Photocatalytic degradation of phenol from industrial effluent using titania-zirconia nanocomposite catalyst
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ABSTRACT

Nowadays, there are increasingly stringent regulations requiring more and more treatment of industrial effluents to generate product waters which could be easily reused or disposed to the environment without any harmful effects. Therefore, different advanced oxidation processes were investigated for treatment of industrial effluents containing phenol. In this study, the photo degradation of phenol in an industrial effluent was studied in a batch reactor, using titania-zirconia nano composite catalyst, which was prepared by sol-gel method using titanium isopropoxide and zirconium oxychloride octahydrate. The catalysts were characterized by transmission electron microscopy and BET analysis. The industrial effluent was also characterized. The highest photocatalytic performance for the reduction of COD as well as phenol in an industrial effluent was observed for an 11.8% zirconia in a zirconia-titania nano composite under UV irradiation. A maximum COD removal of 80% from the effluent was achieved in 150 min at 25°C. The better performance of photocatalytic degradation was achieved in case of UV light than sunlight and dark condition. The reaction was influenced by the process parameters such as catalyst loading, initial pH and COD of the solution and the reaction rate was found to follow the first order kinetics. So, Photodegradation can be an alternative method for the treatment of phenol containing wastewaters.

Keywords: Titania-zirconia catalyst; Sol-gel method; Phenol based effluent; Photo catalysis, Rate kinetics

1. Introduction

The phenolic compounds are present in the effluents of various industries such as petrochemicals, petroleum refining, pharmaceuticals, papers and resin manufacturing industries. The contamination of water bodies with phenol causes significant environmental problems due to its high toxicity and carcinogenic nature (Yavuz et al., 2006). Exposure to phenolic compounds can cause liver damage, hemolytic anemia, paralysis and severer damage to the internal organs in human body. As per the Environmental Protection Agency the maximum allowable limit for the concentration of phenol in water is restricted to 1-5 mg/L (Gupta et al., 2006). Therefore, attention should be given to reduce the concentration of phenols in industrial effluents below the allowable limit.

Several conventional processes such as, chemical oxidation (Comninellis et al., 1993; Comninellis et al., 1991; Cooper et al., 1996), biological treatment (Vijayagopal et al., 2008; Silva et al., 2002), wet oxidation (Su’arez-Ojeda et al., 2007; Miroa et al., 1999), activated carbon adsorption (Qadeer et al., 2002), chlorination (Gea et al., 2008), solvent extraction (Egorov et al., 2008) and membrane process (Lee et al., 2008) may be employed for the
removal of phenol from industrial effluents. These processes have some major drawbacks such as they are sensitive to operating conditions and tendency to the formation of secondary toxic materials (Busca et al., 2008). In recent years, a new treatment technology, known as Advanced Oxidation Processes (AOPs), capable of the destruction of a wide range of organic compounds was developed (Munter, 2001; Poyatos et al., 2010). Alternatively, a novel and economical advanced oxidation technique; the semiconductor mediated photo-catalysis is a promising technology for the treatment of organic contaminants in wastewater (Mills et al., 1993; Sobczynski et al., 2001; Ray et al., 1998). In this approach, harmful organics are degraded in the presence of a catalyst and ultraviolet (UV) irradiation without generating secondary harmful pollutants. It has been extensively studied during the last few years because of its ability to totally oxidise organic molecules at a low energy cost (Linsebigler et al., 1995; Robertson et al., 1996). Titania (TiO$_2$) is found to be an effective photocatalyst with various advantages such as its high activities, low prices and property of tolerating chemical and photo corruptions. It is non-toxic, has excellent biological and chemical inertness, and stability. The UV irradiation of titania upon incidence of photon with an energy higher than its band gap energy results in the formation of electrons (e$^-$) in the conduction band and positive holes (h$^+$) in the valence band, as well as the formation of OH radicals. The OH radicals are responsible for degradation of pollutants (Sayılıkan et al., 2006). But, titania has some disadvantages like lower interface and easy recombination of the h$^+$/e$^-$ pair. Moreover its activity is still not high enough to be suitable for commercial application (Yanqing et al., 2001). In order to enhance the activity of catalyst, many efforts have been paid to modify titania by adding some transition metals (Hernandez-Alonso et al., 2009; Zaleska, 2008; Silija et al., 2012; Vinodgopal et al., 1996; Chen et al., 2002; Klosek et al., 2001; Wang et al., 2003). It has been found that the addition of zirconia could enhance the catalyst activity significantly. Another way to enhance the photocatalytic activity is the coating and doping of other materials, including metal ions and semiconductors, onto the surface of titania nanoparticles. The coupling of two semiconductors provides a novel approach to achieve a more efficient charge separation, an increased lifetime of the charge carriers, and an enhanced interfacial charge transfer to adsorbed substrates. Different methods (Reddy et al., 2005; Mao et al., 2003) are available for the preparation of titania-zirconia (TiO$_2$/ZrO$_2$) catalyst among these methods, preparation of titania-zirconia catalyst has been done by sol-gel process because sol-gel process has notable advantages such as good product purity, good uniformity and low temperature synthesis, easily controlled kinetics and process can generate hybrid materials that do not exist naturally (Tiejun et al., 2009; Tseng et al., 2010; Akpan et al., 2010).

In the present work, a nanocomposite catalyst of titania and zirconia has been developed by sol-gel method and characterized. The degradation of phenol in an industrial effluent by photocatalytic reaction with prepared catalyst has been studied. The effects of different process parameters and kinetic study are included in this study.

2. Materials and methods

2.1 Materials and catalyst preparation

Titanium isopropoxide (Ti[OCH(CH$_3$)$_2$]$_4$) was procured from Alfa Aesar, A Johnson matthey company, UK. Zirconium oxychloride octahydrate (ZrOCl$_2$, 8H$_2$O) was procured from Loba Chemic Pvt. Ltd., India. Ethanol (C$_2$H$_5$OH), titania (TiO$_2$) and hydrochloric acid (HCl) were procured from Merck Specialties Private Limited, India. The raw effluent was obtained from liquid phenol-formaldehyde resin plant (Allied Resins & Chemicals Limited, Kolkata. The
plant produces liquid resins by the condensation polymerization reaction of phenol and formaldehyde. It was used as a material in this study.

For the preparation of catalyst, titanium isopropoxide and zirconium oxychloride octahydrate were the raw materials. Desired quantity of titanium isopropoxide and anhydrous ethanol were premixed for 45 min by stirring with a magnetic stirrer. Next a certain amount of zirconium oxychloride octahydrate was dissolved in distilled water to form a solution. Under vigorous stirring, the solution is added drop-wise into the previous mixture. Appropriate amount of diluted hydrochloric acid was added to adjust the pH of the solution to 2. The resultant sample was dried at 120°C. Then, the composite powders are calcined at 500°C in a furnace for 3 h (Jung et al., 2004). A series of samples with different mass ratio of Zr/Ti are prepared with different zirconia content such as 6.3%, 11.8% and 24.4% and these were denoted by by Zr/Ti-1, Zr/Ti-2 and Zr/Ti-3 respectively.

2.2 Characterization of catalyst and the industrial effluent

The composite catalysts as well as titania were characterized by transmission electron microscopy (TEM) (JEOL, JEM-2100, Japan) and BET surface area analyzer (Quantachrome, AUTOSORB –1C, USA). TEM was used to determine the morphology and particle size of the catalyst samples. Specific surface area and pore volume of the calcined samples were determined by BET surface area analyzer. Chemical composition of all catalysts was also measured. The effluent was also analyzed its composition was listed in Table 2.

2.3 Photocatalytic reaction process

The photo catalytic degradation of phenol in an industrial effluent was studied in a 500 ml glass reactor. An ultraviolet C light (8 W, 218 nm, Philips, Holland) is placed inside a quartz tube mounted centrally on the axis of the reactor and annular spaced between quartz tube and reactor vessel is used for the reaction. The reaction mixture is agitated by sparging air at the bottom of the reactor. The diluted industrial effluent containing 120 mg/L of phenol of volume 250 ml with a require amount of catalyst is taken in the reactor and air is dispersed at flow rate of 0.25 LPM. The sample was taken at the specific time intervals and was analyzed by UV-vis spectrophotometer (Chemito, India, Model 2600).

3. Results and discussion

3.1 Characterization of catalysts

The morphology of nanocomposite particles are analyzed by TEM technique and shown in the Figure 1 from the figure, it is found that the particles are roughly spherical in shape and almost uniform in size with narrow size distribution. The presence of macro voids and agglomeration of the particles are clearly observed in the figure. It has been observed from the TEM micrograph that the materials are partly composed of clusters containing composite nano particles adhering to each other with a mean size of about 8 nm and the size of TiO$_2$ particles are roughly of 20 nm. The figure also suggests that the incorporation of ZrO$_2$ inhibits the growth of crystallites which leads to the smaller particle size with an increase in the amount of ZrO$_2$ loading.

The catalysts were analyzed for BET and the results are shown in Table 1. BET surface area of titania-zirconia composites depend on the quantity of Zr$^{4+}$. The largest surface area (190m$^2$/g) and pore volume were observed for Zr/Ti-2. It has also been noticed that the pore
volume increases with the increase of Zr content up to Zr/Ti-2 and decreases in Zr/Ti-3 with further addition of more Zr\(^{4+}\). The quantitative analysis of the catalysts are shown in Table 1.

3.2 Selection of catalyst

The photocatalytic activity for titania and various titania-zirconia composite catalysts are presented in Figure 2(a). It is noted that the degradation of phenol is higher for Zr/Ti-2 than other composite catalysts and titania without zirconia. Moreover, the reaction rate of phenol removal for different catalysts in case of 1:1 diluted effluent is shown in the Figure 2(b). The selection of catalyst was performed by comparing the degradation rate for various catalysts determined based on the pseudo-first-order kinetic model:

\[
-r_A = \frac{d[C_{\text{phenol}}]}{dt} = kC_{\text{phenol}}
\]

Where, \(C_{\text{phenol}}\) is the initial concentration of phenol in effluent. The initial rate for the phenol degradation reaction with various Zr-Tr composites were determined from the corresponding concentration versus time plot and the rates were fitted to the first order kinetic model to find the apparent rate constant (k). It is observed that the Zr/Ti-2 shows the better performance than the other Zr-Ti composites in terms of the initial rate and apparent rate constant. Basically, the photocatalytic activity depends on the surface and structural properties of the catalyst such as crystal composition, surface area, particle size distribution, porosity, band gap and surface hydroxyl density. Particle size is a primary importance in heterogeneous catalysis, because it is directly related to the efficiency of a catalyst through the definition of its surface area. The increase in the particle size decreases the net available surface area of the catalyst, which in turn decreases the number of available active sites for the reaction. The results of the BET experiments show both the higher pore volume and a surface area of Zr/Ti-2 nano composite. Hence, the Zr/Ti-2 was chosen as the best catalyst for the photocatalytic reaction.

3.3 Effect of photocatalyst loading

Photocatalytic degradation of phenol in industrial effluent was studied by varying the catalyst loading from 0.15gm/L to 0.5gm/L. A set of experiments were conducted under UV light with the industrial effluent at a 1:1 dilution in neutral pH. The results are shown in Figure 3. Here, the photocatalytic degradation is observed to increase as the catalyst loading increases and the percentage removal of phenol reaches to a maximum for a catalyst loading of 0.35gm/L. Beyond 0.35gm/L, the degradation further decreases (shown in the inset of Figure 3). The initial rise in percentage removal of phenol may be explained by the increase in number of active sites available on the surface of photo catalysts. The low photocatalytic reaction rate at catalyst loading of 0.15gm/L is due to less availability of active sites. However, the large number of active sites with the increase of catalyst loading upto 0.35 gm/L, the rate of radical formation in the aqueous solution increses. For to high catalyst loading beyond 0.35 up to 0.5gm/L, the photocatalytic reaction rate reduces. It may be due to light scattering effect and reduction in light penetration through the effluent due to the obstruction of large number of solid particles.

3.4 Effect of concentration

The effect of initial concentration on the removal of phenol is shown in Figure 4(a). It is noted that the percentage removal of phenol decreases as the initial concentration of phenol increases. It is observed that the percentage removals of phenol at 150 min become 85.18%.
83.71%, 82.5% and 77.94% at 1:3, 1:2, 1:1 and zero dilution (raw effluent) respectively. A possible reason for increasing degradation of phenol may be due to the decrease in the formation of hydroxyl radicals on the catalyst surface with the increase in phenol concentration and at the same time the available active sites decrease by the increase of adsorbed phenol on the catalyst surface, which inhibits the direct contact between phenol and hydroxyl radicals. The initial reaction rate also increases with the increase in initial phenol concentration which is shown in Figure 4(b). The reason for this can be explained by considering the formation of hydroxyl radicals in water by the irradiation. For a given irradiation sample and time, it can be expected that the production of OH• radicals remains constant. Under such conditions the extent of reaction between hydroxyl radicals and phenol molecules increases.

3.5 Effect of pH on the removal of phenol

Photo catalytic experiments were carried out varying the initial pH ranging from 3 to 12. After 150 minutes the percentage removal of phenol is 89.73, 85.09, 82.42, 65.12 and 45.63 at 3, 5, 7, 10 and 12 respectively as shown in Figure 5. It is observed that the percentage removal of phenol is higher under acidic medium. The reason is that the pH affects the surface charge for the photocatalyst as well as the organic pollutants.

\[
\text{Catalyst} + \text{H}^+ \rightarrow \text{Catalyst}^+
\]

\[
\text{Catalyst} + \text{OH}^- \rightarrow \text{Catalyst}^- + \text{H}_2\text{O}
\]

Considering the negative charge of phenol and the positive charge of the immobilized catalyst surface, the electrostatic force of absorption exist when these phenol- anions are more likely located at the positive sites. So, the photocatalytic degradation efficiency is higher at acidic medium and confirmed to have better degradation efficiency than either alkaline or neutral media. In alkaline solution, the electrostatic repulsion presents itself between the negative surface of the photocatalyst and the organic pollutants (phenol). On the other hand, the presence of the electrostatic repulsion also retards the adsorption and decreases the phenol degradation efficiency. So, the change in pH can be chosen accordingly to have the maximum efficiency of removal of organic pollutants.

3.6 Effect of irradiation time on the removal of phenol

The required duration for the complete photocatalytic reaction was also observed. The reaction irradiation time was varied from 1 h to 4 h under the UV light source by loading of 0.25 g/L catalyst into 250 mL of 1:1 diluted effluent. Results represented that phenol removal efficiency increases with time as shown in Figure 6 and photocatalytic reaction of the industrial effluent needs longer irradiation time due to the fact that these effluents commonly contain high molecular weight and complex structured organic pollutants such as phenols and so many phenolic compound and they are not directly converted into CO₂ under photo catalytic reactions. These molecules first disintegrate to different molecules those are called secondary pollutants and photo degradation of these secondary pollutants required long irradiation time for the complete conversion into CO₂ and mineral salts.

4. Comparison of the phenol removal from synthetic solution with an industrial effluent

The percentage removal of phenol from synthetic aqueous solution as well as from the industrial effluent was investigated. The reaction was carried out at initial concentration of
phenol 60 mg/L and the industrial effluent was diluted to obtain the concentration of phenol as same as the synthetic solution. The plot of percentage removal as a function of time is shown in Figure 7. It is observed that the percentage removal of phenol is 95.47 and 82.42 for the synthetic solution and effluent at 150 min. The degradation of phenol is less for industrial effluents because of the presence of other complex structured organic compounds and they are not directly converted into CO$_2$ under photo catalytic reactions. But in the synthetic aqueous solution pure phenol is used and the degradation rate is higher than the case of industrial effluent.

### 4.1 Effect of oxygen supply

The influence of photo generated electron scavenger (oxygen supply) on the photocatalytic degradation of phenol in the effluent was also investigated. The photocatalytic degradation experiments were carried out for 150 min of irradiation time by adjusting pH (7.0), catalysts loading (0.25 mg/L), reactant concentration (1:1 dilution) and temperature (30$^\circ$C) as constant. For the photo generated electron scavenger, the air was bubbled into the experimental solution continuously using a compressor which acts as a source of oxygen. A set of photocatalytic degradation experiments were also carried out without supplying air under the same experimental conditions to know the influence of oxygen supply on the photocatalytic degradation. Figure 8 shows the influence of oxygen on the percentage removal of phenol with respect to time under different light sources such as UV light, sun light and dark place in the form of histogram. From the figure it is observed that the percentage removal of phenol is higher in presence of air, i.e. at oxygen supply than without air supply. It is seen in the figure that the phenol removal is also higher in presence of UV light than the reaction carried out in sun light. It is due to the presence of oxygen is known to be beneficial in the photocatalytic degradation systems and supplied oxygen acts as photo generated electron scavengers, which forms superoxide radicals and it has provided more sites for photo generated electrons to be efficiently transferred away from the photocatalysts to subsequently interact with oxygen or to react with other electron acceptors in the system. Either path leads to improved charge separation so that the more numbers of photos generated holes are available to take part in the photo oxidation reactions (Eq. (2) – (10)).

\begin{align*}
\text{UV} + \text{photocatalyst} & \rightarrow \text{photocatalyst}(h^+ + e^-) & (2) \\
\text{photocatalyst}(e^-) + O_2 & \rightarrow O_2^- & (3) \\
O_2^- + 2H^+ & \rightarrow H_2O_2 & (4) \\
H_2O_2 + \text{photocatalyst}(e^-) & \rightarrow 'OH + HO^- & (5) \\
O_2^- + H_2O_2 & \rightarrow 'OH + HO^- + O_2 & (6) \\
O_2^- + H^+ & \rightarrow 'HO_2 & (7) \\
'HO_2 + \text{photocatalyst} (e^-) & \rightarrow HO_2^- & (8) \\
HO_2^- + H^+ & \rightarrow H_2O_2 & (9) \\
2'HO_2 & \rightarrow O_2 + H_2O_2 & (10)
\end{align*}
4.2 COD measurement at various effluent concentrations

The photocatalytic experiments were undertaken with various effluent concentrations under UV light at pH 7 with a 0.25gm/L of catalyst loading for 150 minutes. The COD of solution was estimated before and after the reactions. Based on the COD values, the photo catalytic degradation efficiency was calculated by using the equation:

\[
\text{Degradation efficiency} = \left(\frac{\text{Initial COD} - \text{Final COD}}{\text{Initial COD}}\right) \times 100\% \quad (11)
\]

The results of COD removal at various effluent concentrations are shown in Table 3. It is observed that the initial concentration increases as the degradation efficiency decreases up to 1:2 dilution, whereas at 1:2 and 1:3 dilutions, the degradation efficiency remains constant. It may be due to the fact that as the concentration of the effluent decreases with dilution 1:2 the availability of the light intensities will be more as less molecules are present in the solution and due to this fact the degradation efficiency increases at this dilution. Whereas for the dilutions of 1:2 and 1:3, the constant value of degradation efficiency is observed. Under this condition, the effluent concentration exceeds the concentration of hydroxyl radicals produced by water irradiation beyond 1:2 dilutions and the effluent itself will start acting as a filter for the incident light. It will not permit the desired intensity of light to reach the catalytic materials.

4.3 Effects of light sources on COD removal of phenol based effluents

The effect of light sources on the photocatalytic degradation efficiency was studied under different light sources. The degradation was also carried out in absence of light under identical process conditions such as, temperature, catalyst loading, and pH to observe the importance of light in presence of same photocatalyst. The UV light source of intensity of 2.3775 x 10^{15} \text{ quanta sec}^{-1} \text{m}^{-2} was also compared with the sunlight whose average intensity is 2.918 x 10^{15} \text{ quanta sec}^{-1} \text{m}^{-2}. The results presented in Table 2 show that the COD removal and degradation efficiency for UV light source (70.05%) is greater than that of sunlight (63.52%) for reaction time 150 min and the reaction conducted in dark shows very poor degradation efficiency of 25 %. Due to the lower rate of electron hole formation by the low absorption of photon energy in presence of sun light, the degradation efficiency is lower. Whereas, in case of UV light source, the rate of photoelectron and photo-hole generation is predominant and the rate of recombination of photo-electron and photo-hole is negligible, which results in higher degradation efficiency. In case of dark condition, there will be absence of photon energy for the activation of catalyst and the photo-electron and photo-hole generation or recombination will not occur on the photocatalyst.

5. Conclusion

The titania-zirconia nano composite catalyst exhibits higher activity than titania for the photocatalytic oxidation of phenolic contaminants under UV–vis light. The pore volume and BET surface area of titania-zirconia nanocomposite catalyst are high compared to the titania catalyst and improve the photocatalytic activity. The findings from the study also suggest that various operating parameters such as initial concentration, amount of catalyst, initial pH and irradiation time of the reaction medium can influence significantly the photocatalytic degradation of phenols. Photo catalytic degradation efficiency was gradually increased up to catalyst loading was 0.35gm/L and then the photocatalytic degradation efficiency slightly decreased at 0.5gm/L of catalyst using. The phenol degradation efficiency decreased as the
initial phenol concentration increased and the percentage removal of phenol was higher in acidic than basic medium.

References


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Figure 1: TEM image of catalysts (a) TiO$_2$ only (b) Zr/Ti-2

![TEM image of catalysts](image)

![Graph showing removal of phenol over time](image)
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Figure 2(a): Comparison of removal of phenol for different catalysts and (b) Comparison of Initial rate for different catalysts

Figure 3: Effect of photocatalyst loading on phenol degradation as a function of time and the inset represents the initial rate versus catalyst loading for 1:1 diluted effluent
Photocatalytic degradation of phenol from industrial effluent using titania-zirconia nanocomposite catalyst

Figure 4(a): Initial concentration effects for phenol removal: (a) removal of phenol-time profiles and (b) initial rate versus initial concentration of effluent at 0.25 gm/L catalyst loading
Figure 5: Effect of pH on phenol degradation as a function of time

Figure 6: Effect of irradiation time for phenol removal
Photocatalytic degradation of phenol from industrial effluent using titania-zirconia nanocomposite catalyst

Figure 7: Phenol degradation from various sources

Figure 8: Effect of aeration on the photocatalytic degradation efficiency under different light sources
Table 1: BET surface analyzer and quantitative analysis data of all catalysts

<table>
<thead>
<tr>
<th>Type of Characterization</th>
<th>Catalysts</th>
<th></th>
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<tbody>
<tr>
<td>a) BET surface analyzer</td>
<td>Zr/Ti-1</td>
<td>Zr/Ti-2</td>
<td>Zr/Ti-3</td>
<td>titania</td>
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<tr>
<td>BET surface area (m²/g)</td>
<td>125</td>
<td>190</td>
<td>85</td>
<td>110</td>
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<td>Pore volume (ml/g)</td>
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<td>0.72</td>
<td>0.18</td>
<td>0.34</td>
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<td>b) Chemical composition (wt %)</td>
<td>Zr</td>
<td>2.9</td>
<td>5.49</td>
<td>11.1</td>
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<tr>
<td></td>
<td>Ti</td>
<td>45.45</td>
<td>46.37</td>
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</tr>
<tr>
<td></td>
<td>O</td>
<td>51.65</td>
<td>48.14</td>
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Table 2: Composition of industrial effluent without dilution

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<td>pH</td>
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<td>Phenol</td>
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<td>Formaldehyde</td>
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<td>TS (total solid)</td>
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<td>TSS (total suspended solid)</td>
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Table 3: COD measurements of effluent at different concentrations

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<table>
<thead>
<tr>
<th>Concentration (effluent solution) (mg/L)</th>
<th>Initial COD</th>
<th>Final COD</th>
<th>% Removal of COD</th>
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<td>Undiluted (raw effluent)</td>
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<tr>
<td>1:1 dilution</td>
<td>1425</td>
<td>274.31</td>
<td>70.05</td>
</tr>
<tr>
<td>1:2 dilution</td>
<td>950</td>
<td>135.37</td>
<td>75.76</td>
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<td>1:3 dilution</td>
<td>618</td>
<td>29.16</td>
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**Table 4:** Table showing the photocatalytic degradation efficiency (η) of 1:1 diluted effluent with under different light sources

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<th>Irradiation time(min)</th>
<th>UV light</th>
<th>COD (mg/L)</th>
<th>η (%)</th>
<th>Sun light</th>
<th>COD (mg/L)</th>
<th>η (%)</th>
<th>Dark place</th>
<th>COD (mg/L)</th>
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