Treatment of municipal sewage wastewater by TiO$_2$ based heterogeneous photocatalysis

Sachin Madhavrao Kanawade

Abstract
This paper describes the photo catalytic degradation of organic pollutants present in them municipal sewage water by using hydrothermally prepared supported photo catalyst. TiO$_2$ deposited calcium aluminosilicate beads (CASB) supports were prepared by hydrothermal technique under mild preparation conditions. The photo catalytic degradation of organic pollutants in the sewage water was investigated under several experimental parameters such as catalyst load, pH, organic concentration, Irradiation time, aeration, stirring, and light sources. The photo catalytic removal of organics and its degradation efficiency was evaluated by determination of reduction in the chemical oxygen demand (COD) values. The organic pollutant degradation efficiency was over a wide range of pH values, irradiation time and optimum catalyst load. In additional effects like aeration and stirring increase the photodegradation efficiency of organic. Easy recovery and reuse of supported photo catalyst, along with higher degradation efficiency is the major advantages and it reduces the over treatment cost.

Keywords: Hydrothermal, Municipal sewage, Calcium aluminosilicate beads, Photocatalysis, Chemical oxygen demand, Recovery.

1. Introduction
In recent years many natural and synthetic pollutants are not generally monitored and controlled, although they are known or suspected to cause harmful ecological effects and can be deleterious to human health. Sewage water contains large amount of organic load and cause harmful effects to the surrounding environment and human life. Sewage, defined correctly, is a type of wastewater that is contaminated with urine and faeces, but the term is often used to mean any wastewater. "Sewage" includes liquid waste produced from domestic residences, institutions, and in many areas also from business properties and industry, and usually discharged via a pipe or sewer or similar structure. Residential sewage is a mixture of two fractions of wastewater, household or grey water (from baths, showers, sinks, dishwashers, kitchen, etc.) and sanitary or black water (from toilets). Frequently, one can use the term sewage meaning the municipal wastewater that consists of a broad range of contaminants resulting from the combination of wastewaters from various sources. Occasionally, this combination may also include storm water runoff. Sewage treatment, or domestic wastewater treatment, is a process for removing pollutants from sewage and consists of physical, chemical and biological processes to produce effluent and solid waste (sludge) appropriate to be released back into the environment or reused. However, both effluent and sludge often remain contaminated with toxic organic and inorganic compounds. The conventional treatment methods have failed to complete degradation of dissolved micro organic pollutants in the municipal waste water effectively. Most of the conventional treatment methods are not designed to remove trace organic contaminants and relatively high amounts of these pollutants and their metabolites can be released into the aquatic environment via effluents. They are only partially removed and can resist in conventional water treatment processes. These traditional treatment techniques take long duration for the complete degradation of organic pollutants and also highly difficult to implement for the small scale applications (at residential level). In the conventional treatment methods large amount of secondary pollutants are released to the environment such as toxic gases and odours during the biological treatment of organic pollutants and it produces large amount of sludge after treatment of waste water. Hence, it becomes necessary for a treatment process to
overcome all these shortcomings effectively by photocatalytic treatment. Photocatalytic degradation method provides a satisfactory and economically viable solution in the removal of organic pollutants and harmful bacteria in the aqueous medium (Fengna et al., 2010, Cho et al., 2005, Gomathi Devi et al., 2009, Ireland et al., 1993, Kim and Kwak, 2009, Rajeev and Shalini, 2005, Byrappa et al., 2007 and Brijesh et al., 2008). The photocatalytic degradation method is fast, effective, ecofriendly, economically viable and efficient method in the waste water treatment. Fig. 1 shows the schematic representation of the advantages of photocatalysis in the treatment of organic pollutants in waste water.

![Figure 1: Schematic diagram showing the advantages of photocatalysis in the treatment of organic pollutants in waste water](image)

Most of the photocatalytic application based studies were carried out by employing traditional approaches and methods like slurry type, particles suspended form and particles immobilization on a fixed bed. These traditional approaches have many limitations such as recovery of the photo catalysts after completion of photoreaction, agglomeration of the particles and poorly exposed to the light source. To solve these problems, many attempts have been made based on the immobilization/deposition of the photo catalysts on various supporting materials such as activated carbon, silica, zeolite, polymers and other porous materials (Selvarani et al., 2010, Phanikrishna Sharma et al., 2008 and 2010, Shivaraju et al., 2010, Okte and Sayinsoz, 2008, Neatu et al., 2009, Zhong et al., 2009 and Li et al., 2007). The present research work highlights the novel supported photocatalytic composites and their photocatalytic degradation efficiency. The active photo catalyst TiO2 was deposited on the surface of calcium aluminosilicate beads as a floating support using hydrothermal technique. The size of the CASB supports was typically in the range of 0.5 to 1 mm in diameter. CASB supports are spherical in shape and highly porous in structure along with rough surface area. The phase compositions (alumina, Cao and silica), specific surface area, porosity, low density, and surface roughness of CASB support promising for deposition of active photocatalyst (TiO2). The lower density, higher porosity and pore size distribution of CASB support enhances the deposition rate of photocatalytic materials under the hydrothermal conditions and the surface roughness of the CASB supports minimizes the Gibbs free energy.

2. Material and Method

CASB supports (0.5–1 mm in diameter) were obtained through standard ball milling technique (MTEC, Thailand) and these beads are used as a supporting material for TiO2 deposition. These CASB supports have lower density and float in water. Also they show rough surface and contain a large volume of pores. Reagent grade TiO2 of purity greater than 99.5% was obtained from Loba Chemie, India. All the reagents were used without further purification and all solutions were prepared with double distilled and deionized water. The real time municipal sewage waste water was collected from the inlet of sewage treatment plant located in outskirt of Mysore city, India. The collected real time municipal sewage water was blackish in colour and pH 9.7. As received raw municipal sewage water was filtered to separate floating and visible materials using polythene filter (1 mm in pore size).

2.1 Hydrothermal Preparation of supported Photo Catalyst

Hydrothermal preparation of TiO2 deposited CASB supported photo catalyst was carried out General Purpose autoclave provided with Teflon liner. Reagent grade TiO2 powder was used as a source of TiO2 along with 1M NaOH solution as an effective solvent. 0.25gm reagent grade TiO2 powder was taken in a Teflon liner and mixed with 25 ml of 1M NaOH of solvent and it was kept for the continuous stirring to achieve homogeneous solution. 0.5gm of CASB supports were added into the Teflon liner containing homogeneous solution of TiO2 and 1M NaOH. The CASB were floating over the saturated solution before hydrothermal treatment due to the large volume of pores in the beads. For the comparative study a set of hydrothermal experiment was carried out for the CASB support without adding TiO2 source. After that the Teflon liners were inserted into the stainless steel autoclaves and kept it for heating in a preheated furnace at 200°C for 24 h. After the hydrothermal experimental run the autoclaves were suddenly quenched to the room temperature. Teflon liners were carefully opened and in the hydrothermal experiment with TiO2 source, the run product of TiO2 deposited CASB supports settled down at the bottom of solution in the Teflon liners. But in the hydrothermal experiment without TiO2 source, the CASB supports were still float in the solvent. As obtained TiO2 deposited CASB supports were subjected to 10 to 15 min for water washing in ultrasonic water bath to remove loosely deposited TiO2 particles on the surface of CASB supports. After that the product obtained was dried in a dustproof environment to remove water completely. The dried TiO2 deposited CASB supports were used for the photocatalytic degradation of organic pollutants in the municipal sewage water as an effective supported photo...
catalyst. TiO2 deposited CASB supports are normally more efficient than TiO2 powder in the aqueous solution due to the close and rapid contact of substrate to the deposited TiO2 on supported material. The TiO2 deposited on CASB supports allow more numbers of photons hit to the TiO2 and achieved large absorption capacity under light source.

2.2 Photo Catalytic Degradation Experiment

The photodegradation treatment experiments were carried out using laboratory batch scale Photo reactor under different light sources. The photo reactor made up a reaction vessel which consisted of a standard 100 ml borosilicate glass vessel and it was kept on heating plate with temperature controlling system. The sewage water and suspended photo catalysts were continuously mixed by a magnetic stirrer using teflon coated stirrer bar. The reactor vessel was exposed to the light sources in a closed chamber provided with UV light source (Sankyo Denki, Japan, 8W) and visible light source (Philips, 230V, 15W, India). The collected municipal sewage water showed alkaline in nature and initial COD was 4200 mg/L. As received sewage water was suitably diluted in order to facilitate the enough light penetration through the solution and the initial COD of diluted sewage water showed 2980 mg/L. 50 ml of as diluted municipal sewage water was taken in the reaction vessel and suspended a known amount of supported photo catalyst. The contents of reaction vessel were continuously stirred by means of magnetic stirrer and reaction vessel was exposed to the light source in a closed chamber for 5 h irradiation. The photo degradation experiment was also carried out under the natural sunlight. In addition, a set of experiment was carried out under dark in a closed chamber to know the adsorption efficiency of the supported photo catalyst. COD was estimated for the municipal sewage water before and after the photo degradation experiments (K2Cr2O7 oxidation method) to observe reduction of carbon contents in the effluent. The reduction in COD values confirmed the destruction of organic pollutants in the sewage water during photo catalytic treatment process. The photo catalytic degradation of organic pollutants in the sewage water was evaluated by monitoring the maximum reduction of carbon content in the effluent after photo catalytic degradation. Based on the COD results the photocatalytic degradation efficiency was calculated by following Equation

\[
\eta = \frac{\text{Initial COD} - \text{Final COD}}{\text{Initial COD}} \times 100
\]

3. Results and Discussion

Photocatalytic treatment of the sewage waste water assisted by semiconductor based photo catalysts depend on various experimental parameters like amount of photo catalysts load, concentration of organic substrates, initial pH, irradiation time, aeration, stirring and different light sources (Gomathi Devi et al., 2009, Mills and Hunte, 2007, Moshe et al., 2009, Serpone and Pelizzetti, 1998). The effect of photo degradation experimental factors on the degradation efficiency of organic pollutants in the sewage water was studied using TiO2 deposited CASB supported composite.

3.1 Effect of Photo Catalyst Load

For economic removal of pollutants from the municipal sewage water, it is necessary to find the optimum amount of photo catalyst load for efficient photo catalytic degradation. The effect of photo catalyst load on the photo catalytic degradation efficiency of sewage water was studied by using hydrothermally prepared TiO2 deposited CASB supported composite. The photo catalytic degradation experiments were carried out under the UV light by varying the amount of photo catalyst load from 10 mg to 100 mg and the illumination time was fixed for 5 h. Fig. 2 shows the effect of photo catalysts load on the photo catalytic degradation efficiency. When the amount of photo catalyst load was increased in the waste water, photo catalytic degradation efficiency was significantly increased and degradation rate constant was found at 70 mg of photo catalyst load. Further increase in the amount of photo catalyst load (beyond 70 mg) does not increase the photo catalytic degradation efficiency significantly. The photo degradation rate was slightly reduced beyond the 70 mg of photo catalysts load (80 to 100 mg), this is due to the large amount of photo catalyst load in solution leads to light scattering and reduction in light penetration through the aqueous medium by decrease in transparency of sewage water. An amount of 70 mg/50 ml of photo catalyst was used for the subsequent photo degradation experiments. This observation can be explained in terms of availability of active sites on the photo catalyst surface and the penetration of UV light through the sewage water.
3.2 Effect of initial pH
pH of the aqueous solution is an important variable in the evaluation of aqueous phase mediated photocatalytic reactions. The effect of pH on the photocatalytic degradation efficiency of organic pollutants in the sewage water was studied under constant experimental conditions such as photo catalyst load (70 mg), irradiation time (5 h) and temperature (28°C). The experiments were carried out by changing in the initial pH value of diluted sewage water from 2 to 12 and the pH of sewage water was adjusted using varying concentration of HNO₃ or NaOH. All the photo degradation experiments were carried out under UV light source of intensity 2.3775 x 10¹⁵ quanta sec⁻¹ m⁻². The photocatalytic degradation efficiency was considerably increased with an increased pH of sewage from 2 to 4 (Fig. 3) and it showed higher degradation efficiency at strong acidic condition than the neutral pH. The photocatalytic degradation efficiency was significantly increased when the pH of the sewage was increases from 8 to 12 (Fig. 3) and it showed that an increased rate of degradation efficiency under strong alkaline conditions. Under acidic and alkaline conditions, the concentrations of perhydroxyl radicals and hydroxide ions are increase respectively. During catalyst based photochemical reactions, both perhydroxyl as well as hydroxyl ions produces large number of hydroxyl radicals in the aqueous medium, which effectively take part in the degradation of organic pollutants present in the sewage water. When deposited TiO₂ on the surface of CASB support contact with aqueous solution it shows amphoteric nature and the amphoteric surface functionality is the titanol and denoted as >TiOH. The hydroxyl group on the TiO₂ surface undergoes in the acid base equilibrium Equations 
\[
>\text{TiOH}^- \leftrightarrow \text{TiO}^- + \text{H}^+ \quad \text{(acidic condition)}
\]
\[
>\text{TiOH} \leftrightarrow \text{TiO}^+ + \text{H}^- \quad \text{(basic condition)}
\]
Below the neutral pH the TiO₂ surface is positively charged and above this neutral pH the TiO₂ surface is negatively charged. In particular, for organic compounds that undergo photoreaction, the variations in the pH not only influence the quantity of organic pollutants, but also surface properties of the photo catalysts. In addition the band edge energy of TiO₂ will change with pH and thermodynamically this change would lead to a change in photo catalytic degradation efficiency.

![Figure 3: Effect of initial pH on the photocatalytic degradation efficiency of organic pollutants in the sewage water](image)

3.3 Effect of Organic Substrate Concentration
The municipal sewage water commonly contains human wastes such as urea, saccharose, human urine and other organic substrates. Higher concentrations of organic load in the sewage water can dramatically slow down the photocatalytic degradation efficiency of organics in the sewage water. The effect of organic substrate concentration on the photocatalytic degradation efficiency was studied by dilution of raw sewage water in different dilution ratios (1:0, 1:1, 1:2, 1:3, and 1:4). A set of photocatalytic degradation experiment was carried out for the raw sewage water without dilution and Fig. 4 shows the effect of concentration of substrates on the photo catalytic degradation efficiency. The photo catalytic degradation efficiency was considerably increased when the concentration of organic substrate decreased in the sewage water by suitable dilution. When the raw sewage water was subjected for photo degradation without dilution the degradation efficiency was very poor due to the more scattering of light by higher concentration of organic substrate and less transmission of light through the raw sewage.
3.4 Effect of Irradiation Time
The required duration for the complete photo catalytic treatment of organic pollutants in the municipal waste water was studied based on the duration of catalyst irradiation to the light source. The catalysts irradiation time was varied from 2 h to 8 h under the UV light source by loading 70 mg of supported photo catalyst into 50 ml of diluted sewage water. In the present study the results obtained represented that highest degradation efficiency when the irradiation of photo catalyst was continued till 8 h under UV light source and the organic pollutants removal efficiency reached upto 97% for 8 h irradiation time. The photo degradation efficiency increased with respect to irradiation time of photo catalyst and the results obtained are shown in Fig. 5.

3.5 Effect of Oxygen Supply
The photo catalytic degradation rate at semiconductor surfaces depends on the photo catalytic generation and recombination of electronhole. In the present study the influence of photo generated electron scavenger on the photo catalytic degradation rate of organic pollutants in the sewage water was investigated. The photo catalytic degradation experiments were carried out at constant experimental parameters like pH (9.0), photo catalysts load (70 mg) and temperature (28°C) for 5 h irradiation duration. For the photo generated electron scavenger, ambient air was bubbled into the sewage water continuously using an air pump (AC 100240V, 12W motor) as a source of oxygen with continuous stirring. A set of photo catalytic degradation experiments were carried out without supplying ambient air at the same experimental parameters to know the influence of oxygen supply on the photo catalytic degradation rate. Fig. 6 shows the influence of oxygen on the photo catalytic degradation of organics in the sewage water with respect to time under different light sources. The complete photo catalytic degradation of organics in the sewage water was observed within 2 to 3 h, when the external air was bubbled as source of oxygen to the photo catalytic reactions. The photo catalytic degradation of organics in the sewage water takes 6 to 7 h for the complete degradation in the absence of oxygen supply (Fig. 6). This is because the presence of oxygen is known to be beneficial in certain photo catalytic degradation systems and supplied oxygen acts as photo generated electron scavengers, which forms superoxide radicals. It is believed, it has provided more sites for photo generated electrons to be efficiently transferred away from the photo catalysts to subsequently interact with oxygen or to react with other electron acceptors in the system (Gerischer and Heller, 1991). Either path leads to improved charge separation so that the more numbers of photo generated holes are available to take part in photo oxidation reactions.

![Figure 4: Effect of organic substrate concentration on the photocatalytic degradation efficiency of organics in the sewage water](image1)

![Figure 5: Effect of irradiation time on the photocatalytic degradation efficiency of organics in the sewage water](image2)
3.6 Effects of Stirring

The effect of stirring on the photo catalytic degradation of organics in the sewage water was studied under different light sources with continuous stirring in the photo reactor using a magnetic stirrer. The continuous stirring also increases the solution flow along the photo catalysts surfaces and homogeneous distribution of photo catalysts in the solution. A set of photo catalytic experiments were carried out without stirring mechanism and other experimental parameters were kept constant in all the experiment runs. Fig. 7 shows the effect of stirring mechanism on the photo catalytic degradation efficiency under different light sources. The photo catalytic degradation efficiency considerably increased with stirring process during photoreaction. Stirring creates localized turbulence near the base of the photo catalyst and enhances the micro mixing of organic substrate in the sewage water. Stirring mechanism also brings the organic pollutants into contact with photo catalysts in the aqueous solution and decreasing the boundary layer distance leading to an increase in the photo catalytic degradation efficiency of organic pollutants in the aqueous medium.
3.7 Photo catalytic Degradation of Organic Pollutants under different Light Sources
The effect of light sources on the photo catalytic degradation efficiency was studied under different light sources with different intensity. A set of experiment was carried out in a dark chamber to study the important of light for the activation of photo catalyst. All the photo catalytic experiments were conducted under the same experimental conditions such as constant temperature, photo catalyst load, pH and irradiation time. Light sources like UV light of intensity $2.3775 \times 10^{15}$ quanta sec$^{-1}$m$^{-2}$, visible light of intensity $1.7481 \times 10^{15}$ quanta sec$^{-1}$ m$^{-2}$ and sunlight of average intensity $2.918 \times 10^{15}$ quanta sec$^{-1}$ m$^{-2}$ were used for the photo catalytic degradation study. Under the UV light and the sunlight the photo degradation rate considerably increased when compared with the photo degradation rate under visible light source (Table 1). Under dark, the degradation efficiency of organic pollutants was very poor due to the lack of photon energy for the activation of deposited TiO$_2$ on CASB supports and it showed 16% removal of organic pollutants from the sewage water, it was expected due to the surface adsorption of organics by suspended photo catalyst. The incident light intensity determines the rate of photoelectron and photo hole generation and consequently photoelectron and photo hole concentration in an illuminated semiconductor. It influences not only the rate of photo catalytic degradation of organic pollutants, but also the rate of photoelectron and photohole recombination. The photo catalytic degradation efficiency of organic pollutants in the aqueous solution was very less under the visible light (Table 1) this is due to less rate of electron hole formation by less absorption photon energy in the visible light. At lower intensity, the rate of photoelectron and photo hole generation considerably decreased and it leads to a decrease in the photo catalytic degradation efficiency. The photocatalytic degradation efficiency was very high under the UV light (Table 1) because, in the medium intensity of UV light source the rate of photoelectron and photohole generation is predominant and the rate of photoelectron and photohole recombination is negligible. But in case of photo catalytic degradation efficiency under sunlight, the rate of photoelectron and photohole generation may compete with the recombination, thereby causing less photo degradation efficiency than UV light source. Without light source degradation efficiency was neglected, because, without light the photoelectron and photohole generation or recombination will not occur on the photo catalyst.

### Table 1: Table showing the photocatalytic degradation efficiency ($\eta$) and COD values of sewage water under different light source

<table>
<thead>
<tr>
<th>Irradiation time</th>
<th>COD (mg l$^{-1}$)</th>
<th>UV light</th>
<th>COD (mg l$^{-1}$)</th>
<th>Visible light</th>
<th>COD (mg l$^{-1}$)</th>
<th>Sunlight</th>
<th>COD (mg l$^{-1}$)</th>
<th>Dark place</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>2487</td>
<td>0</td>
<td>2487</td>
<td>0</td>
<td>2487</td>
<td>0</td>
<td>2487</td>
<td>0</td>
</tr>
<tr>
<td>1 h</td>
<td>1591</td>
<td>36</td>
<td>1890</td>
<td>24</td>
<td>1517</td>
<td>39</td>
<td>2288</td>
<td>8</td>
</tr>
<tr>
<td>2 h</td>
<td>1044</td>
<td>58</td>
<td>1417</td>
<td>43</td>
<td>994</td>
<td>60</td>
<td>2213</td>
<td>11</td>
</tr>
<tr>
<td>3 h</td>
<td>596</td>
<td>76</td>
<td>1044</td>
<td>58</td>
<td>621</td>
<td>75</td>
<td>2188</td>
<td>12</td>
</tr>
<tr>
<td>4 h</td>
<td>373</td>
<td>85</td>
<td>746</td>
<td>70</td>
<td>472</td>
<td>81</td>
<td>2114</td>
<td>15</td>
</tr>
<tr>
<td>5 h</td>
<td>149.2</td>
<td>94</td>
<td>522</td>
<td>79</td>
<td>271</td>
<td>89</td>
<td>2089</td>
<td>16</td>
</tr>
</tbody>
</table>

3.8 Recovery and reuse of supported photo catalyst
The recovery of the suspended photo catalyst after photo catalytic treatment in the aqueous medium is very difficult and it is one of the major problems in the photo catalytic treatment of waste water. In the present work the recovery of the suspended photo catalyst was easily achieved by common filtration method using polythene microfilters. Easy recovery of the catalysts from the aqueous solution after photo catalytic treatment is the major advantage of the deposition of TiO$_2$ on the supporting material. The photo catalytic degradation efficiency of once, twice and thrice recycled supported photo catalyst was carried out under UV light. Recovered supported photo catalysts were washed in ultrasonic water bath and dried in a hot air oven at 80-100°C for 12 h in each experimental run. Recycled TiO$_2$ deposited CASB supports by once, twice and thrice recycled has shown 90%, 87% and 81% of photo degradation efficiency respectively for about 5 h irradiation time (Table 2). These tests showed that the photo catalytic treatment efficiency of recycled photo catalyst is almost nearest to the photo catalytic treatment efficiency of fresh photo catalyst. Thus, TiO$_2$ deposited CASB supports can be recycled without causing any decline in the photo catalytic activity. These results indicate economic advantages of hydrothermally prepared supported Photo catalyst in degradation of organic pollutants in the municipal sewage and such procedure reduces the treatment cost.

### Table 2: Table showing the photocatalytic degradation efficiency of recovered supported photocatalyst under UV light source

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>Photocatalytic degradation efficiency ($\eta$) under UV light of 5 h irradiation time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial COD in mg l$^{-1}$</td>
</tr>
<tr>
<td>Once recycled photocatalyst</td>
<td></td>
</tr>
<tr>
<td>Twice recycled photocatalyst</td>
<td></td>
</tr>
<tr>
<td>Thrice recycled photocatalyst</td>
<td></td>
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<tr>
<td>Fresh photocatalyst</td>
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</table>
4. Conclusion
A simple method of photo catalytic degradation of organic pollutants by using hydrothermally prepared supported photo catalyst is described. Photo catalytic degradation of organic pollutants in the municipal sewage water studied under different experimental factors and moderate experimental conditions have been proposed for the effective degradation of organic pollutants. Hydrothermally prepared supported photo catalyst (Both fresh and recovered) showed higher degradation efficiency under UV light as well as under natural sunlight. Easy recovery and reuse of as recovered supported photo catalyst in several treatment cycles are the major advantages along with higher degradation efficiency.

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6. References