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FABRICATION AND STRUCTURAL CHARACTERIZATION OF $SrSiO_3/TiO_2$ PHOTOCATALYST FOR THE DEGRADATION OF CONGO RED DYE UNDER SUNLIGHT

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ABSTRACT

Titanium dioxide and strontium silicate-loaded titanium dioxide photocatalysts are prepared via a simple chemical precipitation technique using titanium tetrachloride as the precursor solution in an alkaline medium. Different characterization techniques such as x-ray diffraction analyses, field emission scanning electron microscopic analyses, transmission electron microscopic analyses, energy dispersive x-ray analyses and bet surface area studies are carried out for the synthesized photocatalysts. The enhancement in the photocatalytic activity of the strontium silicate loaded titanium dioxide against the bare titanium dioxide catalyst is investigated using congo red dye as a model pollutant. The parameters such as catalyst concentration, pH and initial dye concentration are optimized to achieve maximum degradation of congo red dye using the modified titanium dioxide photocatalyst. The kinetic studies using the Langmuir-Hinshelwood model are investigated to study the rate and order of the photocatalytic dye degradation process.

Keywords: $SrSiO_3/TiO_2$Composite, Photodegradation, Congo Red Dye, XRD, HRTEM, Air Oxidation, Solar Radiation.

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INTRODUCTION

Water pollution problems have increased continuously over the past decades due to the extensive development of textile, printing and dyeing units. The unfixed dyes and toxic chemical compounds released into the aquatic system from the textile industries are a major cause of water pollution.[1-3] A wide variety of synthetic dyes used in the textile and dyeing industries are non-biodegradable in nature. When these non-biodegradable dyes are released into the water bodies, they persist in the environment for a long period of time, posing serious health hazards to the aquatic and human life.[4,5]Among the wide variety of dyestuffs, the azo dyes constitute a major class, they are widely employed in the dyeing industries due to the intensity of the colors, fast fixation of the dyes to the fabric. Congo red is one such azo class of dye widely employed in the textile and dyeing industries. Due to the thermal and optical stability of congo red dye, it is not readily degradable. They are highly toxic and are suspected carcinogens that create serious environmental and health concerns. Conventional water treatment techniques such as sedimentation, flocculation, membrane filtration and adsorption are found to be less effective in the removal of toxic synthetic dyes from the environment and under anaerobic conditions the dyes are transformed to aromatic amines which are also potentially carcinogenic in nature.[6-9] Hence, an investigation into the advanced technologies for the abatement of these organic pollutants is widely researched by scientists all over the world. The advanced oxidation processes such as heterogeneous catalysis is a clean and commercially scalable method for the degradation of toxic organic pollutants.[10]Titanium dioxide catalystis one of the best semiconductor photocatalysts widely employed for the removal of azo dyes. However, the wide bandgap of titanium dioxide catalysts (3.2eV) makes it less favorable for photocatalytic process.[11-13] Hence, in recent years researchers have focused on modifying TiO_2 catalyst in order to improve its photocatalytic response. Recently, Himanshu Narayan *et al.*, reported the photocatalytic degradation of congo red dye using Nd^{2+}, Er^{3+} loaded TiO_2 photocatalyst.[14]Adiyansyah *et al.*, reported a faster photocatalytic activity for the degradation of reactive black 5 dye using sulphurdoped TiO_2 photocatalyst.[15] Similarly, silicon oxide supported TiO_2 photocatalyst also exhibited excellent

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photocatalytic activity against the removal of ammonia in aqueous solution within 24 hours.[16] In our present study, the photocatalytic activity of strontium silicate incorporated TiO_2 photocatalyst prepared via simple chemical precipitation technique is employed for the degradation of congo red dye under natural sunlight.

EXPERIMENTAL

Material and Methods

The titanium tetrachloride solution and sodium hydroxide were purchased from Sisco Research Laboratories Pvt. Ltd. Congo red dye is purchased from S.D. Fine chemicals. The chemical structure of the Congo red dye is shown in Fig.-1.

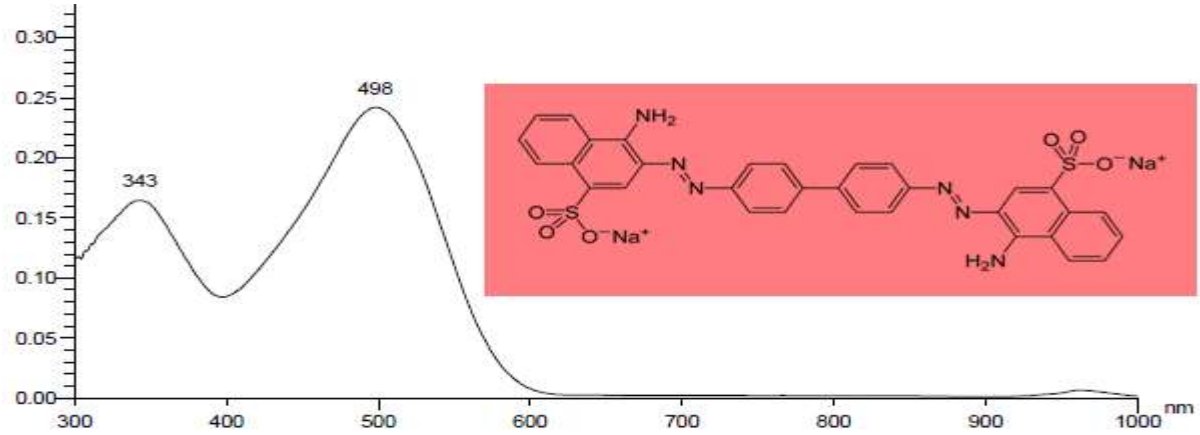

Fig.-1: UV-Visible Absorption Spectrum and Chemical Structure of the Congo Red Dye

Synthesis of $SrSiO_3/TiO_2$Photocatalyst

Titanium tetrachloride solution (1M) is used as a precursor solution to prepare titanium dioxide nanoparticles. One weight percent of strontium silicate powder is added to the precursor solution and it is magnetically stirred for 30 minutes. Slowly the temperature of the solution is raised to 60° C and sodium hydroxide is added as a precipitating agent and the stirring is continued for another half an hour. The thick white precipitate obtained is washed repeatedly with distilled water and dried in the oven for 6 hours and finally, it is calcined at 400°C to obtain powders of 1wt% $SrSiO_3/TiO_2$ photocatalyst. Similarly, different weight ratios (0.5, 2 and 3%) of strontium silicate-loaded titanium dioxide photocatalysts are prepared and the bare TiO_2 photocatalyst is prepared without the addition of the strontium silicate.

Photocatalytic Degradation Experiments

The stock solution of congo red dye ($1.43x10^{-5}$mol/L) is prepared, from which 50mL was withdrawn for each photocatalytic experiment. All the photocatalytic experiments were carried out under sunlightbetween 11 am to 2 pm. The reaction was carried out in the open air and the solution was continuously mixed by aeration. The photocatalytic experiment was carried out for three hours and at different time intervals,approximately 2mL of the dye solution was taken and centrifuged so that it was free from the catalyst. The pH optimization of the solution is done by adjusting the solution to appropriate pH levels using 0.1N NaOH and 0.1N HCl. A similar procedure was carried out at room temperature to get the blank experimental value. The percentage decolorization was calculated using the formula A_o - $A/A_o x100$ where A_0 is the initial absorbance and A is the absorbance of the solution at a time 't'.

RESULTS AND DISCUSSION

Catalyst Characterization

The morphology of the synthesized titanium dioxide and strontium silicate loaded titanium dioxide photocatalysts was examined by Field Emission-Scanning Electron Microscopy and Transmission Electron Microscopy analysis.

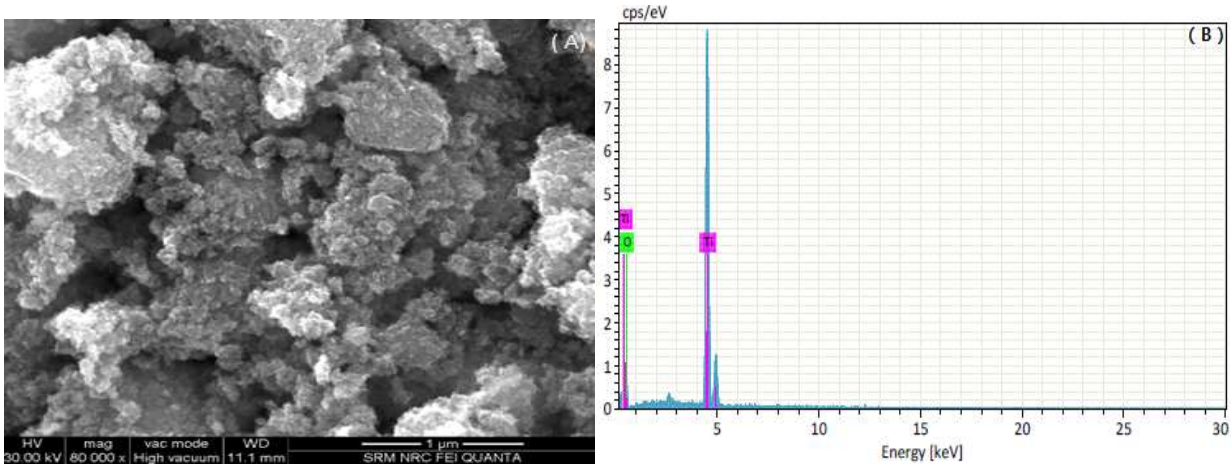

Fig.-2: A and B shows the FE-SEM Image and the EDAX Spectrum of the Synthesized Titanium dioxide photocatalyst

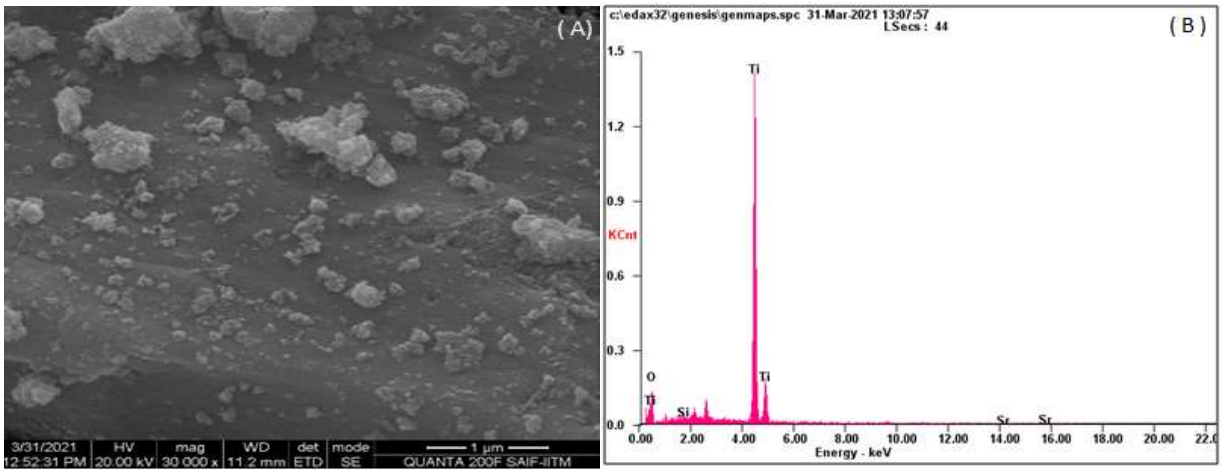

Fig.-3: A and B show the FE-SEM image and the EDAX Spectrum of the synthesized Strontium silicate loaded Titanium dioxide Photocatalyst.

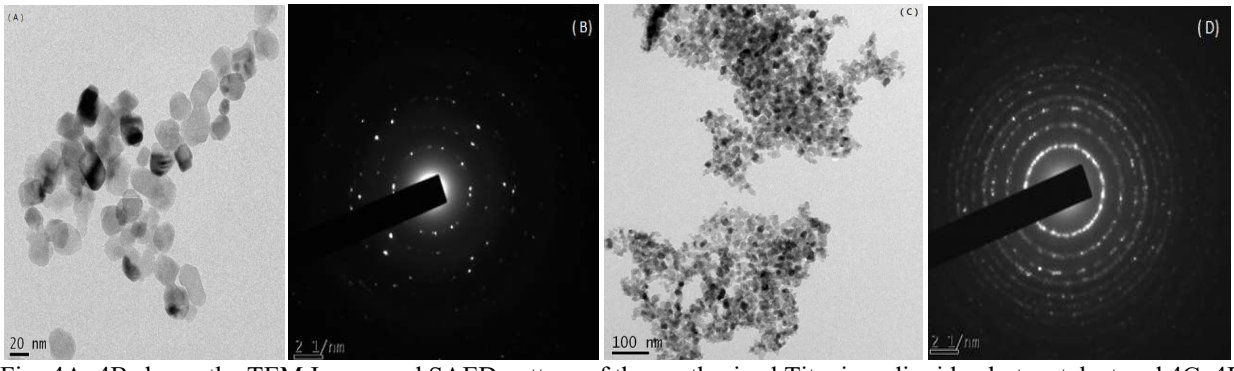

Fig.-4A, 4B shows the TEM Image and SAED pattern of the synthesized Titanium dioxide photocatalyst and 4C, 4D shows the TEM Image and SAED pattern of the strontium silicate loaded titanium dioxide photocatalyst.

From the FE-SEM and TEM images shown in Figs.-2a,3a and 4a,4c it is found that the synthesized bare titaniumdioxide particles and strontium silicate loaded titanium dioxide catalyst are moderatelyspherical in shape with the particle size ranging from 12.5nm to 33.8 nm for the undoped titanium dioxide photocatalyst. Additionally, the rings and dark-spotted circles inthe SAED pattern of the synthesized TiO_2 and $SrSiO_3/TiO_2$ photocatalysts indicate the crystalline nature of the titanium dioxide particles and it also reveals that the crystallinity of titanium dioxide particles is still retained even after modification with

strontium silicate. This result is in agreementwith that found in titaniumdioxide nanoparticles prepared from similar precursors.[17,18] The typical EDAXspectrum of the titanium dioxide particles and strontium silicate loaded titanium dioxide particles are shown in Fig.-2b,3bwhich confirms the presence of titanium and oxygen elements in majorcomposition in the synthesized TiO_2 photocatalyst and the presence of titanium and oxygen in major with less intense peaks of strontium and silicon are also detected in the EDAX spectrum for the synthesized $SrSiO_3/TiO_2$ photocatalyst. This indicates that the synthesized TiO_2 and $SrSiO_3/TiO_2$ photocatalysts are obtained without any impurities.

Further, the crystallinity and surface area properties of the as-synthesized TiO_2 and $SrSiO_3/TiO_2$ photocatalysts were examined by XRD and nitrogen adsorption-desorptionanalyzer, respectively.XRD spectrum of the synthesized TiO_2 and $SrSiO_3/TiO_2$ photocatalysts are shown in Fig.-5a and 5b. The crystal planes (101), (004), (200), (204), (220), (215) represent the anatase phase[19] which is in accordance with the standard JCPDS [21-1272] and the crystal planes (110), (103), (105), (211) representing the rutile phase[20] and the crystal planes (121) and (032) representing the brookite phase[21]are evidenced in the synthesized materials.From the obtained XRD results, it is found that (101) peak representing the anatase is the most intense one, which is also the preferred growth plane of bare titanium dioxidenanoparticles, however, in the strontium silicate loaded titanium dioxide nanoparticles the crystal plane (121) representing the brookite phase is found with maximum intensity indicating it as the preferred growth plane. The sharpness and intensity of all the peaks in both TiO_2 and $SrSi/TiO_2$ photocatalysts once again confirm the crystalline nature of the synthesized materials. The average crystallite calculated from the debye scherrer's equation for bare titanium dioxide catalystis 20.2 nm and for $SrSiO_3/TiO_2$ catalysts the crystallite size decreased to 17.85 nm. The catalytic activity of a photocatalyst can be correlated to the surface area of the catalyst;the higher the surface area greater will be the photocatalytic activity.[22,23]The nitrogen adsorption-desorption isotherms of the as-synthesized TiO_2 and $SrSiO_3/TiO_2$ photocatalysts are shown in Fig.-6a and 6b.From the BET surface area measurements, it is found that thespecific surface area of the bare titanium dioxide catalyst is 61.006m^2/g and the surface area of the strontium silicate loaded titanium dioxide catalyst increased to 78.295m^2/g respectively.

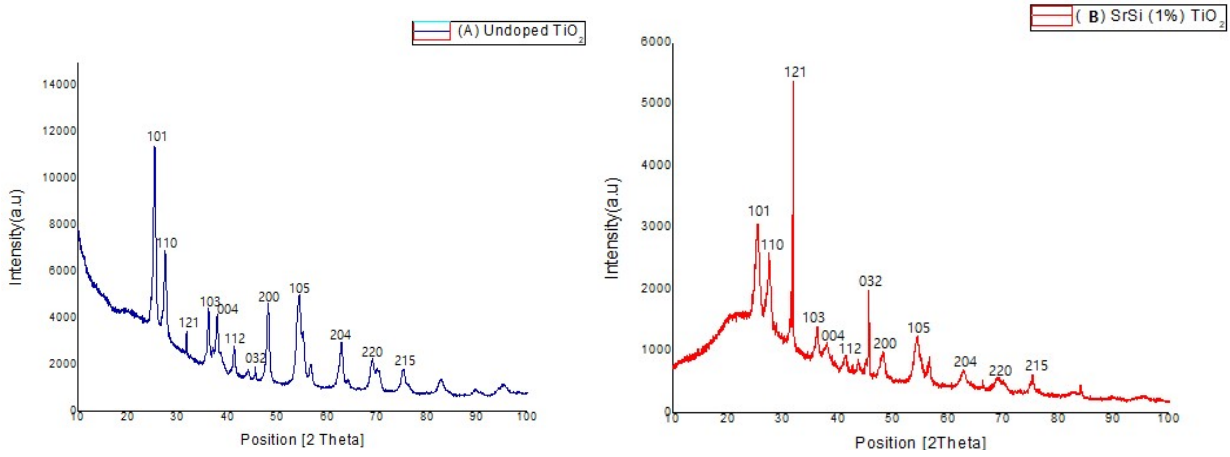

Fig.-5 A and B shows the XRD Pattern of the synthesized Titanium dioxide and the 1% strontium silicate loaded titanium dioxide photocatalyst.

Photocatalytic Degradation of Congo Red Dye

Effect of pH

The effect of pH in the range of 4–9 is studied for 10 mg/L(50ml) of congo red dye solution. The maximum decolorization efficiency was observed in neutral pH=7.5 as shown in Fig.-7. In neutral and acidic pH the anionic congo red dye gets easily adsorbed to the positively charged surface of titanium dioxide nanoparticles and hence good decolorization efficiency is achieved at acidic and neutral pH levels however, at alkaline pH levels beyond pH8 the titania catalyst with negatively charged surface repels the anionic congo red dye and thus a decrease in the photocatalytic decolorization of the dye is observed.[24,25]

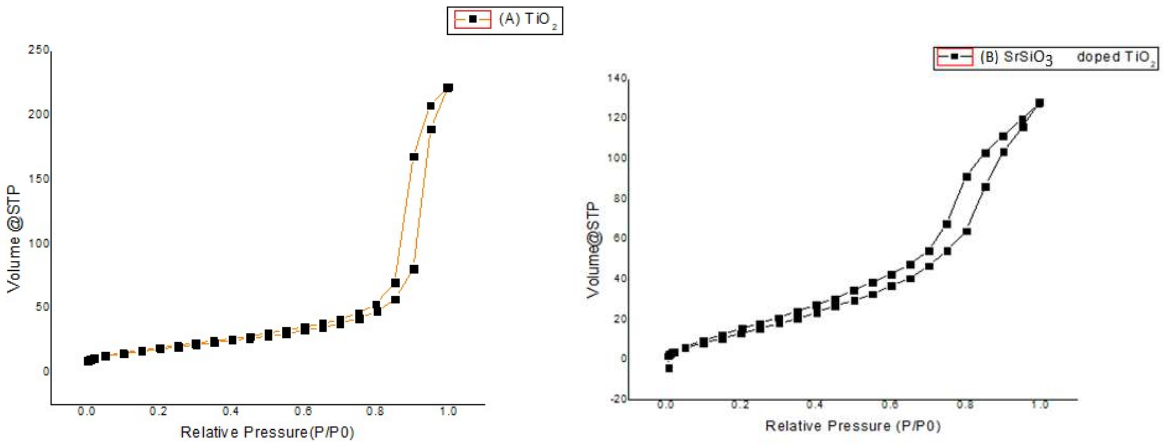

Fig.-6 A and B shows the Nitrogen Adsorption-Desorption isotherm of the synthesized Titanium dioxide and the 1% strontium silicate loaded titanium dioxide photocatalyst. (Figure (B) changed)

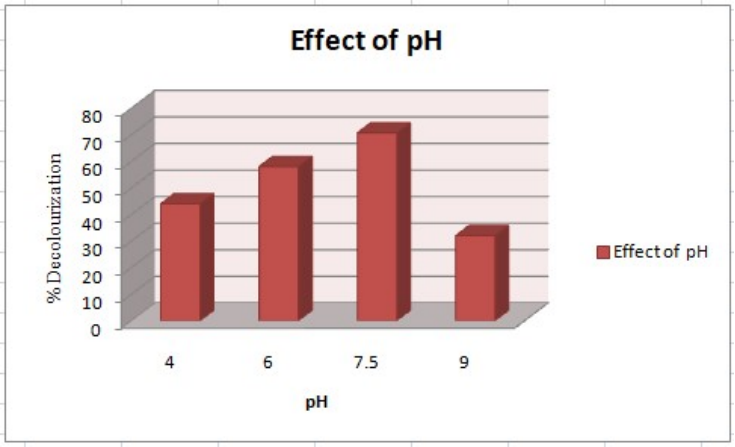

Fig.-7: 0.01g/L Congo Red Dye Solution, 25mg of TiO_2catalyst, pH varied from 4 to 9, airflow rate =2.5L/min under Sunlight.

Effect of Catalyst Dosage

The optimum amount of titanium dioxide catalyst for the effective decolorization of congo red dye is found by varying the weight of TiO_2 catalyst from 15mg to 35mg as shown in Fig.-8. The maximum decolorization of congo red dye is achieved with 25 mg of the titanium dioxide catalyst beyond which a decrease in the decolorization rate is observed. This is due to fact that active sites required for the photocatalytic dye decolorization increase by increasing the catalyst concentration and beyond the addition of a certain amount of the catalyst to the dye solution there will be an increase in the turbidity of the suspension and hence decreases the sunlight penetration. This decrease in sunlight penetration in the dye solution brings about a decrease in the photodecolorization process.[26, 27]

Effect of Initial Dye Concentration and Effect of Loading Strontium Silicate onto TiO_2 Photocatalyst

To find out the optimum concentration of congo red dye, the concentration of the dye is varied from 10-50mg/L and the maximum dye decolorization efficiency is evaluated using 25mg of bare titanium dioxide at an optimum pH of 7.5 by effective air purging under sunlight. About 94% of 10mg/L of congo red dye got decolorized within 90 minutes. The interaction of the hydroxyl radicals with the dye molecules decreases on increasing the congo red dye concentration and the turbidity of the solution blocks the sunlight penetration path, which also accounts for the photodecolourization of the dye at higher concentrations.[28,29] Under similar conditions, 95% of dye decolorization took place within 40 minutes using 1% strontium silicate loaded titanium dioxide photocatalyst, whereas under room temperature only

12% of the dye decolorization took place. This clearly shows that the dye is resistant to self-photolysis and that both TiO_2 catalyst and effective air purging under sunlight are essential for efficient photocatalytic decolorization of congo red dye. Further modifying the titanium dioxide catalyst loading different weight percent of strontium silicate has also reduced the time taken for the photocatalytic dye decolorization process.

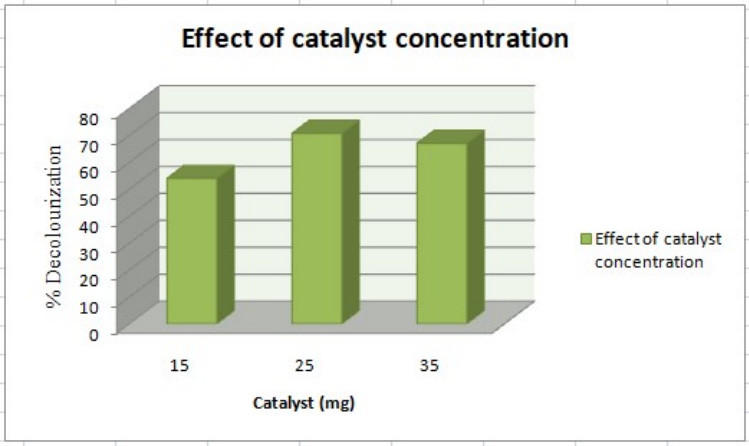

Fig.-8: 0.01g/L Congo Red Dye Solution, TiO_2 catalyst dosage varied from 15mg to 35mg, pH = 7.5, Air Flow Rate = 2.5L/min under Sunlight.

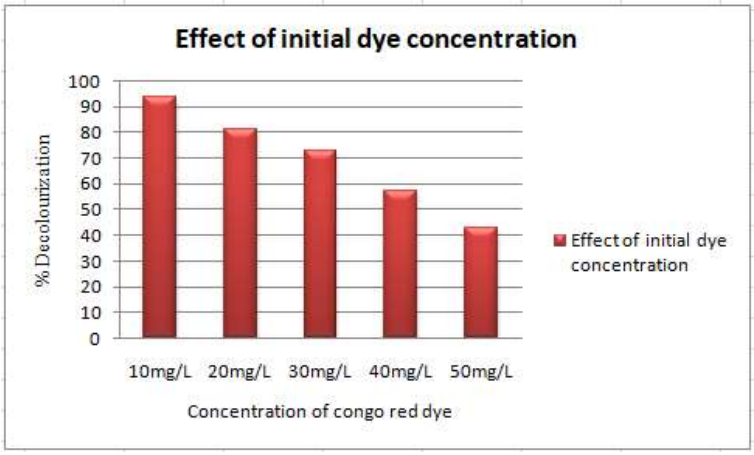

Fig.-9:25mg of TiO_2Catalyst, pH=7.5, initial Congo Red Dye concentration varied from 0.01g/L to 0.05g/L, airflow rate = 2.5L/min under Sunlight.

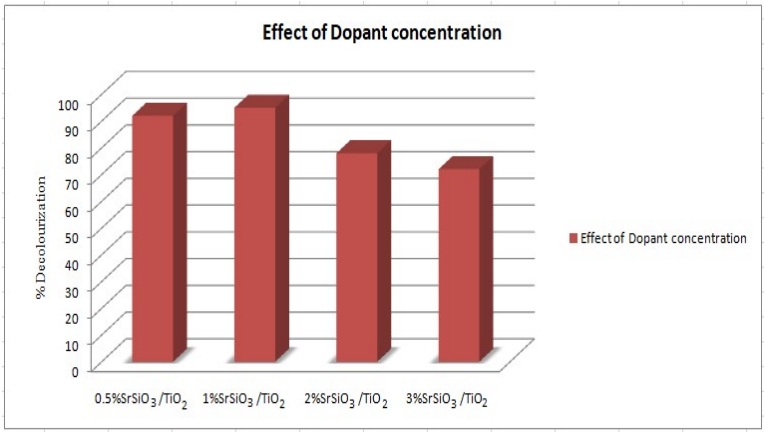

Fig.-10: Initial Congo Red Dye concentration (10mg/L), strontium silicate weight varied from 0.5-3% on TiO_2 catalyst(25mg), pH=7.5, airflow rate = 2.5L/min under Sunlight. (Figure changed)

Kinetic Studies

The kinetics for the degradation of congo red dye using titanium dioxide and strontium silicate loaded TiO_2 photocatalyst is studied by Langmuir Hinshelwood kinetic model. According to the (L-H model), the integrated form of pseudo-first order kinetics[30-32] is as follows:

$$\ln [C_0]/[C] = kt$$

Where, k is the pseudo-first-order rate constant (min^{-1}), C_0 is the initial concentration of dyes ($g\ L^{-1}$), C is the concentration of the congo red dye at time't' (minutes).
The linear fit between ln $[C_0/C]$ and irradiation time't' under different weight percent of strontium silicate loaded TiO_2 photocatalysts was plotted to understand the pseudo-first-order rate equation. The photocatalytic experiments for degradation of congo red dye solution followed pseudo first order kinetics shown in Fig.-11. The calculated average R^2 values are 0.966, 0.960, 0.904 and 0.865 for 0.5-3% strontium silicate incorporated titanium dioxide photocatalysts respectively.

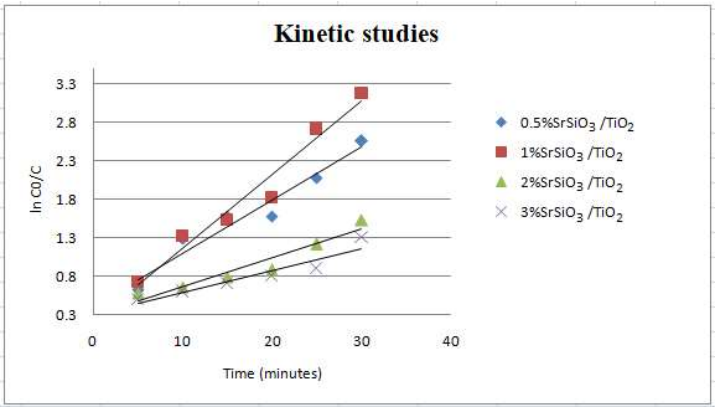

Fig.-11: The Plots of ln($[C_0]/[C]$) versus Time for different weight percent of strontium silicate loaded TiO_2 photocatalyst. (Figure changed)

CONCLUSION

$SrSiO_3/TiO_2$ composite photocatalyst was successfully synthesized by a simple chemical precipitation method. Effective degradation of Congo red dye is achieved by effective air purging under solar irradiation within a very short span of time. Thus, this simplest, low-cost and effective technique can be employed for thedegradation of the azo class of dyes from the aqueous solution.

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REFERENCES

1. A. Riga, K. Soutsas, K. Ntampegliotis, V. Karayannis and G. Papapolymerou, *Desalination*, **211**, 72(2007), https://doi.org/10.1016/j.desal.2006.04.082
2. MehtapEjder-Korucu, Ahmet Gurses, Cetin Dogar, Sanjay K. Sharma and MetinAcikyildiz, 2015, Removal of Organic Dyes from Industrial Effluents: An Overview of Physical and Biotechnological Applications, Scrivener Publishing LLC, Beverly, pp.1-34.
3. H. Ali, *Water Air Soil Pollution*, **213**, 251(2010), https://doi.org/10.1007/s11270-010-0382-4
4. H.Lachheb, E.Puzenat, A.Houas, M.Ksibi, E.Elaloui, C.Guillard and J.M.Herrmann, *Appl. Catal., B*, **39**, 75(2002), https://doi.org/10.1016/j.desal.2005.04.048
5. Y.Wang, *Water Research,***34(3)**, 990(2000).

6. A. Mittal, V. Thakur and V. Gajbe, *Environmental Science and Pollution Research*, **20(1)**,260(2013), https://doi.org/10.1007/s11356-012-0843-y
7. N. Barka, S. Qourzal, A. Assabbane, A. Nounah and Y. Ait-Ichou, *Arabian Journal of Chemistry*, **3(4)**, 279(2010), https://doi.org/10.1016/j.arabjc.2010.06.016
8. N. Saibaba KV and R.V. Kandisa, *Rasāyan Journal of Chemistry*, **12(4)**, 2176(2019), https://doi.org/10.31788/RJC.2019.1245478
9. M.Stylidi, D.I. Kondarides and X.E.Verkyios, *Applied catalysis B. Environmental*, **40**, 271(2003)
10. Y.G.Wang, B.Li, C.L.Zhang, L.F.Cui, S.F.Kang, X.Liand L.H.Zhou, *Appl. Catal. B* **131**, 277(2013), https://doi.org/10.1016/j.jsamd.2018.07.003
11. H. Narayan, H. Alemu, L. Macheli, M. Thakurdesai and T. K. Gundu Rao, *Nanotechnology*, **20**, 255601(2009), https://doi.org/10.1088/0957-4484/20/25/255601
12. F. Han, V. S. Kambala, M. Srinivasan, D. Rajarathnam and R. Naidu , *Applied Catalysis A: General*, **359**, 25(2009), https://doi.org/10.1016/j.apcata.2009.02.043
13. A. G. Agrios, P. J. Pichat, *Journal of Applied Electrochemistry*, **35**, 655(2005).
14. Himanshu Narayan and Hailemichael Alemu¸ *IOP Conf. Series: Journal of Physics: Conference Series,* **82**, 394 (526071879).
15. Adiansyah, I. Elisabeth Purba , M. Tarigan , Lisnadiyanti, Yusnaidar and I.P. Mahendra, *Rasayan Journal of Chemistry*, **13(1)**, 757(2020), http://dx.doi.org/10.31788/RJC.2020.1315461
16. E.T. Wahyuni, S. Suherman, D. Satyawati, R. Puspita and M. Mudasir, *Rasayan Journal of Chemistry*, **13(1)**, 574(2020), http://dx.doi.org/10.31788/RJC.2020.1315464
17. V.P. Muhamedshajudheen, K. Viswanathan, K. Aniatha Rani, A. Uma Maheswari and S. Saravana Kumar, *International Journal of Chemical and Molecular Engineering*,**10(5)**, 2016.
18. R. Desai, S. K. Gupta, S.Mishra, P.K. Jha and A. Pratap, *International Journal of Nanoscience*,**10**, 1249(2011), https://doi.org/10.1142/S0219581X11008381
19. Y. Han, H. S. Kim and H. Kim, *Journal of Nanomaterials*, **Volume 2012**, Article ID 427453(2012), https://doi.org/10.1155/2012/427453
20. R. Kaplan, B. Erjavec, G. Draˇzi´c, J. Grdadolnik, and A. Pintar, *Applied Catalysis B, Environmental*, (2015), http://dx.doi.org/10.1016/j.apcatb.2015.08.027
21. H. Lee, S. C. Lee, J. H. Seo, W. G. Hong, H. Kim, H. J. Yun, H. J. Kim, and J. Lee, *Chemical Engineering Journal,*(2013), http://dx.doi.org/10.1016/j.cej.2013.02.099
22. S. C. Lee , H. U. Lee, S. M. Lee, G. Lee, W. G. Hong, J. Lee, and H. J. Kim, *Materials Letters*,**79** 191(2012).
23. L. Mateˇjova, Zdeneˇk Mate and Olga Šolcova, *Microporous and Mesoporous Materials*,**154** 187(2012).
24. S. Erdemoˇglu, S. K. Aksub, F. Sayılkan, B. Izgi, M. Asiltˈurk, H. Sayılkan, F. Frimmel and S¸ erefGˈuc¸er , *Journal of Hazardous Materials*, **155**, 469(2008).
25. N. J. Bejarno-Perez and M. F. Suarez-Herrera, *Ultrasonics Sonochemistry*, **14**, 589(2007), https://doi.org/10.1016/j.ultsonch.2006.09.011
26. Y. Ou, J. Lin, S. Fang and D. Liao, *Catalysis Communications,***8**, 936(2007).
27. T. Peng, D. Zhao, K. Dai, W. Shi and K. Hirao, *The Journal of Physical Chemistry B,***109**, 4947(2005), https://doi.org/10.1021/jp044771r
28. S. A. Qaradawi and S. R. Salman, *Journal of Photochemistry and Photobiology A*,**148**, 161(2002), http://dx.doi.org/10.1016/S1010-6030(02)00086-2
29. X. W. Zhang, Y. Z. Wang and G. T. Li, *Journal of Molecular Catalysis A: Chemical*, **237**, 199(2005), https://doi.org/10.1016/j.molcata.2005.03.043
30. Y. Caoa, X. Lia, Z. Biana, A. Fuhrb, D. Zhang, J. Zhu, *Applied Catalysis B: Environmental,***180**, 551(2016), https://doi.org/10.1016/j.apcatb.2012.09.005
31. Ruby Chauhan, Ashavani Kumar, Ram Pal Chaudhary, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,***98**, 256(2012), https://doi.org/10.1016/j.saa.2012.08.009
32. S. K. Kansal, M. Singh, D. Sud, *Journal of Hazardous Materials*,**141**, 581(2007), https://doi.org/10.1016/j.jhazmat.2006.07.035

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