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Preparation and characterization of supported photocatalytic composite and its decomposition and disinfection effect on bacteria in municipal sewage water

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ABSTRACT

TiO_2/CASB composite was prepared by straight forward mild hydrothermal processes. As prepared photocatalytic materials were characterized by powder X-ray diffraction (XRD), Scanning Electron Microcopy (SEM), Fourier Transform Infrared spectroscopy (FTIR), Positrons Annihilation Lifetime Spectroscopy (PALS) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) to assess their physicochemical properties. Their photocatalytic decomposition and disinfection activity of bacteria in municipal sewage water was studied. The XRD studies reveal the presence of TiO_2 in the form of anatase phase in the supported composite. The XRD studies further suggested that well crystalline form of TiO_2 onto calcium alumino silicate beads (CASB) supports. FTIR results revealed the presence of Ti-O-Si linkages in the TiO_2/CASB composite, which are responsible for its higher photocatalytic activity in the destruction of bacterial mass in the sewage water. TiO_2 deposited CASB composite showed drastic reduction in the colony forming unit (CFU) of sewage water with UV light.

KEYWORDS

Hydrothermal;
Photocatalytic;
Disinfection;
Sewage water;
Composite.

INTRODUCTION

In the field of preparation of photocatalyst, there is lots of growing interest on the preparation of highly active and easily recoverable metal oxides for the exploration, either as photocatalysts or as catalyst supports[1-5]. The degree of physicochemical and the catalytic activity of the photocatalysts are highly influenced by the preparation methodology[3]. Sol–gel[6], metal oxide chemical vapor deposition[7], spry deposition[8], atomic layer deposition[9], chemical reduction method[10], and decomposition of the precipitates obtained by non-aqueous precipitation method[11] are some of the common preparation methods. Among these methods, hydrothermal technique is most widely used due to its promising capability in controlling the textural and surface properties of the photocatalyst. Furthermore, all the wet chemical methods in general, to some extent, still need calcinations at relatively higher temperatures along with longer duration of soaking to obtained final products with good crystallinity. Since raising the calcinations temperature and prolonging the soak time makes the crystalline grains grow larger in size and weaken the reactivity, obtaining nanosized particles has been difficult. Recently, hydrothermal synthesis has emerged as an effective catalyst synthesis route, which is simple and economic. This process does not require any complicated procedure and expensive experimental set up. The products obtained do not require further high temperature treatment or calcinations or sintering, etc., which in turn leads to conservation of time and energy[12,13]. Several research articles report the sterilization and decomposition using this novel photocatalytic technology for disinfecting drinking water and removing bioaerosols from indoor air environments[14-16]. Killing of cancer cells with the TiO_2 photocatalyst for medical applications has also been reported[17]. Since photo-electrochemical disinfection with platinum doped TiO_2 was first reported almost 20 years ago[18], many photocatalytic-inactivation studies with TiO_2 have been conducted. In the present work, TiO_2 deposited CASB supports were prepared under mild hydrothermal conditions. Highly photocatalytic active and well crystallized TiO_2 particle were well deposited on the surface of CASB to increase the photocatalytic performance and easy recovery of suspended catalysts after completion of photocatalytic reaction. As prepared TiO_2 based supported photocatalysts were used for the decomposition of bacterial mass present in the municipal sewage water.

MATERIALS AND METHODS

Material preparation and characterization

TiO_2 deposited CASB supporting photocatalytic composite was prepared by hydrothermal technique using general purposes autoclaves. Schematic diagram of general purposes autoclaves provided with Teflon liner is shown in Figure 1. In a typical experiment a known amount of reagent grade titanium oxide powder (Aldrich, USA) was taken in a Teflon liner and adds a known volume of 1M HCl solution and stirred well to get homogeneous solution. Then a known amount (Same amount of TiO_2 powder) of CASB supports (MTEC, Thailand) was added into the solution. Teflon liner was tightly closed and inserted into the stainless autoclave, then placed inside the preheated furnace. The hydrothermal temperature was fixed at 200 ^{O}C for 24 h experimental duration. After the experimental run, the autoclave was suddenly quenched to room temperature by blowing air using air jet and the products obtained was carefully recovered from the Teflon liners. As obtained product was washed continuously with double deionized water, ultrasonicated and dried at room temperature.

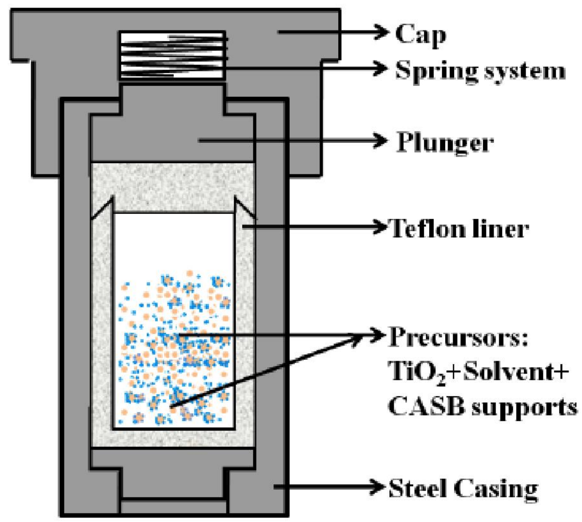


Figure 1 : Schematic diagram of general purposes autoclaves provided with teflon liner

As prepared supported photocatalysts were characteristics by using powder X-ray diffraction (Model-MAC Science Company Limited, Japan) with Bragg's angle ranging from 10–70°. The strongest peaks corresponding to TiO_2 were selected to evaluate the crystalline phases and identification of the crystalline phases was compared with JCPDS using PCPDF Win version 2.01. General morphology and structural details of TiO_2 deposited onto CASB supports were determined using scanning electron microscope (Hitachi, Model S-4000, Japan). Functional group and structural elucidation of the hydrothermally prepared TiO_2 deposited onto CASB supports were characterized by the Fourier transform infrared spectroscopy in the range of 400–4000 cm^{-1} (JASCO-460 PLUS, Japan.). The pore volume and the positron lifetime measurements of were studied by the positron annihilation lifetime spectroscopy and the pore size has been evaluated as per the Jean model[19]. The amount of TiO_2 deposited onto CASB supports under the hydrothermally conditions was determined by using inductively coupled plasma mass spectrometer (Model ICP-MS/ELAN-6100).

Photocatalytic experiment

The real time sewage water was collected from the municipal sewage waste water treatment plant located in southern part of Mysore city using polythene bottle. As collected sewage water was filtered to remove suspended solids and suitably diluted with distilled water so that the total number of colonies on a plate will be 30 to 300. The photocatalytic experiments were carried out by using batch photoreactor under the UV light source for decomposition of total bacterial contents in the sewage water. A small scale batch photoreactor setup includes a borosilicate reaction vessel placed on the magnetic stirrer and reaction vessel was covered with a thin glass lid to avoid contact with the ambient conditions. 50 ml of as diluted municipal sewage water was taken in the reaction vessel and suspended 80 mg of supported photocatalyst. 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 provided with UV light source (Sankyo Denki, G8T5, 8W, Japan,) for 4 to 5 h irradiation. Evaluation of bacterial concentration in the sewage water was determined by the standard plating method (pour plate method) using nutrients agar medium. During the determination of total bacteria, 1 ml of sewage water which was subjected to the photocatalytic experiment was pour into each sterilized petri dish using 1 ml sterilized pipette before adding melted culture media. Pour at least 10 to 12 ml liquefied medium maintained at 44 to 46°C into each petri dish by gently lifting cover just high enough to pour. Carefully avoid spilling medium on outside of container or on inside of dish lid when pouring. When pouring agar from flasks that have been held in a water bath, wipe with clean paper towel and flame the neck before pouring. As each plate is poured mix melted medium thoroughly with test portions in petri dish, taking care not to splash mixture over the edge, by rotating the dish first in one direction and then in the opposite direction, or by rotating and tilting. Do not let more than 20 min elapse between starting pipetting and pouring plates. Let plates solidify (within 10 min) on a level surface. After medium solidifies, invert plates and place in incubator for 24 -48 h at 36^{O}C. Check sterility of medium and dilution water blanks by pouring control plates for each series of samples (blank). After incubation time all the colonies obtained were counted on the selected portion using microscope. Then calculate the bacterial concentration per milliliter using following formula:

$$\mathbf{CFU / mL} = \frac{\textbf{Colonies counted}}{\textbf{Actual volume of sample in dish in mL}}$$

Where CFU is colony forming unit

Evaluation of bacterial concentration in the sewage water was determined both before and after photocatalytic experiments. Effect of photocatalysts load and irradiation time on the photocatalytic decomposition of bacteria in sewage water was studied by varied in photocatalysts load (20 to 100 mg/50 mL) and irradiation time (1 to 5 h). The reduction in CFU values confirmed the decomposition of total bacteria in the sewage water during photocatalytic process.

RESULTS AND DISCUSSION

Characterization study

Usually catalytic supports are classified by their chemical nature to organic and inorganic supports. No matter what the support is, it plays an important role in immobilizing active catalyst. Principally, the support should be increase the surface area of catalytic material, decrease sintering, improve the chemical stability of the catalytic material, govern the useful lifetime of the catalyst and increase the overall photocatalytic activity. Support may also improve the activity of the catalyst by acting as a co-catalyst. Reducing the particle size increases the surface area. Other possibilities to increase the active surface area are to increase porosity or to apply appropriate support. By increasing the porosity, the surface area of many common supports may be increased to a great extent. In the present work amorphous CASB supports were obtained by the fusion of several inorganic substances mainly calcia (CaO), silica (SiO_2), and alumina (Al_2O_3) with lesser amounts of potassium oxide and magnesium oxide. The free oxides are not present and they are fully combined in the fused silicate. The fused mass is quenched to ambient temperature at a fast rate to prevent crystallization. Then the bulk calcium alumino-silicate is subjected for the standard ball milling technique to obtain required size of grains. In the present study the calcium alumino-silicate are obtained in the spherical shape and these beads measures 1.5 to 2 mm in diameters. The CASB are white in colour with rough surface and floats in the water due to the low density. In this study, the CASB are used as an effective supports for the hydrothermal deposition of active photocatalysts on their surface. CASB contains 96 % of $CaO-Al_2O_3-SiO_2$ composition. Other trace oxides are present in the CASB system in the fused form with SiO_2. Over 73.64 % of silica is present in the CASB along with 5.86 % of alumina and 16.70 % of CaO. The silica and alumina have been widely reported as a good adsorbent for the organic compounds.

The powder XRD pattern of hydrothermally prepared TiO_2 deposited CASB supported composite is shown in Figure 2. The strongest peaks corresponding to TiO_2 was identified along with calcium alumino-silicate peaks and as identified strong peaks of TiO_2 were matched with PCPDF-782485 and it confirmed as anatase phase of TiO_2 obtained on the surface of CASB supports during hydrothermal preparation. The powder XRD pattern of TiO_2 deposited CASB supported composite clearly indicates the presence of well developed anatase phase of TiO_2 structures on the surface of CASB supports which greatly influenced on photocatalytic activities.

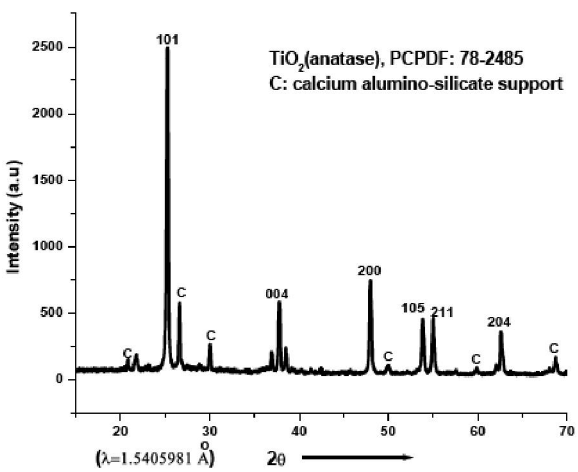
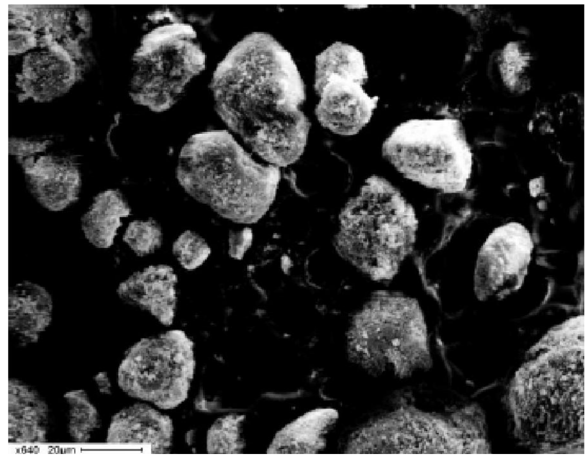
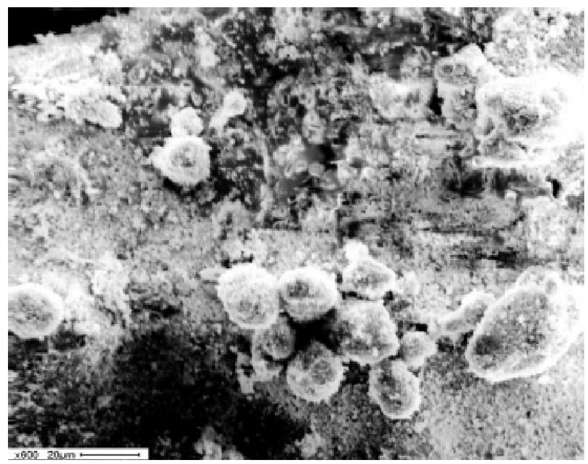


Figure 2 : Powder x-ray diffraction pattern of hydrothermally prepared TiO_2 deposited CASB supported composite

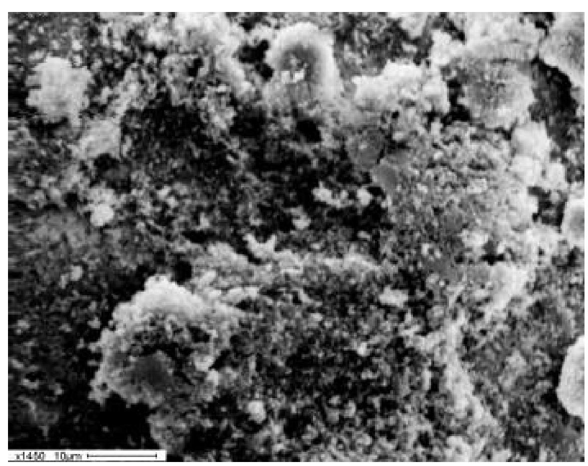
The most intense anatase peak is present at $2\theta = 25.3^{O}$. The morphology and detailed surface structure of hydrothermally prepared TiO_2 deposited CASB supported composites were determined using scanning electron microscope. The SEM images are depicts the effective and homogeneous deposition of TiO_2 on the surface of CASB support. Figures 3(a, b & c) show the scanning electron micrographs of TiO_2 deposited CASB supported composite prepared under hydrothermal conditions (Temperature: 200°C, Duration: 24 h and Solvent: 1M HCl) and it clearly shows deposi-



(a)



(b)



(c)

Figure 3 : SEM images of: (a) TiO_2 deposited CASB supports; (b) surface of TiO_2 deposited CASB support; and (c) enlarged portion of TiO_2 deposited CASB support

tion of TiO_2 micro-particles on the surface of CASB supports under mild hydrothermal conditions. The SEM images of TiO_2 deposited CASB support composites indicate that the deposition of well crystallized phase and microstructure of TiO_2 on the surface of CASB supports under mild temperature and it was confirmed by corresponding powder X-ray diffraction results. FTIR spectra of CASB supports, directly mixed TiO_2 and CASB supports powder and TiO_2 deposited CASB supported composite are shown in Figure 4. All the samples exhibit two broad and strong peaks at 3400 and 1625 cm^{-1}. The band at 3400 cm^{-1} could be attributed to stretching vibration of d (–OH) groups and band at 1625 cm^{-1} is due to bending vibration of the d (–OH) groups of the Ti–OH and hydrated species[20]. There is a noticeable difference in the intensity of these peaks. These peaks are quite intense in supported composite compared to CASB supports. The difference in the peak intensities clearly demonstrates that CASB contain less hydroxyl groups in comparison. CASB exhibits another few peaks at 450, 850, and 1098 cm^{-1} of SiO_2 which is the major composition of CASB supports and stretching bands at 587 cm^{-1} corresponding to CaO. The absorption peaks at 800 and 1098 cm-1 were assigned to symmetric m(Si–O–Si) stretching vibration and asymmetric m(Si–O–Si) stretching vibration of the $SiO4^{4-}$ structural unit, respectively[21] in CASB supports. Additionally, the band at 450 cm^{-1} is assigned for Si–O–Si bending modes[22]. It is interesting to note that the peak at 1098 cm^{-1} is observed only in the FTIR spectrum of CASB. It is often used as evidence for Ti incorporation into the silica lattice. This band has been ascribed to a vibration involving SiO_4 tetrahedra bonded to a titanium atom through Si–O–Ti bonds. The presence, in the same region, of a band at 1098 cm^{-1} arising from Si–OH groups prevents quantitative analysis; however, the high intensity band in between 1000 t0 1200 950 cm^{-1} found in TiO_2 deposited CASB supported composite and it clearly indicates to the presence of a large amount of Si–O–Ti linkages[23-25]. It has been reported that the surface hydroxyl groups and Si–O–Ti linkages play an important role in the photodecomposition processes through their interaction with photo-generated holes. The decrease in the intensities of the 1240 cm^{-1} absorption peaks, indicating a the strong deposition of TiO_2 during the hydrothermal treatment and it is connected with the formation of titanium oxide, as evidenced by the appearance of the broad absorption band in the region of 400 cm^{-1} corresponding to TiO_2.

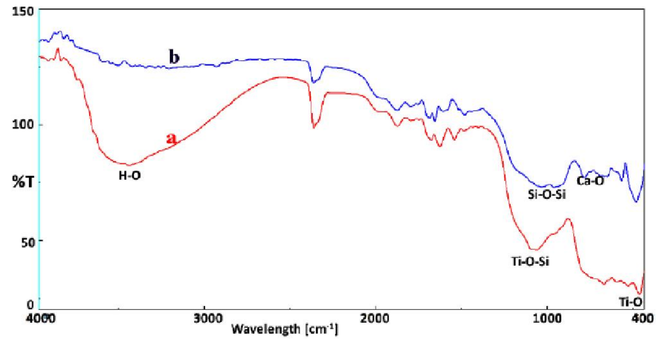


Figure 4 : FTIR spectra of: (a) Hydrothermally prepared TiO_2 deposited CASB support (b) CASB supports

The bulk porosity of TiO_2 deposited CASB supported composite prepared under hydrothermal conditions was studied based on the PALS measurements and the obtained results are tabulated in TABLE 1. The effect of hydrothermal conditions on the bulk porosity of TiO_2 deposited CASB supported composites were studied by means of pore size volume (V_f) and pores concentration (Fv). The measured positron lifetime has been resolved by lifetime components τ_2 with relative intensity I_2. The lifetime τ_2 is due to annihilation of positron trapped at defect in the product and it represented as pore distribution in the system and based on the τ_2 values, the pore size volume (V_f) and pores concentration (Fv) has been evaluated as per the Jean model[19]. The PALS measurements were carried out for the pure CASB supports and directly mixed TiO_2 with CASB supports without hydrothermal treatment. The PALS results of CASB support and directly mixed TiO_2 with CASB support shows 16.055 Å^3 and 19.656 Å^3 respectively. PALS measurements of hydrothermally prepared TiO_2 deposited CASB supported composites showed highest porosity (61.375 Å^3) and drastic difference in the bulk porosity when compared to directly mixed TiO_2 with CASB supports. The evaluation of deposited rate of TiO_2 onto CASB supports under mild hydrothermal conditions was carried out using analytical techniques like ICP-MS and results obtained are shown in TABLE 2. The ICP-MS results obtained are showed very minute quantity of Ti in the raw CASB supports and hydrothermally prepared TiO_2 deposited CASB supported composite showed 19.67 weight percent of Ti presence in the bulk composite. It clearly confirmed that well deposition of required amount of highly active TiO_2 onto CASB supports which further increases the photocatalytic performance.

TABLE 1 : Positron annihilation lifetime spectroscopic results

Materials	Positron annihilation lifetime measurement details			
	$\tau_3 \pm 0.03$ ns	$I_3 \pm 0.29$ (%)	$V_f \pm 0.6$ (Å^3)	F_V (%)
Pure CASB supports	0.947	5.071	16.055	0.147
Direct mixed TiO_2 powder with CASB supports	1.011	2.726	19.656	0.096
Hydrothermally prepared TiO_2 deposited CASB composite	1.598	1.449	61.375	0.160

TABLE 2 : Inductively coupled plasma mass spectrometry results

Photocatalytic materials	Hydrothermal preparation conditions			Ti in weight %
	Temperature in ?C	Duration in h	Solvents	
CASB supports	---	---	---	0.07
TiO_2 deposited CASB supported composite	200	24	1 M HCl	19.67

Photocatalytic decomposition of bacteria in municipal sewage water

Bactericidal effect of TiO_2 deposited CASB supported composite was studied by photodecomposition of bacterial mass in the sewage water under ultraviolet light. The photocatalytic decomposition experiments were carried out with different amount of photocatalyst load and irradiation time at constant temperature and *pH*. The effect of photocatalytic activities on the total bacterial concentration in the sewage water are shown in TABLE 3. The colonies obtained in the standard plate technique (Figure 5) clearly indicate higher rate of photocatalytic decomposition efficiency of TiO_2 deposited CASB supported composite under UV light. The photocatalytic inactivation of microorganisms that consider the role of complex photooxidants which are released during photoreaction and such photooxidants are the hydroxyl radical ($^{\cdot}OH$), the superoxide radical ($O_2^{\cdot-}$), and hydrogen peroxide (H_2O_2), etc. It is frequently assumed that the hydroxyl radical is the major factor responsible for the antimicrobial activity observed in the TiO_2 photocatalytic reaction[26-28]. Other reactive oxygen species such as H_2O_2 and $O_2^{\cdot-}$ etc. as well as the hydroxyl radical are also play significant roles in microorganism inactivation. The results obtained showed that upto 95.56 % of decomposition rate of total bacterial content in the sewage water. The disinfection studies were carried out either to identify the optimum catalyst load for effective disinfection of bacteria in sewage water

TABLE 3 : Photocatalytic decomposition rate of bacteria in sewage water at different irradiation time and different amount of catalyst load

Photocatalyst load/50 mL for 4h duration	CFU mL^{-1}	Irradiation time and 80 mg/mL catalyst	CFU mL^{-1}
Blank	293	Blank	293
20 mg	21	1 h	19
40 mg	17	2 h	18
60 mg	15	3 h	15
80 mg	13	4 h	13
100 mg	14	5 h	12

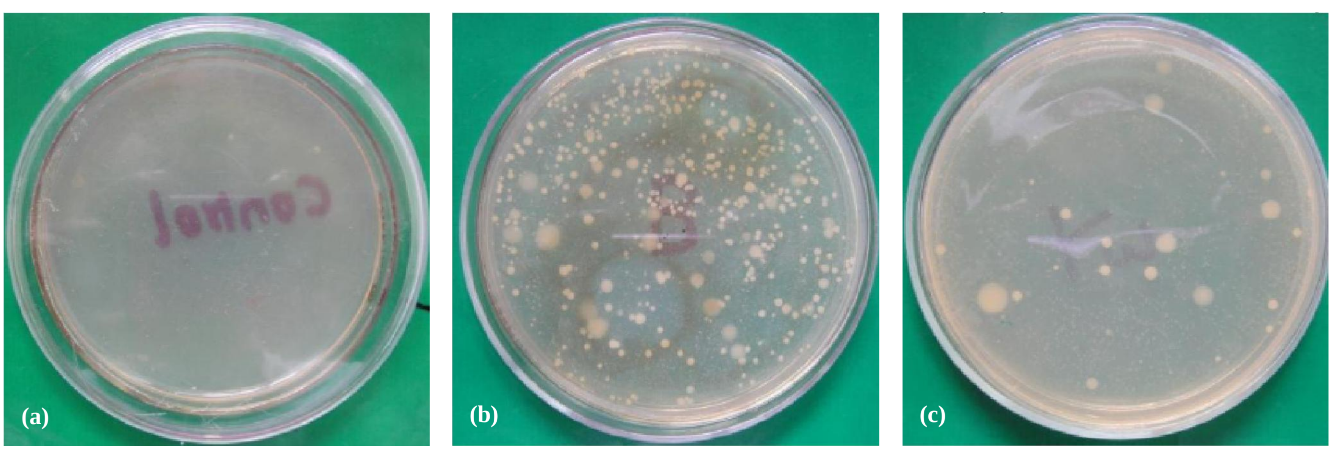


Figure 5 : Colonies forming unit (CFU) on nutrient agar medium in the: (a) Control without sewage water sample; (b) Sewage water without addition of supported photocatalytic composite; (c) Sewage water with addition of supported photocatalytic composite

and 80 mg/50 mL was found to be optimum amount of catalyst load for 4 h duration. The hydrothermally prepared supported photocatalyst performed significant rate of bacterial disinfection properties and it decreases the number of CFU in 1 mL of sewage water from 293 to 12 under UV light for 5 h experimental duration. In addition, it is confirmed that increased rate of decomposition efficiency with increased irradiation time.

CONCLUSION

By adopting hydrothermal techniques with mild experimental conditions TiO_2 deposited CASB supported photocatalytic composite was successfully prepared. As prepared photocatalytic composite showed higher porosity, well crystalline structure, well microstructure and morphology. In addition, FTIR results revealed the presence of more number of hydroxyl groups and Ti–O–Si linkages in the TiO_2 deposited CASB composite, which increases the photocatalytic activities. ICP-MS indicated that the sufficient amount of TiO_2 deposited onto CASB supports under mild hydrothermal conditions. TiO_2 deposited CASB supported photocatalytic composite showed highest activity for the bacterial decomposition, which might be due to its higher bulk porosity, well crystalline structure and easy irradiation to light source. In conclusion, our findings suggest that TiO_2 deposited CASB supported photocatalytic composite photocatalysis may be a viable process for disinfection of bacteria in waste water treatment systems.

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