ISSN : 0974 - 7451 Volume 6 Issue 2

Trade Science Inc.

Environmental Science

An Indian Journal

Current Research Papers

ESAIJ, 6(2), 2011 [67-74]

Photocatalytic removal of fast green FCF dye from water using hydrothermally prepared TiO_2 deposited CASB supported composite

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Received: 20th January, 2011 ; Accepted: 30th January, 2011

ABSTRACT

A supporting photocatalyst was prepared by depositing anatase phase of TiO_2 on the surface of calcium alumino-silicate beads supports that made easy recoverable and highly active photocatalyst in the aqueous medium. Supporting photocatalyst was prepared by hydrothermal technique using General Purpose autoclaves under mild hydrothermal conditions (temperature-200^{O}C, solvent-1M HCl, duration-24 h). The photocatalytic degradation of industrial dye Fast Green FCF in aqueous medium was studied in a batch photoreactor under different light sources. The decomposition of dye molecules in water by UV/deposited TiO_2 process was studied under various conditions such as photocatalyst load, initial dye concentration, initial *pH* and temperature.

KEYWORDS

Photocatalyst;
Hydrothermal;
Fast green FCF;
Autoclaves.

INTRODUCTION

Synthetic dyes are massively produced to meet the need of colorful household products around the world. Fast Green FCF is a commonly used dye in food, chocolate, plastic and pharmaceutical industries as a colorant in large scale. Fast Green FCF is poorly absorbed by the intestines[1] and its use as a food dye has been prohibited in European Union and some other countries. This substance has been found to have tumorigenic effects in experimental animals, as well as mutagenic effects in both experimental animals and humans. It furthermore risks are the irritation of eyes, skin, digestive tract and respiratory tract in its undiluted form[2]. Many industries like plastics, paper, textile and cosmetic industries use large numbers of dyes to colour their products. These dyes are common water pollutants and they may be frequently found in trace quantities in the industrial wastewater. Their presence in water, even at very low concentrations is highly visible and undesirable. In addition, Fast Green FCF is highly difficult to degrade due to their complex aromatic structure and they tend to persist in the environment and creating serious water quality and public health problems. The heterocyclic dye Fast Green FCF is also using in dyeing, printing, leather processing, fluorescent pigments and widely used as a colorant in the cosmetics and drug industries. During the manufacturing and processing operations a significant percentage of dyes are lost as effluent[3-6] and cause considerable environmental concerns. The direct release of wastewater containing Fast Green FCF causes serious environmental problems due to its strong colour and toxicity. Fast Green FCF, for an instance, a widely used colorant in textiles and foodstuffs, can induce irritation to human skin, eyes and respiratory tract. Also it is carcinogenic and chronically toxic toward human beings[7].

Many technologies currently using for the treatment of synthetic dyes and organic colorants, such as carbon adsorption or biodegradation, merely showed less efficiency and failed complete removal. In recent years, the photocatalytic technologies are studied and reported to be effective on oxidizing several synthetic dyes and colorants at mild conditions. Anatase form of titanium dioxide (TiO_2) is the most frequent studied photocatalyst for environmental applications, because it is stable, non-toxic and is capable of degrading a wide range of organic pollutants. However, the practical application of photocatalytic processes for the treatment of organic pollutants in aqueous streams is hindered by the development of effective photocatalysts. This process has been intensively investigated for the remediation of dyestuffs from wastewater[8-12] but its application is impeded by the inefficient recovery of suspended fine catalyst powder. Recently, photocatalysts on supporting materials have been proposed to solve this problem[13-17]. In the present study, calcium alumino-silicate beads (CASB) were used as a supporting material for the deposition of highly active TiO_2 particles. The compositions (73.64 % of silica; 5.86 % of alumina and 16.70 % of CaO), specific surface area, pore volume, low density, surface roughness, shape (spherical) and size (0.5-1 mm in diameter) of CASB supports promise as potential supports for deposition of active photocatalysts.

EXPERIMENTAL

Preparation of photocatalyst

Preparation of highly active photocatalytic particles under hydrothermal conditions have been reported by our group before[18-20]. In this research work, anatase phase of TiO_2 particles were deposited on the surface of CASB supports under mild hydrothermal conditions using General Purposes autoclaves. During the hydrothermal preparation of supported photocatalyst, a known weight of reagent grade TiO_2 powder (Loba Chemie, India) was taken in a Teflon liner and mixed with 1M HCl solution with continuous stirring for homogenous mixing. In to the homogeneous solution a known amount of CASB supports (MTEC, Thailand) were added and the Teflon liner was tightly closed, then Teflon liner was inserted into the stainless steel autoclave. Finally the autoclave assembly was placed inside the furnace at a desired temperature (200°C) over a given experimental duration (24 h). After hydrothermal experimental run, the autoclave was suddenly quenched to room temperature by blowing air through air jet. The resultant products were carefully recovered from Teflon liner and washed repeatedly with deionized water. The resultant products were rinsed with mild alkaline solution to neutralize the *pH* and ultrasonicated to remove the excess acidic or basic solutions. The resultant product obtained were rinsed again with double distilled water and dried in dust free environment at room temperature in a hot air oven. Figure 1 shows the schematic representation of hydrothermal preparation of TiO_2 deposited CASB supported photocatalytic composite. The crystalline phase of TiO_2 deposited on the surface CASB supports were determined by powder X-ray diffractometer (Model-MAC Science Company lim-

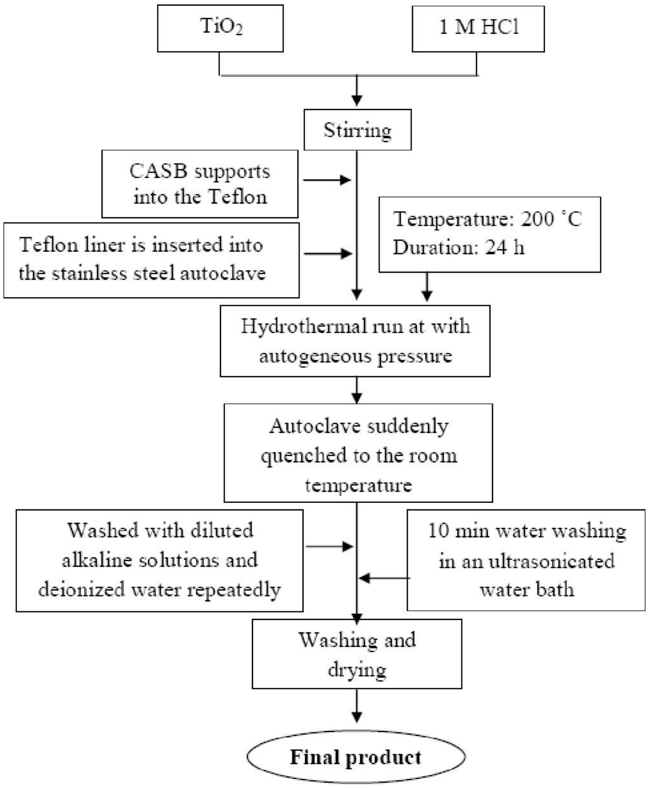


Figure 1 : Schematic representation of hydrothermal preparation of TiO_2 deposited CASB supported photocatalytic composite

ited, Japan) with Bragg angle ranging from 10–70°. The strongest peaks corresponding to TiO_2 were selected to evaluate the crystalline structure of TiO_2 deposited on the surface of CASB supports. The identification of the crystalline phase of TiO_2 deposited was accomplished by comparison with JCPDS using PCPDF Win version 2.01. Inductively Coupled Plasma-Mass Spectroscopy (Model ICP-MS/ELAN-6100) was employed to determine the contents of Ti (in weight %) on the surface of CASB supports.

Removal of dye

In the present study industrial dye Fast Green FCF was used as a model pollutant for the photocatalytic degradation studies and chemical structure of Fast Green FCF dye is shown in Figure 2. The photocatalytic degradation of dye was carried out in a small scale photoreactor and the schematic of photoreactor used is shown in Figure 3. TiO_2 deposited CASB supported composite (70 mg) was suspended in a borosilicate reaction vessel (100 ml capacity) containing 50 ml of 0.00001 M aqueous Fast Green FCF dye solution. The contents of the reaction vessel were kept under continuous stirring by means of magnetic stirrer bar inside the reaction vessel. The photoreactor assemble was irradiated to the light source in a closed chamber at 12 cm distance. The degradation experiments were carried out for 5 h irradiation time under different light sources. At 1 h time interval, 5 ml of dye solution was removed and the suspended photocatalysts were separated by filtration using polythene micro filter. Reduction of dye concentration in aqueous dye solutions was observed from its characteristic percent transmission (%T) at respective λ_{max} (360 nm) using UV Visible spectrophotometer (Model: Minispec SL 171, Elico, India). Chemical oxygen demand (COD) was estimated before and after the photocatalytic degradation experiments to observe reduction of carbon contents in dye solution. The reduction in the COD and increase in %T of dye solution indicated a removal of dye in aqueous solution. The photocatalytic degradation efficiency was calculated by using the following equation:

$$\begin{array}{c}\textbf{Photocatalytic degradation}\\ \textbf{efficiency}\ (\eta)\end{array} = \frac{\begin{array}{c}\text{Initial}\\ \text{COD}\end{array} - \begin{array}{c}\text{Final}\\ \text{COD}\end{array}}{\text{Initial COD}} \times 100$$

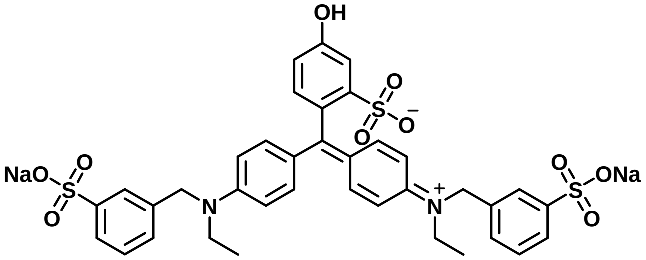


Figure 2 : Chemical structure of industrial dye fast green FCF ($C_{37}H_{34}N_2Na_2S_3$)

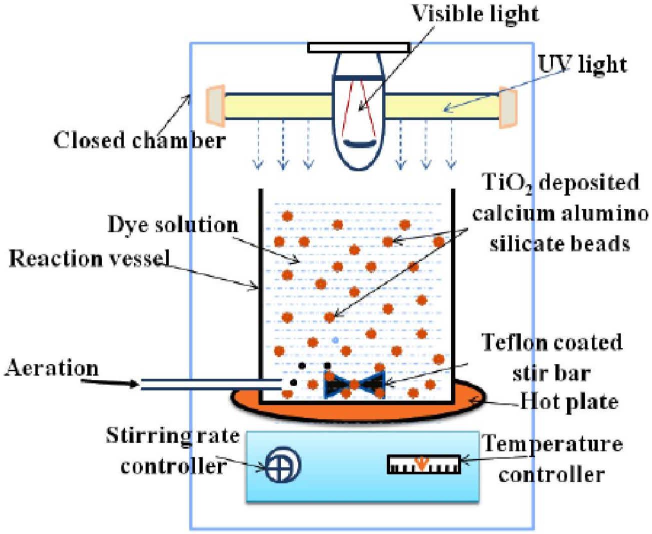


Figure 3 : Schematic of batch photoreactor

RESULTS AND DISCUSSION

Hydrothermally prepared supported photocatalytic composite shows well developed and desired crystalline phases of TiO_2 deposited on the surface of CASB supports. The strongest peaks of TiO_2 corresponding to anatase (A) was identified without contamination along with calcium alumino-silicate peaks. The identified crystalline phases of TiO_2 deposited are well matched with PCPDF-841285 and confirmed anatase phase of TiO_2 deposited on the surface of CASB supports. The powder XRD spectra of TiO_2 deposited CASB supported composite is shown in Figure 4. The Inductively Coupled Plasma-Mass Spectroscopic measurements showed 19.67 wt % of Ti (TiO_2) deposited onto CASB supports

TABLE 1 : Contents of Ti on the surface of CASB supports (in weight percent)

	Ti in wt %
CASB supports	0.03
TiO_2 deposited CASB supported composite	19.67

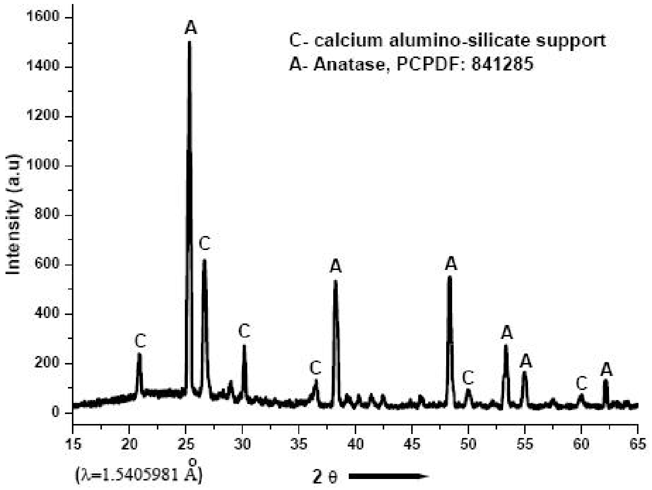
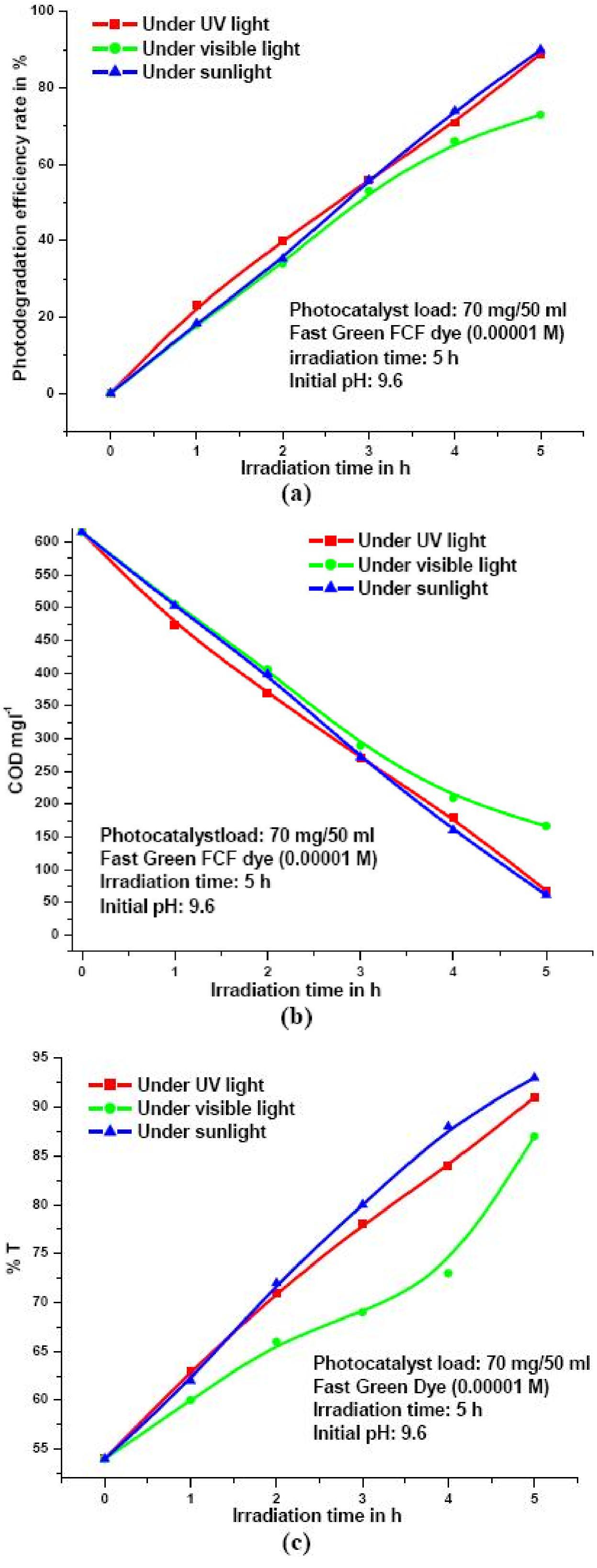


Figure 4 : Powder x-ray diffraction pattern of TiO_2 deposited CASB supported composite

under mild hydrothermal conditions and the results obtained are given in TABLE 1.

The photocatalytic degradation experiments were carried out under different light sources and about 70 mg of supported photocatalytic composite was loaded for each experimental run. Different light sources such as UV light (Sankyo Denki, G8T5, 8W, Japan), visible light (Philips, 230V, 15W, India) and the natural sunlight (between 10 am to 3 pm on a sunny day) were used for the photocatalytic degradation studies. The results obtained are given in TABLE 2 and these results showed high rate of photocatalytic degradation efficiency under both sunlight and UV light when compared to visible light (Figures 5). At low light intensity and correspondingly low carrier concentrations, the rate of oxidation of a particular compound is proportional to light intensity. Decrease in COD value and increase in %T of dye solution indicate the effective photodegradation of Fast Green FCF dye under different light sources and the results obtained are shown in Figures 5. The photocatalysts deposited on the surface of CASB supports are easily exposed to the light source without any agglomeration and it achieved easy surface contact of dye molecules in aqueous medium. The shape of the CASB supporting material increases the irradiation rate of photocatalyst deposited to the light source by its easy movements and spinning along with photocatalysts in aqueous medium. High rate of irradiation enhances the production rate of OH radicals on the surface of catalysts, which actively taken part in the photocatalytic degradation of dye molecules in the medium. Silica and alumina, which are the major com-



(a)

(b)

(c)

Figures 5 : Effect of light sources on: (a) photocatalytic degradation rate of fast green FCF dye; (b) COD values of fast green FCF dye solution; (c) percent transmission (%T) of the fast green FCF dye solution

TABLE 2 : Photocatalytic degradation rate (η) of fast green FCF dye under different light sources

Irradiation time in h	Under UV light			Visible light			Under natural sunlight		
	COD mg/l	%T	η (%)	COD mg/l	%T	η (%)	COD mg/l	%T	η (%)
Initial	615	54	0	615	54	0	615	54	0
1	472	63	23.20	504.5	60	18	502	62	18.37
2	370	71	39.83	405	66	34	398	72	35.28
3	270	78	56.01	289.05	69	53	271	80	55.85
4	179	84	70.89	209.1	73	66	160	88	73.98
5	67.5	91	89.01	166.05	87	73	61	93	89.96

ponents of CASB supports, are widely reported as the good adsorbents for the organic molecules[21-24]. More importantly these supporting materials composition form a good media, which not only facilitate the adsorbing organic compounds (organic dyes and colorants) but also transfers those adsorbed organic compounds to active sites on TiO_2 deposited. In addition, the hydrothermally prepared supported composite was found to be easy to handle and recover from aqueous solution after the photocatalytic reaction. Figure 6 shows the interaction of dye molecules with active sites of TiO_2 deposited on the surface of CASB supports in aqueous medium. The possible reaction scheme for the photocatalytic degradation of Fast Green FCF dye is given in the following equations (Eqs. 1 to 3).

$$TiO_2 + hv \longrightarrow TiO_2^{\bullet} \qquad (1)$$

$$TiO_2^{\bullet} + OH_2O \longrightarrow H^+ + {}^{\bullet}OH \qquad (2)$$

$$\begin{aligned} &{}^{\bullet}OH + C_{37}H_{34}N_2Na_3S_3 + O_2 + H_2O \longrightarrow \\ &CO_2 + NO_3^- + SO_4^{2-} + NaHSO_4 + H_2O \end{aligned} \qquad (3)$$

In the present study the effect of experimental parameters such as photocatalyst load, *pH* of the medium, experimental temperature, initial dye concentration and irradiation time on the photocatalytic degradation rate of Fast Green FCF dye in aqueous solution was investigated.

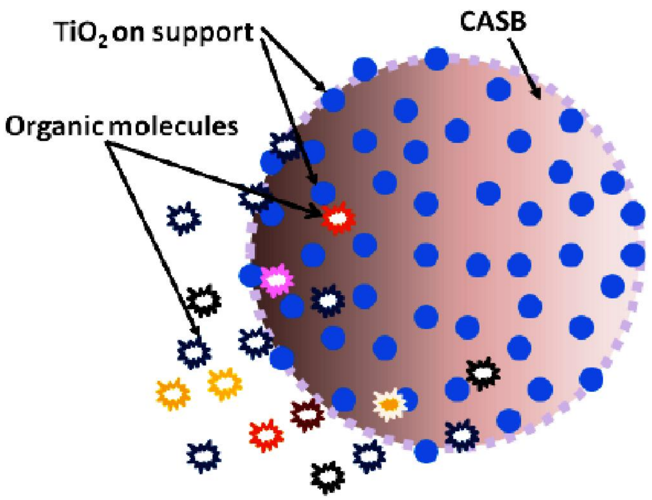


Figure 6 : Illustration of the interaction between dye and deposited TiO_2 on the surface of CASB support

Effect of photocatalyst load

The photocatalytic degradation experiments were carried out using hydrothermally prepared TiO_2 deposited CASB supported composite and the effect of its amount on the photocatalytic degradation rate constant was determined. The amount of photocatalysts load was varied from 10 to 100 mg into 50 ml of aqueous dye solution and an experiment was carried out without adding photocatalyst. During the photocatalytic degradation study 0.00001M of aqueous Fast Green FCF dye solution was used under constant experimental conditions for all the photocatalytic experiments by adding different amounts of photocatalyst. The photocatalytic experiments were carried out under the UV light source and irradia-

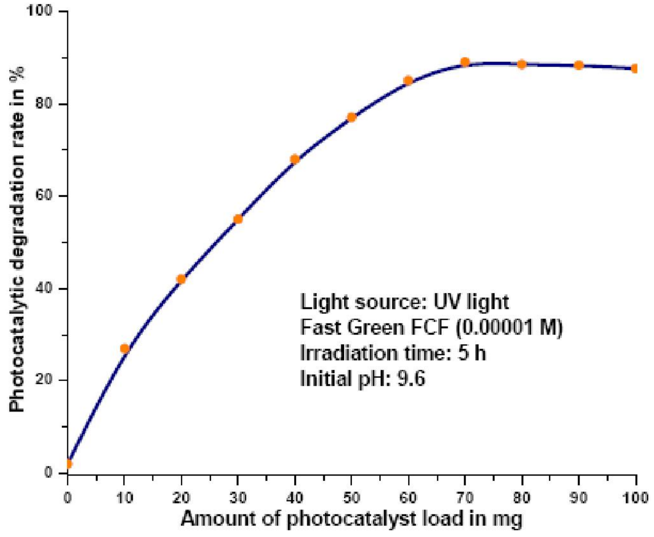


Figure 7 : Effect of TiO_2 deposited CASB supports load on the photocatalytic degradation rate constant of fast green FCF dye

tion time was fixed for 5 h. A significant enhancement of photocatalytic degradation rate was observed at 70 mg of TiO$_2$ deposited CASB supported composite load and the results obtained are shown in Figure 7. The photocatalytic degradation rate was not further enhanced significantly beyond 70 mg of photocatalyst load and initiate slightly reduction in the degradation rate beyond this amount of photocatalyst load. This is due to the increased diffusion time of photon to reach the active sites at the range of super saturation point of photocatalyst load in aqueous dye solution. Moreover, the high amount of photocatalyst load in the aqueous dye solution than its saturation amount leads to reduction in the transmission of light through the aqueous dye solution.

Effect of initial dye concentration

The effect of initial concentration of Fast Green FCF dye in the aqueous solution on the photocatalytic degradation efficiency was studied under UV light for 5 h irradiation time. The photocatalytic degradation experiments were carried out by varying in the concentration of dyes from 1 x 0.00001M to 10 x 0.00001M and about 70 mg photocatalytic composite was loaded into each photocatalytic reaction experiment. The photocatalytic degradation experimental results obtained are shown in Figure 8 and it shows decreased rate of photodegradation efficiency at higher concentrations of dye in the aqueous solution. The decreased rate of photodegradation efficiency was evident for the effect of initial concentration of Fast Green FCF dye on the photocatalytic degradation rate under UV light. The reaction rate was significantly influenced by the light intensity, therefore, at higher initial dye concentration in the aqueous medium the solution becomes more intense coloured and the path length of photons entering through the dye solution decreases thereby fewer photons reach catalysts surface. Due to insufficient photons, the available active sites on the catalysts for the photoreactions are very crucial and the productions of hydroxyl and superoxide radicals are limited.

Effect of temperature

The photocatalytic degradation efficiency of Fast Green FCF dye has been studied at different temperatures (283 to 333 K). The constant and different range of temperature (> 303 K) was achieved by keeping the reaction vessel on a heating plate provided with temperature controller and the low temperature (= 303 K) was maintained by keeping the reaction vessel in a cold water bath with continuous stirring (200 rpm). About 70 mg of hydrothermally prepared TiO$_2$ deposited CASB supported composite was loaded into 50 ml of dye solution and the photoreaction was carried out under UV light source. The photocatalytic degradation results obtained at different experimental temperatures are shown in TABLE 3. Figure 9 shows the effect of experimental temperature on the photocatalytic degradation efficiency with respect to irradiation time. The results obtained show the photocatalytic degradation rate of dye significantly increased with increased experimental temperature and complete degradation of Fast Green FCF dye has been observed within 2 and 3 h irradiation time at the temperature 333 K and 323 K respectively.

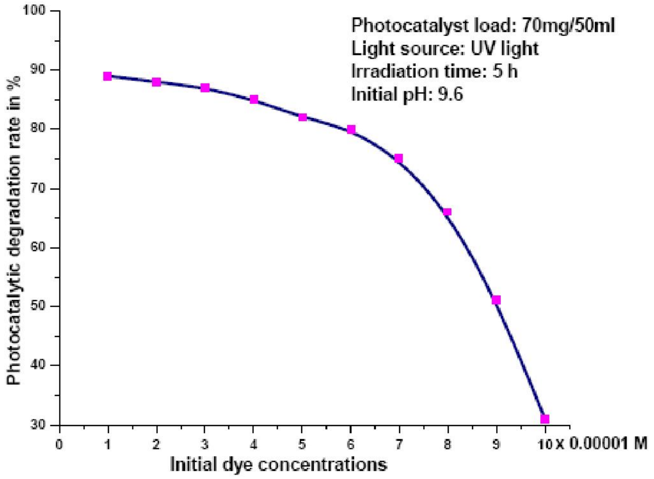


Figure 8 : Effect of initial dye concentrations on the photocatalytic degradation rate of fast green FCF dye

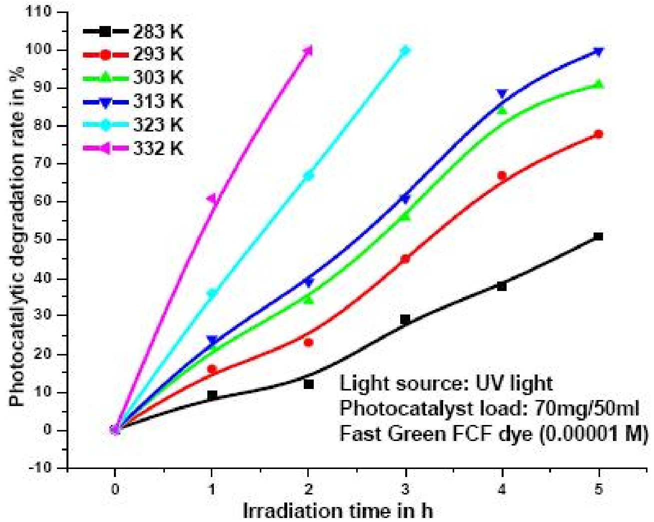


Figure 9 : Effect of different temperature on the photocatalytic degradation rate of fast green FCF

TABLE 3 : Effect of temperature on the photocatalytic degradation rate of fast green FCF dye under UV light

Irradiation time in h	Photocatalytic experimental temperature (K) and degradation efficiency in %					
	283 K	293 K	303 K	313 K	323 K	333 K
1	9	16	22	24	36	61
2	12	23	34	39	67	99
3	29	45	56	61	99	--
4	38	67	84	89	--	--
5	51	78	91	99	--	--

As seen from TABLE 3 the rate of photocatalytic reaction was very less at low temperature because, at low temperature the supplied energy may be utilized for the equilibrium process. Due to lack of sufficient energy for the activation of photocatalysts in aqueous medium may reduce the photocatalytic reaction rate at low temperature. An increase in temperature favours the photodegradation reaction, due to increased oxidation rate of dye substrate at the interface of the TiO_2 photocatalyst under high degree experimental temperature.

Effect of initial *pH*

The *pH* of aqueous solution significantly affects on all the metal oxide semiconductors, including the surface charge on the semiconductor particles, the size of the aggregates formed and the energies of conduction and valence bands. The effect of *pH* on the photocatalytic degradation rate of Fast Green FCF dye was studied at different level of initial *pH* of dye solution. The initial *pH* of dye solution was varied from 2 to 12 and the *pH* of dye solution was adjusted using diluted HNO_3 or NaOH solutions. The photocatalytic degradation experiments were carried out under the UV light source by loading 70 mg of photocatalysts into the 50 ml of 0.00001M dye solution. The minimum photocatalytic degradation rate was recorded at *pH* 6 and photodegradation rate was considerably increased with increased *pH* of dye solution (alkaline condition). At *pH* < 6 the TiO_2 surface accumulates a net positive charge, while at high *pH* the surface has a net negative charge. In accordance with Nernst's law, varying the *pH* of the solution shifts the energies of the valence and conduction band edges by 0.059 V per *pH* unit (at ambient temperature). This results in the valence band electrons becoming more potent and the conduction band holes less potent at higher *pH*. Under the acidic condition of dye solution, the photocatalytic degradation rate was high and this is because, the perhydroxyl radical is formed by the protonation of the superoxide radical. Consequently, the perhydroxyl radical can form hydrogen peroxide that in turn dissociates to give hydroxyl radicals (Eqs. 4 to 9), which result in the degradation of dye. In the alkaline *pH* range the increased concentration of hydroxide ions results in the production of hydroxyl radicals (Eq. 10), which increase the photocatalytic degradation efficiency. An increase in the concentration of hydroxide ion increases the rate of reaction, which increases the concentration of OH radicals with time. Thus, the photocatalytic degradation of Fast Green FCF dye can be enhanced by both H^+ and OH^-. Even though there is an increase in the degradation efficiency at higher acidic and alkaline *pH*, it is not suggested to use such *pH* range in waste water treatment, because it may cause corrosion of the entire waste treatment system. Figure 10 shows the effect of initial *pH* of dye solution on the photocatalytic degradation efficiency.

$$O_2 + e^- + h\nu \longrightarrow O^{\bullet -}_2 \qquad (4)$$

$$O^{\bullet -}_2 + H^+ \longrightarrow HO^{\bullet}_2 \qquad (5)$$

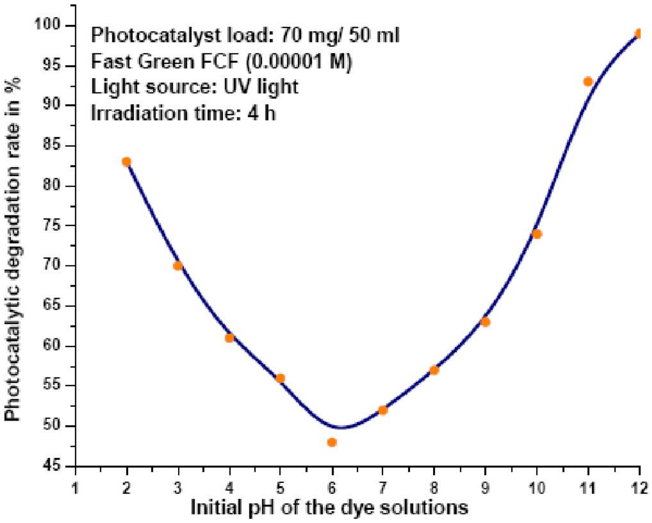


Figure 10 : Effect of initial *pH* of fast green FCF dye solution on the photocatalytic degradation rate constant

$$HO^{\bullet}_2 + HO^{\bullet}_2 \longrightarrow H_2O_2 + O_2 \qquad (6)$$

$$H_2O_2 + e^-_{CB} + h\nu \longrightarrow HO^{\bullet} + HO^- \qquad (7)$$

$$H_2O_2 + O^{\bullet-}_2 \longrightarrow HO^{\bullet} + HO^- + O_2 \qquad (8)$$

$$H_2O_2 + h\nu \longrightarrow 2\,HO^{\bullet} \qquad (9)$$

$$HO^- + O_2 + h\nu \longrightarrow HO^{\bullet} + O^{\bullet-}_2 \qquad (10)$$

CONCLUSION

A photocatalytic composite of TiO_2 deposited CASB supports was prepared, which can be easily recoverable from aqueous medium. An enhancement of the photocatalytic activity of TiO_2 materials was achieved by deposition of highly active anatase phase of TiO_2 onto CASB supports under mild hydrothermal conditions. The characterization results indicated that the deposition of 19.67 Wt % TiO_2 on the surface of CASB supports, which showed the highest photocatalytic activity during removal of dye from the aqueous medium. According to these observations, we could conclude that hydrothermally prepared TiO_2 deposited CASB supported composite promote the better photocatalytic activity for the removal of industrial dyes under both UV light and natural sunlight. As far as the industrial application is concerned, easy recoveries and handling of supported photocatalyst during treatment process reduces the treatment cost in large scale applications.

REFERENCES

[1] IPCS, Fast Green FCF; INchem., Retrieved **(2007)**.

[2] Fast Green FCF; Food and Agriculture Organisation of the United Nations, Retrieved, INS, 143 **(2007)**.

[3] I.Arslan, I.A.Balcioglu, D.W.Bahnemann; J.Dyes.Pigmen., **47**, 207 **(2000)**.

[4] E.Forgacs, T.Cserháti, G.Oros; J.Environ.Intern., **30**, 953 **(2004)**.

[5] J.Abhishek, J.Abhilasha, L.Savitri, B.Pinki, R.C.Ameta; Bull.Cat.Soci.Ind., **7**, 160 **(2008)**.

[6] J.Rajeev, S.Shalini; In.J.Phys.Sci., **3(12)**, 299 **(2008)**.

[7] R.Jain, M.Mathur, S.Sikarwar, A.Mittal; J.Environ.Manag., **85**, 956 **(2007)**.

[8] M.Chih-Ming, K.Young, K.Yu-Lin, C.Yiang-Chen, J.Fu-Tien; J.Wat.Air.Soil.Poll., **197**, 313 **(2009)**.

[9] V.K.Gupta, R.Jain, A.Mittal, M.Mathur, S.Sikarwar; J.Collo.Inter.Sci., **309**, 464 **(2007)**.

[10] I.Ikuichiro, W.D.Wendell, O.W.Keith, F.F.Fu-Ren, J.B.Allen; J.Phys.Chem., **84(24)**, 3207 **(1980)**.

[11] S.Chunyan, Z.Dan, C.Chuncheng, M.Wanhong, Z.Jincai; J.Environ.Sci.Tech., **43(1)**, 157 **(2009)**.

[12] T.Ben-Moshe, D.Ishai, B.Brian; J.Appl.Cat.B: Environ., **85**, 207 **(2009)**.

[13] K.V.Subba Rao, A.Rachel, M.Subrahmanyam, P.Boule; J.Appl.Cat.B: Environ., **46**, 77 **(2003)**.

[14] S.R.Sadhana, D.Nidhi, V.C.Ravikrishna, V.J.Meenal, K.L.Nitin, D.Sukumar; Curr.Scie., **93(10)**, 1376 **(2007)**.

[15] C.Aiping, L.Guanzhong, T.Yong, D.Zhiming, G.Hongchen; J.Mat.Phys.Mech., **4**, 121 **(2001)**.

[16] L.Mingliang, B.Derek, B.Peter; J.Wat.Air.Soil.Poll., **198**, 233 **(2009)**.

[17] T.An, J.Chen, G.Li, X.Ding, G.Sheng, J.Fu, B.Mai, K.E.O'Shea; J.Cat.Today, **139**, 69 **(2008)**.

[18] H.P.Shivaraju, K.Byrappa, M.B.Shayan, T.Rungnapa, S.Pakamard, M.S.Vijay Kumar, S.Ananda; Mat.Res.Innov., **14(1)**, 73 **(2010)**.

[19] H.P.Shivaraju, C.P.Sajan, T.Rungnapa, M.S.Vijay Kumar, C.Ranganathaiah, K.Byrappa; Mat.Res.Innov., **14(1)**, 80 **(2010)**.

[20] B.Shahmorady, C.P.Sajan, H.P.Shivaraju, K.M.Lokanatha Rai, S.Ananda, M.B.Shayan, T.Tonthai, G.V.Narasimha Rao, K.Byrappa; Mat.Res.Innov., **14(1)**, 6 **(2010)**.

[21] Q.Zhou, P.Somasundaran; J.Coll.Inter.Scie., **331(2)**, 288 **(2008)**.

[22] L.E.Paul, A.U.Laura; J.Separ.Purif.Tech., **66(3)**, 532 **(2009)**.

[23] S.C.Abraham, L.S.Vernon, F.Francois; J.Environ.Sci.Tech., **21(1)**, 83 **(1987)**.

[24] M.Domenico, L.P.Nello, B.Luca, P.Pietro, I.Gianfranco, B.Simone, E.M.Massimo; J.Sens.Actuat.B: Chem., **137(1)**, 76 **(2009)**.