the absence of suitable scavengers, the stored energy is dissipated within a few nanoseconds by recombination. If a suitable scavenger is available to trap the electron or hole, recombination is prevented and

subsequent redox reactions may occur. The valance band holes are powerful oxidants (+1.0 to +3.5V vs. NHE depending on the semiconductor and pH), while the conduction band electrons are good reductants (+0.5 to -1.5V vs NHE). Most organic photo degradation reactions utilize the oxidizing power of the holes either directly or indirectly. In bulk semiconductor electrodes only one species, either the hole or electron, is available for reaction due to band bending. However in every small semiconductor particle suspensions both species are present on the surface. Hence both oxidative and reductive pathways are possible in semiconductor particle suspensions.

Fig. 1 illustrates the typical photocatalytic process. It consists of superposition of the energy bands of semiconductors and the geometrical image of a spherical particle.
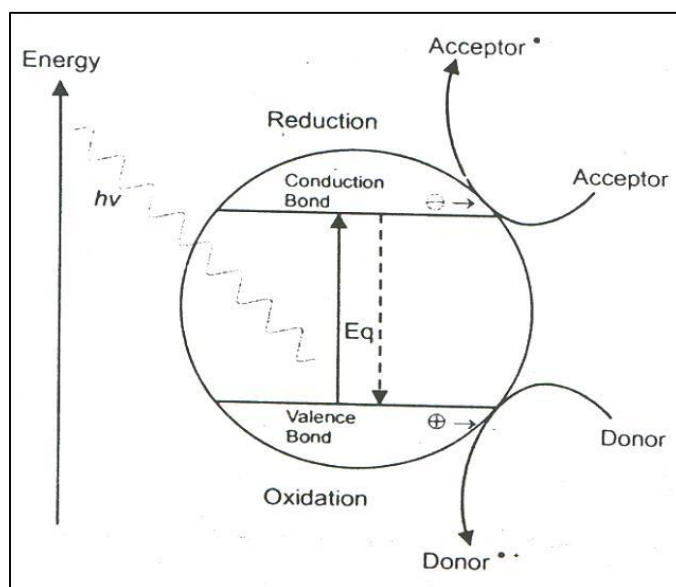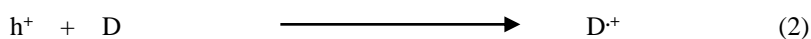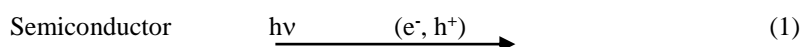

Fig. 1: Typical Photo-catalysis Process

Unlike metals, semiconductors lack a continuum of inter-band states to assist the recombination of the electron hole pair. This assures an electron-hole pair lifetime sufficiency long enough to allow these species to participate in interfacial electron transfer [40]. Thus, the act of photo excitation usually generates an electron-hole pair poised

respectively at the conduction band and valence band edges (**1**). The components of this activation pair, when transferred across the interface, are capable of, reducing and oxidizing a surface-adsorbed substrate forming on a common surface a singly oxidized electron donor and singly reduced electron acceptor respectively (**2** and **3**).

$$Semiconductor \xrightarrow{\quad h\nu \quad} (e^-, h^+) \qquad (1)$$

$$h^+ + D \longrightarrow D^{\cdot+} \qquad (2)$$

$$e^- + A \longrightarrow A^{\cdot-} \qquad (3)$$

If a photo-generated hole reaches the surface of the semiconductor, it can react with an adsorbed substrate by

interfacial electron transfer, assuming that the adsorbate possesses a redox potential appropriate for a

thermodynamically allowed reaction. Thus, an adsorbed electron donor can be oxidized by transferring an electron to a photo-generated hole on the surface and an adsorbed acceptor can be reduced by accepting an electron from the surface. Hole trapping generates a cation radical $D^{.+}$ (**2**) and electron trapping generates an anion radical A (**3**). These radical ions can participate in several pathways as follows:

1. They may react chemically with themselves or other adsorbates.
2. They may recombine by back electron transfer to form the excited state of one of the reactants or waste the excitation energy by a non-radiative pathway.
3. They may diffuse from the semiconductor surface and participate in chemical reactions in the bulk solution.
4. If the rate of formation of $D^{.+}$ (cation radical) is kinetically competitive with the rate of back electron transfer, photo-induced oxidation will occur for any molecule with an oxidation potential less positive than the semiconductor valence band edge, since under these conditions interfacial electron transfer at the illuminated interface is thermodynamically allowed.

By similar considerations, photo-induced reduction can occur, barring kinetic restraints, to any molecule possessing a reduction potential less negative than the conduction band edge.

1.2. TiO₂ as the catalytic material

Photo-catalysts other than TiO_2 have been used although none have matched the attributes of TiO_2 in terms of stability, performance and cost. In this regard, it is pertinent to note that the paint and pigment industry has long attempted to suppress the photo-activity of TiO_2 (by passivating its surface) in product formulations. In environmental pollution abatement, it is this very property of TiO_2 that is crucial.

TiO_2 is a complex material because it opacifies, variegates and crystallizes glazes. It also modifies existing colours from metals like Cr, Mn, Co, Ni, and Cu. TiO_2 belongs to the family 3 OPACIFIER with atomic weight 79.9 and fusion temperature 1830^0C. TiO_2 group is composed of rutile, anatase and brookite. The characteristics of each phase are given in **TABLE 1**.

Table 1. Characteristics of the various phases of TiO₂.

Parameters	Rutile	Anatase	Brookite
Formula Weight	79.890	79.890	79.890
Z	2	4	8
Crystal System	Tet	Tet	Tet
Point Group	4/mmm	4/mmm	4/mmm
Space Group	$P4_2/mnm$	$I4_1/amd$	Pbca
Unit Cell a(^{o}A) b c	4.5845 2.9533	3.7842 9.5146	9.1840 5.4470 5.1450
Volume	62.070	136.25	257.38
Molar Volume	18.693	20.156	19.377
Density	4.2743	3.8950	4.1230

Although other photocatalytic materials such as ZnO and CDS have been used, TiO_2 continues to hold a dominant position in photo-catalysis. Interestingly, according to numerous reports [6], [53] the activity of the anatase phase of TiO_2 for photo degradation of various pollutants is in general much higher than that of rutile. It has been shown that the photocatalytic activity of TiO_2 is influenced by the crystal structure, surface area, crystallinity and porosity [9], [20], [39].

All of the extensive knowledge that was gained during the development of semiconductor photo-electrochemistry during the 1970 and 1980s has greatly assisted the development of photo-catalysis [21]. In particular, it turned out that TiO_2 is excellent for photo-catalytically breaking down organic compounds. For example, if one puts catalytically active TiO_2 powder into a shallow pool of polluted water and allows it to be illuminated with sunlight, the water will gradually become purified [18].

Ever since 1977, when Frank and Bard first examined the possibilities of using TiO2 to decompose cyanide in water there has been interest in environmental applications [14]. These authors quite correctly pointed out the implications of their results for the field of environmental purification and their prediction has indeed been borne out, as evidenced by the extensive global efforts in this area [4], [13], [15], [16], [17], [21], [22], [24], [25], [26], [27], [29], [35], [36], [41], [42], [45], [46], [49], [52], [53], [54], [57], [58], [60], [62], [63], [64], [65], [66], [67].

One of the most important aspects of environmental photo-catalysis is the availability of a material such as titanium dioxide, which is close to being an ideal photo-catalyst in several respects. For example, it is relatively inexpensive, highly stable chemically and the photo-generated holes are highly oxidizing. In addition, the photo-generated electrons are reducing enough to produce superoxide from dioxygen.

The energy band diagram for TiO_2 in pH 7 solution is shown in Fig. 2**.** As shown, the redox potential for photo-generated holes is +2.53 V versus the standard hydrogen electrode (SHE). After reaction with water, these holes produce hydroxyl radicals ($\cdot OH$) whose redox potential is only slightly decreased. Both are more positive than that for ozone. The redox potential for conduction band electrons is -0.52 V which is in principle negative enough to evolve hydrogen from water, but the electrons can become trapped and lose some of their reducing power, as shown. However, even after trapping, a significant number are still able to reduce dioxygen to superoxide O_2^- or to hydrogen peroxide (H_2O_2). Depending upon the exact conditions, the holes, $\cdot OH$ radicals, O_2^-, H_2O_2 and O_2 can all play important roles in the photocatalytic reaction mechanisms.
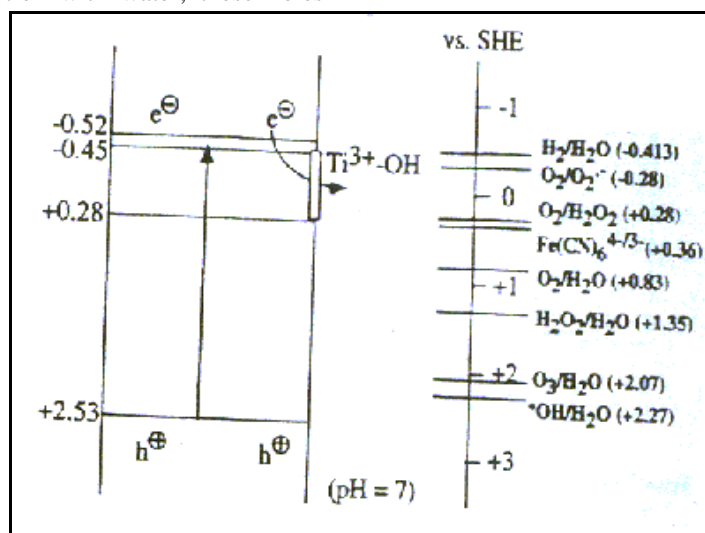

Fig. 2: Energy Diagram for TiO_2

Organic contaminants can be completely mineralized by irradiation in presence of semiconductor, TiO_2 [32], [23], [61].

1.3. Mechanism of TiO_2 catalysis

As a result of the quantized nature of photocatalytic process, there is a threshold wavelength beyond which photon absorption will be negligible. For TiO_2 this threshold is in the 380-4l0nm range. While these wavelengths are much longer than the excitation wavelengths needed for the UV/H_2O_2 and UV/O_3 processes, the match of the TiO_2 absorption profile with the solar spectrum is unfortunately rather poor [49]. Otherwise solar/ TiO_2 would be a much better candidate in terms of process economics.

Attempts to extend the TiO_2 spectral response into the red (such as via dye sensitization) have relied on initial excitation of the dye followed by subsequent electron transfer from the dye-excited state into the TiO_2 conduction band. Such strategies have yielded impressive results for photovoltaic applications [43] but are likely to be ill suited for practical applications.

Many of the photo-generated $e^- h^+$ pairs simply recombine. However, a fraction escapes to the TiO_2 surface and then reacts with the solution species or with the hydroxyl groups invariably present at oxide surfaces. Thus, species such as O_2^- and $\cdot OH$ are generated that can in turn be used to break down the pollutant. A crucial advantage with UV/ TiO_2 (unlike UV /H_2O_2 and UV/O_3*)* is that the conduction-band electrons have considerable reducing power and can be used to reduce the pollutant directly. This has been demonstrated. For example, in case of Cr (VI) to Cr (III) conversion [30], and with the simultaneous treatment of toxic metal ions and organic pollutants [48] using UV/ TiO_2.

Interestingly, the reaction pathway of TiO_2 is often different in the various treatment routes. This difference manifests itself in the type and even the number of intermediates that have been identified in various cases. For example, direct photolysis of 4-chlorophenol at wavelengths of 290 nm or greater yielded 12 primary intermediates [2]. On the other hand, only six were

detected when UV/ TiO$_2$ was used. The major intermediate product, hydroquinone was formed in amounts about 20 times greater in direct photolysis than in UV/ TiO$_2$. Incidentally, the UV/TiO$_2$ route (at longer wavelengths. above 340 nm) was faster than the direct photolysis pathway for 2- and 3-chlorophenol [2].

Stafford et al. (1994) at the University Of Notre Dame have found that the concentration of aromatic intermediates is lower for 4 chlorophenol in the UV/TiO$_2$ case compared with y-radiolysis. In general, UV/TiO$_2$ affords complete mineralization in a number of instances, although there are reports from the National Renewable Energy Laboratory (NREL) on the generation of intermediates that are even more toxic than the parent compound [38].

It is again worth noting that UV/TiO$_2$ provides one reaction route that is not available with UV/H$_2$O$_2$or UV/O$_3$) that is the reductive conversion of the substrate. This route is especially important where the OH attack mechanism has rather low rate constants, as with chloroalkanes (such as chloroform). Indeed, both oxidative and reductive conversion has been seen in some cases where UV/TiO$_2$ was used for e.g. tri and tetra chloroethylene in water [19].

II. MATERIALS AND METHODS

Commercially available TiO$_2$ (Glaxo) was used for experimental purpose. The powder was dried at 105°C for an hour followed by experimental evaluation for optimization of the process parameters and efficiencies.

Batch processes were used for the study. In batch experiments, known amounts of fresh effluents were taken in conical flasks and subjected to optimization of individual efficiency parameters such as pH, contact time, sorbent concentration, initial COD load, catalyst concentration and temperature.

pH study was carried out by equilibrating the effluents with the sorbent at different pH from 2 to 13. The pH was adjusted to the required range with HCl and/or NaOH using pH meter prior to the addition of sorbent.

The experiments for sorption studies were performed in rotary shakers by varying desired parameter of study. The reaction mixture consisted of 100 ml fresh effluents collected from the study area having variable COD loads determined separately each time and a particular dose of adsorbent. Flasks were withdrawn from the shaker at different time intervals followed by adsorbent separation using membrane filtration/centrifugation and the residual COD was determined using standard method of analysis.

III. RESULTS AND DISCUSSIONS

3.1. Effect of pH

A common feature of Photocatalytic reactions occurring on metal oxide or metal chalcogenide semiconductor powders suspended in aqueous solution is the weak dependence of the reaction on solution pH [11], [31], [50], [51].

The optimum pH for maximum COD reduction is found to be 7.0. A maximum COD reduction of 91% is achieved for highly coloured chemical mixed effluent collected from the study area.

The particle size, surface charge and band edge positions of TiO$_2$ are strongly influenced by pH [55]. The isoelectric point of TiO$_2$ in water is about pH=6 [5] and positive surface charge is expected at lower pH and negative surface charge is predicted at higher pH values. The effect of pH on the reduction of COD is represented in Fig. 3.
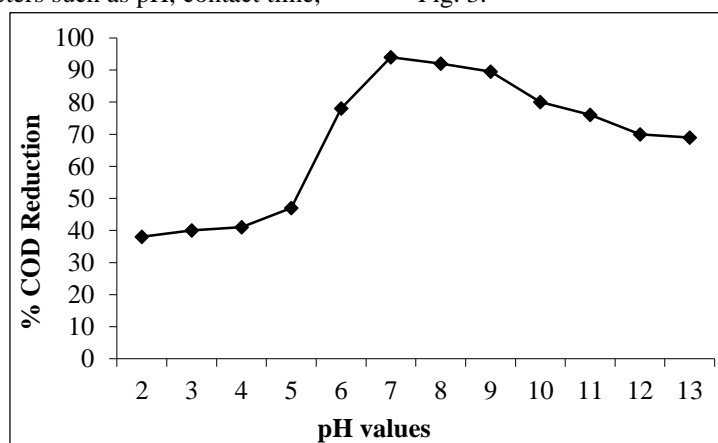

Fig. 3: Effect of pH on COD reduction.

Nonetheless, changes in rate of photo-catalysis activity from one end of the pH range to the other are usually small, often less than 1 order of magnitude. Despite clear evidence for the importance of surface charge on substrate adsorptivity, evidence for higher reaction rates for various photocatalytic conversions at both lower and higher pH can be found in literature. Total metal conversion to metallic state has been reported at pH [48]. Although the zero point

charge for TiO_2 is around 7.0, the abundance of all species as a function of pH is as follows:

When 3< pH <10   -   TiOH $\geq$ 80%
When pH>10   - $TiO^- \geq$ 20%
When pH<3   - $TiOH_2^+$

One of the most important features of photo-catalysis which is normally not taken into consideration is that when it is used for the decontamination of water, a multitude of intermediate products are produced which might behave differently depending upon pH of the solution. It was also observed that TiO_2 remained in dispersed phase in the effluents at pH 7.0. Thus the reduction in COD at different pH is varying to a great extent since the effluents subjected to TiO_2 photo-catalysis is of mixed type and may harbor a variety of synergistic and antagonistic components.

3.2. Effect of Contact Time

As seen in case of any adsorption process the TiO_2 system is contact time dependent. Initially the COD reduction seems to be directly proportional to time. However, after a particular time, the system achieves a stationary phase, and any further increase in contact time does not affect the activity of TiO_2. The equilibrium time in case of mixed effluents is found to be 60 minutes.

Fig. 4 represents the effect of contact time on the COD reduction for the mixed effluents. The reason for such behavior is the saturation of the active groups on the surface. However, as the oxidation proceeds, less and less of the surface of the TiO_2 particles are covered as the contaminant is decomposed. Evidently, at total decomposition the rate of degradation is zero and a decreased photo catalytic rate is to be expected with increasing illumination time. This is confirmed from the gradual reduction in the COD reduction rate with increase in contact time.
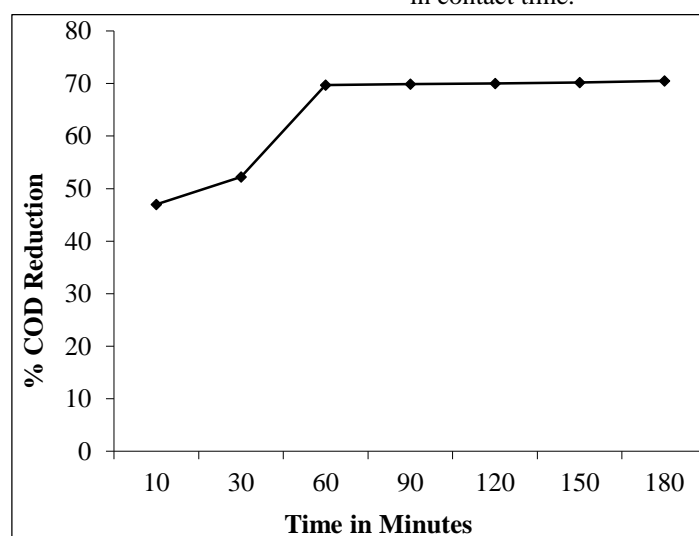

Fig.4: Effect of Contact Time on COD reduction.

3.3. Effect of Catalysts Concentration

The initial reaction rates were found to be directly proportional to catalyst mass. This is indicative of a truly heterogeneous regime. The same behavior is seen in case of the present system under consideration. The optimum catalyst dosage required for maximum COD reduction for the mixed effluents is found to be 0.5 g/l as seen in Fig. 5.

However, above a certain value i.e. 0.5 g/l, the reaction rate levels off and becomes independent of catalyst mass. This limit is achieved when all the particles i.e. the entire surface area is exposed and are totally illuminated. Then the catalyst concentration is very high, after traveling a certain distance on an optical path, turbidity impedes further penetration of light.
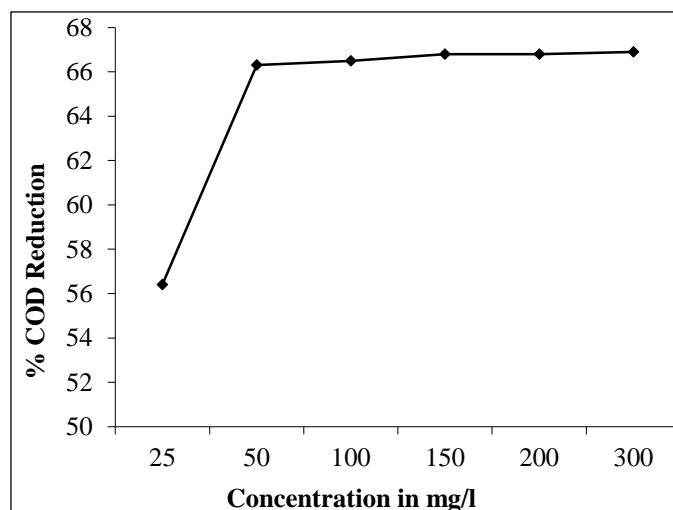
Fig. 5: Effect of Catalyst Concentration on COD reduction.

3.4. Effect of Initial COD Load

The variation in COD reduction with different initial strengths of effluents is represented in Fig. 6.
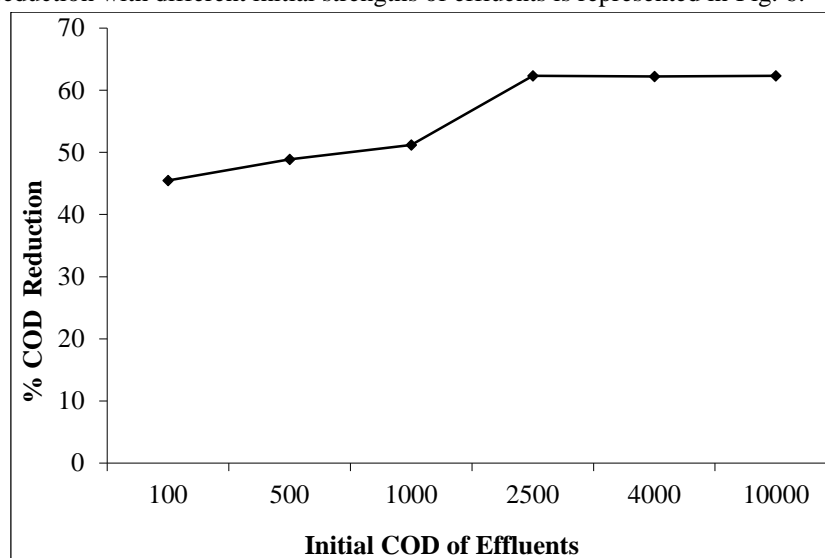

Fig. 6: Effect of Initial Effluent load.

It is observed that as the initial concentration of COD increases, there is a proportionate increase in COD reduction. However the rate of COD reduction is stabilized and independent of COD concentrations with very high loadings. The reason for independency is probably due to the saturation of the surface groups taking part in catalysis.

3.5. Effect of Temperature

Like most photoreactions, photocatalytic reactions are not dramatically sensitive to minor variations in temperature. It has been reported that the rate of photo-assisted decomposition of aliphatic alcohols was insensitive to temperature variation [10], [47]. The present system acts in the same manner as seen in Fig. 7.
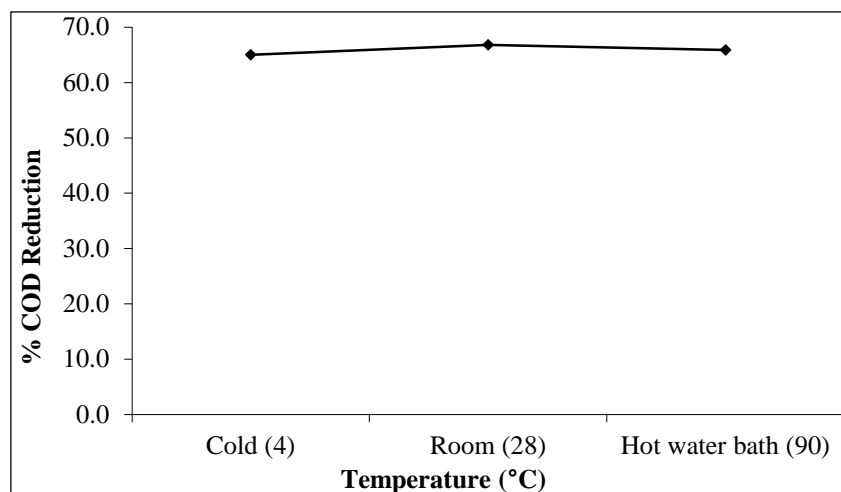
Fig. 7: Effect of temperature on COD reduction.

The optimum efficiency of the system is found to be at room temperature. Because of photonic activation the system does not require heating and hence operates at room temperature. The true activation energy is nil whereas the apparent activation energy is often very low (a few KJ/mol) in the medium temperature range (20°C to 80°C). The activity is reported to be lowered at very low temperatures (-40°C to 0°C).

IV.   CONCLUSIONS

Mixed effluents have always been a cause of concern for treatment using a common facility or an individual system. The most impressive factor making the use of this system for application in the study area is the operation at room temperature since there is no need to waste energy through heating and 92.7% material is regenerated by backwashing simply using water, which can further be improved by using centrifugation and ultra-filtration processes for recovery of the material. The ease of availability of the material in the active phase further enhances the applicability. The mode or form of application such as internal coatings to the treatment tanks and incorporation of the system in the unit processes for wastewater treatment has proven to be a boon for mixed waste treatment. Above all since the system optimizes at neutral pH conditions, it can be clubbed with the neutralization/equalization tank that forms the first step in the treatment of any effluent either of the individual industry or mixed waste at the CETP.

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