www.ijramr.com

ISSN : 2350-0743

International Journal of Recent Advances in Multidisciplinary Research

Vol. 04, Issue 04, pp.2498-2504, April, 2017

RESEARCH ARTICLE

SOLUTION PROCESSING OF RUTHENIUM DOPED ZnO ON CALCIUM ALUMINUM SILICATE BEADS AND THEIR APPLICATION IN PHOTODEGRADATION OF ORGANIC DYES

Namratha, K., *Deepthi, B. K., Deepa, C.S. and Byrappa, K.

Center for Material Science and Technology, Vijnan Bhavan, Manasagangotri, P. B. No 21, University of Mysore, Mysore 570006, India

ARTICLE INFO

Article History:
Received 27th January, 2017
Received in revised form
14th February, 2017
Accepted 28th March, 2017
Published online 30th April, 2017

Keywords:
Solvothermal Synthesis,
Photocatalysis,
Calcium Aluminum Silicate Beads,
Ru^+doped ZnO Nanomaterials,
Organic Dyes.

ABSTRACT

Solution processing of ruthenium (Ru^+) doped ZnO nanoparticles on surface of calcium aluminum silicate beads were carried out under solvothermal conditions (T, 150°C; P, autogenous; duration, 4h). The reagent grade ZnO, ruthenium and calcium aluminum silicate beads (CASB) material were used as starting materials along with methanol as a solvent and thus obtained ruthenium doped ZnO coated calcium aluminum silicate beads were characterized by using X-ray diffraction, SEM, Fourier transform infrared spectroscopy and UV spectroscopy. Solar light mediated Photocatalytic degradation of organic dyes such as brilliant yellow, brilliant blue, rhodamine b and proclor red Mx-5B dye, two mixed dye (rhodamine b and proclor red Mx-5B) and three mixed dye (brilliant blue, brilliant yellow and rhodamine b) were studied using solvothermal prepared Ru^+ doped ZnO coated calcium aluminum silicate beads. The effect of various parameters such as initial dye concentration and Catalyst loading with time duration on photodegradation of organic dyes was investigated.

INTRODUCTION

ZnO is a promising photocatalyst [1-5] and nano particles of ZnO have been employed extensively in studies related to heterogeneous photocatalysis in degradation of environmental contaminants because of their increased surface area [6-11]. The doping of metal ions into ZnO nanoparticles can lead to effects such as enhancement in fluorescence and controlling concentration of surface defects [12]. The Ru^+ doped ZnO is expected to modify absorption and could result in enhanced Photocatalytic activity. Calcium aluminum silicate beads were used as the Photocatalyst support material due to their large surface area and ordered pore structure. In addition, the large pores and high surface area allow nanoparticles of catalyst to be incorporated inside the pores which helps in Photocatalyst processing with highly effective photoctalytic degradation of organic dyes and contaminants (13). Photocatalytic degradation involves absorption of photon by Ru^+ doped ZnO nanoparticles coated on calcium aluminum silicate beads which leads to promotion of electron from valance band to conduction band of the semiconductor particle surface; this electron promoted from the valance band to the conduction band leaves a positive hole (h^+) in the valance band. These electrons and hole pairs can be recombined on the surface or in the bulk of the particle in a few nanoseconds and the energy is dissipated as heat or can be trapped in surface states where they can react with donor or acceptor species like H^+, OH^- or O_2 adsorbed or close to the surface of the particle forming hydroxyl radical or superoxide anion which are strong oxidizing agent capable of oxidizing organic compound into CO_2 and H_2O. In the present work, the authors have employed a mild and environmentally bening technique, namely, solvothermal method for the coating of Ru^+ doped ZnO nanoparticles on surface of calcium aluminum silicate beads. This specially prepared Photocatalytic material was then characterized by various techniques such as powder X-ray diffraction (XRD), SEM, Fourier transform infrared spectroscopy (FTIR) and UV spectroscopy. The Photocatalytic degradation of organic dyes using these Ru^+ doped ZnO coated calcium aluminum silicate beads has been reported. The influence of various parameters such as initial dye concentration and amount of catalyst used with time on Photocatalytic degradation of organic dyes such as brilliant yellow, brilliant blue, rhodamine B, proclor red MX-5B dye, two mixed dye and three mixed dyes has been discussed in detail.

Experimental procedure

Solvothermal preparation of ZnO coated calcium aluminum silicate beads

Ru^+ doped ZnO were coated on surface of calcium aluminum silicate beads supports by solvothermal technique. In solvothermal experiments, required amount of commercially available reagent grade ZnO was taken in teflon liner along

---

***Corresponding author: Deepthi, B. K.,**
Center for Material Science and Technology, Vijnan Bhavan, Manasagangotri, P. B. No 21, University of Mysore, Mysore 570006, India

with ruthenium as dopant and mixed with solvent methanol. A known amount of calcium aluminum silicate beads supports was added into teflon liner containing solution of ZnO, ruthenium and methanol. The teflon liner was inserted into the stainless steel autoclave and kept for heating in a furnace at the desired temperature. The experiment temperature was fixed to 150^{o}C for 4h. After the experimental run the autoclave was quenched at room temperature and the resultant product from teflon liner were carefully recovered. The resultant products were washed with nanopure water repeatedly. Finally the recovered Ru^+ doped ZnO coated on calcium aluminum silicate beads supports were dried at 60^{o}C for 12h.

Characterization of Ru^+ doped ZnO coated calcium aluminum silicate beads

The crystal phases of ruthenium doped ZnO coated on calcium aluminum silicate beads were identified using Rigaku MiniFlex II Desktop X-ray Diffracto meter, Japan, with CuKα, λ=1.542Å radiation, Voltage = 30mV, Current =15mA, Scan speed ~2° min^{-1} with scanning range 20-80^o. The strongest peaks corresponding to ZnO were selected to evaluate crystallinity of Ru^+ doped ZnO coated Calcium aluminum silicate supports. The identification of crystalline phase was accomplished by comparison with JCPDS files. General morphology and detailed structure of Ru^+ doped ZnO coated on calcium aluminum silicate beads support was determined using scanning electron microscope SEM Hitachi, (JAPAN). The structural and quantitative elucidation of Ru^+ doped ZnO coated on calcium aluminum silicate beads was characterized by fourier transform infrared (FTIR) spectroscopy using JASCO-460 PLUS, Japan at a resolution of 4 cm^{-1}. The optical properties were studied using UV-Vis spectrophotometer (Array Spectrometer SA 165 Elico, India).

Photocatalytic experiment

Photocatalytic degradation was carried out for Brilliant Yellow, Brilliant Blue, Rhodamine B and Proclor red MX- 5B, both individually and mixed, where two mixed dyes (Rhodamine B and proclor red Mx-5B) figure 5 and three mixed dye (Brilliant Blue, Brilliant Yellow and Rhodamine B) figure 6 were mixed in the ratio 1:1 and 1:1:1 respectively where emission wavelength of these mixed dye was determined by scanning the dye solution in UV-spectroscopy between wavelength range 300-800. In Photocatalytic experiments, dye solution containing catalyst (ZnO) were taken in a beaker and exposed to sunlight for different time duration till cent percent transmission was achieved. Dye samples of about 2–3 ml were taken out at every 30 min from the test solution and centrifuged for 10 min at 750–800 rpm, their absorbance were recorded at 397 for brilliant yellow, 628 for brilliant blue, 555nm for Rhodamine B dye and 538nm for proclor Red Mx-5B dye, 553 nm for two mixed dyes and 554nm for three mix dye using a spectrophotometer to determine percentage decolorization (Model: SA 165, Array Spectrophotometer Elico, India). Chemical oxygen demand (COD) of the dye solution was estimated before and after the Photocatalytic treatment using $K_2C_{r2}O_7$ oxidation method.

RESULTS AND DISCUSSION

Characterization

The powder XRD pattern of Ru^+ doped ZnO coated on calcium aluminum silicate beads is shown in Figure 1. The identification of crystalline phase of ZnO was accomplished by comparison with JCPDS files. The required phase of ZnO was observed on the surface of calcium aluminum silicate beads. Figure 2 shows FTIR spectrum Ru^+ doped ZnO coated on calcium aluminum silicate beads. The two stretching bands of ZnO are obtained in the range 600 to 400 cm^{-1} in the FTIR spectrum. The stretching mode of vibration of C=O is observed at 1630 cm$^{-1.}$ The FTIR absorption bands of solvothermal process ZnO nanomaterials clearly show stretching band in the range of 3200-3600 cm^{-1} corresponding to O-H group, indicating the existence of adsorbed moisture on the surface.

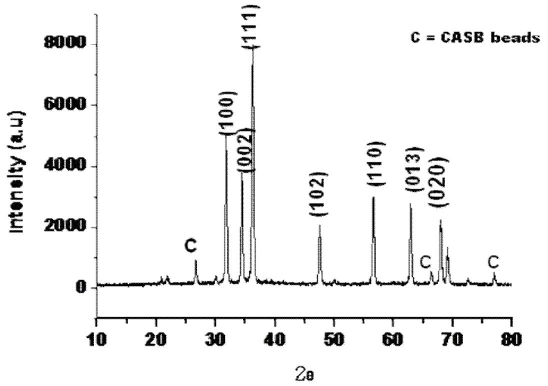

Figure 1. X-ray diffraction pattern of Ru^+ doped ZnO coated calcium aluminum silicate beads

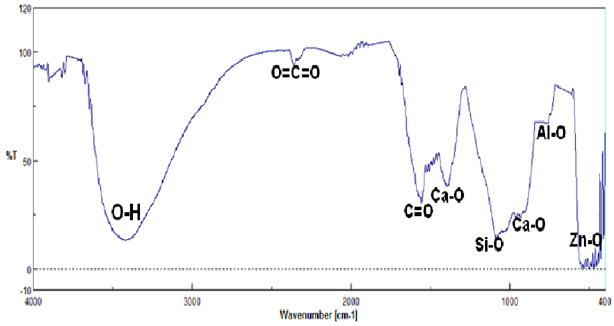

Figure 2. FTIR Spectrum of Ru^+ doped ZnO coated calcium aluminum silicate beads

The absorption bands of Si-O, Al-O and Ca-O are observed in the FTIR spectrum as CASB supports are used in the present work. Figure 3 shows SEM image of solvothermal prepared Ru^+ doped ZnO coated calcium aluminum silicate beads. The particles are in the size range 100nm with lower aspect ratio. And are usually hexagonal shapes, which can be clearly shown in figure. The ultraviolet spectroscopy data is shown in the figure 4. It was observed that the synthesized doped sample had a profound effect on its optical response in the visible length range. Band of the synthesized sample was calculated by using the formula E_g=1240/λ, where E_g is bandgap and λ is wavelength. The band gap of bulk reagent grade ZnO is found to be 3.37 which are comparable with literature data. The ruthenium doped ZnO showed band gap of about 3.24ev which has been reduced by 0.13ev when compared with that of reagent grade ZnO. The narrowing of band gap may due to formation of midgap band above valence band. The electrons are transferred from midgap band to conduction band. Thus by narrowing the band gap, the absorbance has shifted from ultraviolet to near visible region.

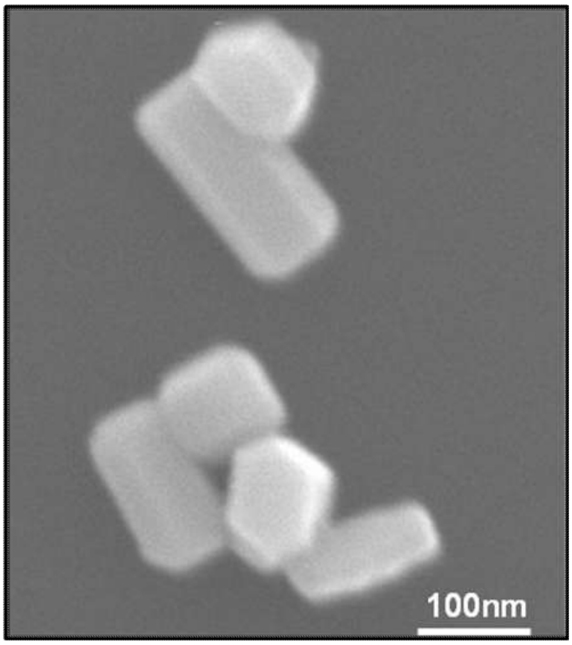

Figure 3. SEM image of Ru$^+$ doped ZnO coated Calcium aluminum silicate beads

Red shift indicates more photogenerated e-/h$^+$ pairs that could be excited by photons with less energy, leading to better Photocatalytic degradation efficiency in visible region (14).

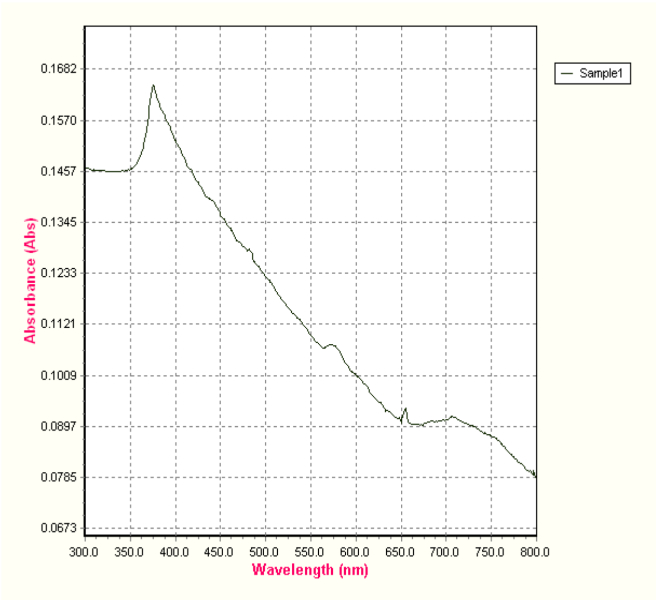

Figure 4. UV-Visible spectroscopy image of Ru$^+$ doped ZnO coated calcium aluminum silicate beads (λ_{max} 382nm)

Photocatalytic activity of ruthenium doped ZnO coated on Calcium aluminum silicate beads

The experiment were conducted to test the photoactivity of Ru$^+$ doped ZnO coated on calcium aluminum silicate beads in the degradation of brilliant yellow, brilliant blue, rhodamine dye, proclor red Mx 5B dye, two mixed dye (rhodanmine B dye and proclor red Mx 5B dye) and three mixed dye (brilliant blue, brilliant yellow and rhodamine B dye) with respect to operating parameter. The emission wave length of two mixed dye and three mixed dye was fixed by scanning different concentration of dye solution in UV-spectroscopy between wavelength ranges 300-800 which showed increase in absorption peak at the same wavelength range i.e 553 (Figure 5) and 554 (Figure 6) for two mixed dye and three mixed dye respectively. Mineralization was estimated by measuring COD before and after experiment run. There are several factors that can affect the Photocatalytic degradation processes. Such factors are nature of the catalyst and target pollutant, catalyst loading, concentration of pollutant, light intenstity and wavelength, interfering species in solution media and solution *pH*. In this present work authors have discussed two important factors which were initial pollutant concentration and catalyst loading with time was chosen to discuss.

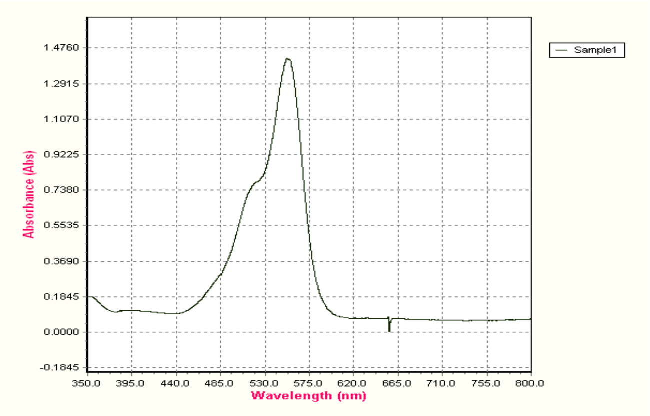

Figure 5. UV-Vis Spectra in ranges 350-800 nm for 2 mix dye (emission wavelength - 553 nm)

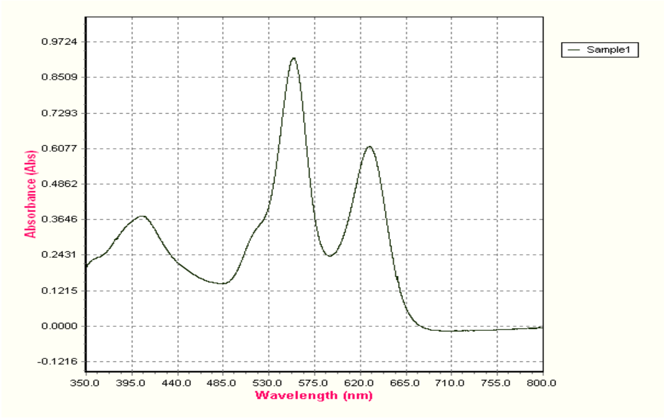

Figure 6. UV-Vis Spectra in ranges 350-800 nm for 3 mix dye (emission wavelength - 554 nm)

Effect of catalyst loading rate

The amount of catalytic loading rate is one of the main parameter for the degradation studies. In order to avoid excess of catalyst it is necessary to find out optimum loading for efficient removal of dye. To determine optimum dosage of the catalyst photodegradtion of brilliant yellow, brilliant blue, rhodamine b, proclor red MX dye, two mixed dye (rhodamine B and Proclor red Mx 5B dye) and three mixed dye (Brillaint blue, Brilliant yellow and rhodamine B dye) Photocatalytic degradation experiment was carried by taking different amount of catalyst i.e. 4,8,12,16 and 20g/l for time duration of 90, 120, 90, 90, 90, and 90 minute respectively by keeping dye concentration constant at 15ppm (Figure 7, 8, 9, 10, 11 and 12).

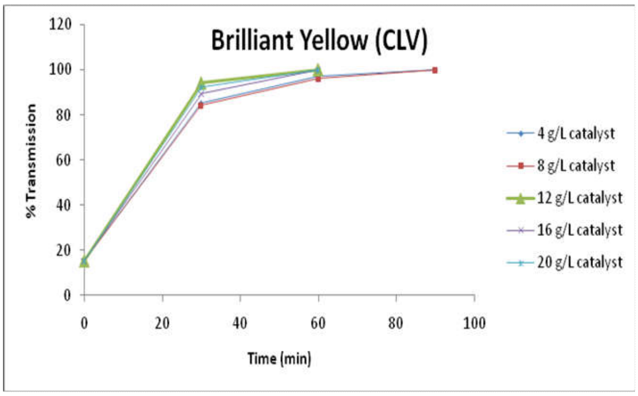

Figure 7. Effect of catalyst loading rate in decolorization of brilliant yellow dye

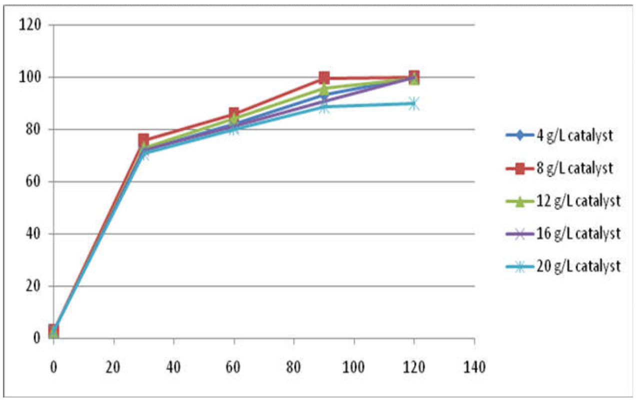

Figure 8. Effect of catalyst loading rate in decolorizatiom of brilliant blue dye

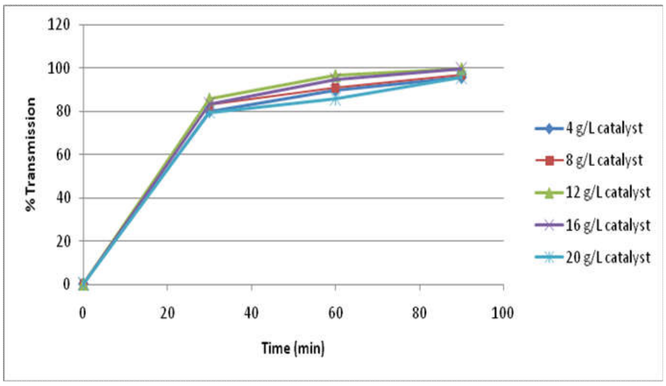

Figure 9. Effect of catalyst loading rate in decolorization of rhodamine B dye

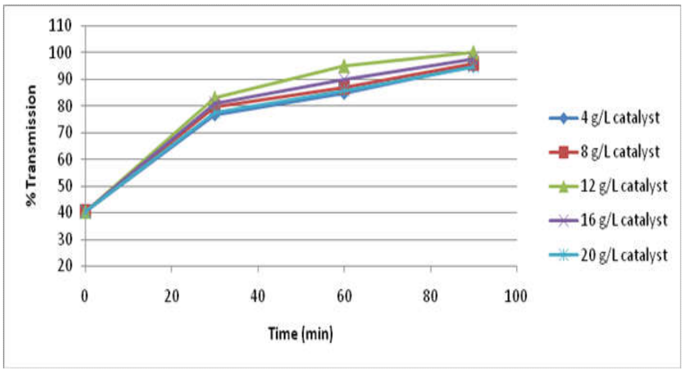

Figure 10. Effect of catalyst loading rate in decolorization of proclor red mx 5B dye

The results of photodegradation studies i.e. % transmission with respect to catalyst variation are represented in figure. Studies reveal that increase in the Photocatalyst loading is able to improve degradation efficiency due large amount of active surface area of the catalyst (i.e. ruthenium doped ZnO) on CASB as well as higher light absorption. The increase of active surface means more active sites for carrying out Photocatalytic reaction. In addition more catalyst is exposed to sunlight so amount of photon being absorbed increases, thus degradation efficiency will be enhanced. However, when the catalyst loading exceed certain amount, degradation slightly reduced because the light penetration slightly decreased because large amount of Photocatalyst load in the dye solution leads to light scattering and reduction in light penetration through the aqueous medium by decrease in transparency of aqueous dye solution.

Effect of initial dye concentration

The effect of initial dye concentration on Photocatalytic degradation of brilliant yellow, brilliant blue, rhodamine b, proclor Red Mx 5B dye , two mixed dye (rhodamine b and proclor red MX 5B dye) and three mixed dye (brilliant blue, brilliant yellow and rhodamine b dye) has been examined. The initial dye concentration was varied from 10ppm, 15ppm, 20ppm, 25 ppm and 30 ppm keeping catalyst dosage constant at 1.2g/l, 0.8g/l, 1.2g/l, 1.2g/l, 0.8g/l and 0.8g/l for time duration of 180 minutes for brilliant blue, brilliant yellow, rhodamine b dye and two mixed dye, 150 minutes for proclor red Mx 5B dye and three mixed dye respectively (Figure 13, 14, 15, 16, 17 and 18). The result of the experiment is shown in figure. The studies reveal that as the concentration increases time required to reach 100% transmission also increases because when the concentration increases amount of available active sites for reaction between active radical and dye molecules decreased because of the competitive adsorption of dye molecule on the surface of ZnO. Furthermore at higher concentrations of dye molecules in aqueous medium restrict the penetration of light through it and light illumination on catalyst is less. Hence the production of hydroxyl and super oxide radicals is limited or reduced. Therefore, the photodegrdation efficiency is reduced.

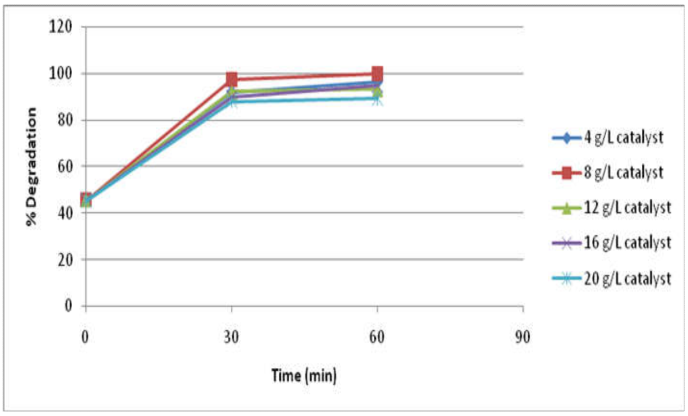

Figure 11: Effect of catalyst loading rate in decolorization of 2 mix dye

Estimation of Chemical oxygen demand (COD)

COD is the measurement of amount of oxygen in water consumed for chemical oxidation total concentration of

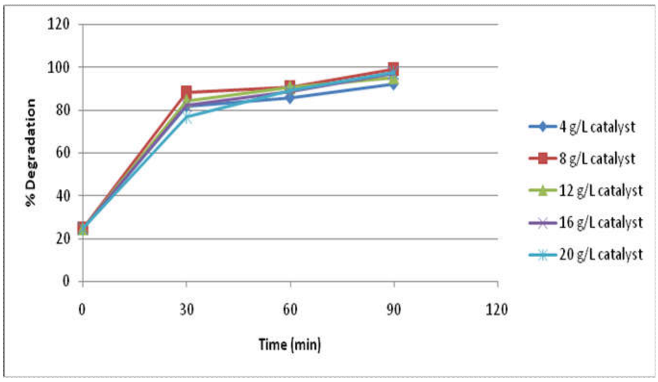

Figure 12. Effect of catalyst loading rate in decolorization of 3 mix dye

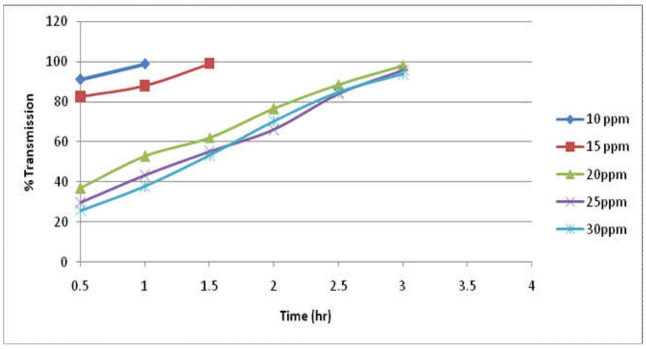

Figure 13. Effect of concentration variation in decolorization of brilliant yellow dye

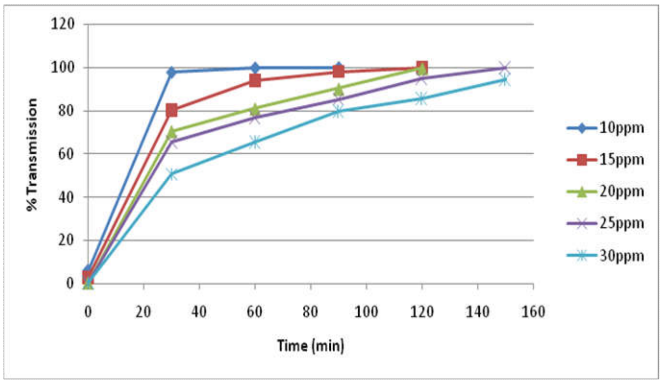

Figure 14: Effect of concentration variation in decolorization of brilliant blue dye

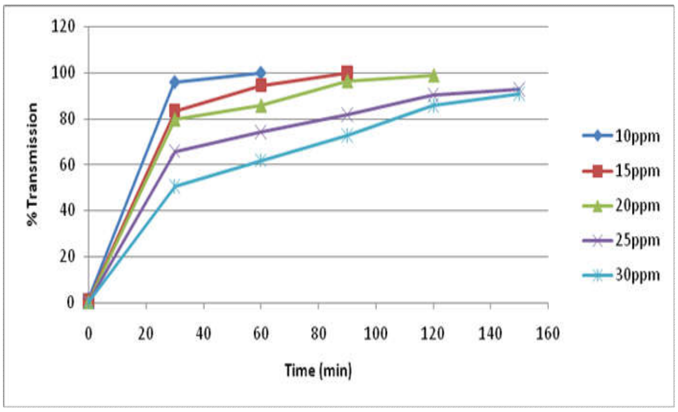

Figure 15. Effect of concentration variation in decolorization of rhodamine B dye

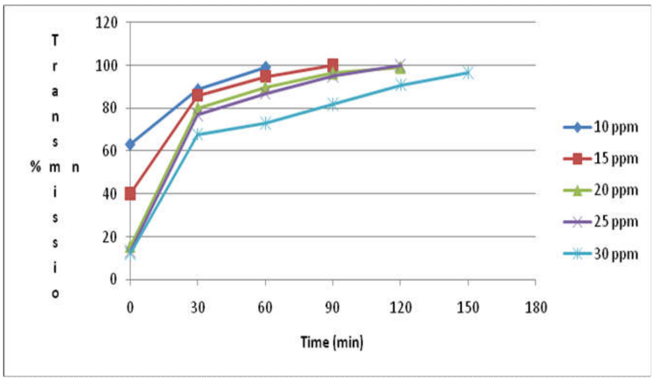

Figure 16: Effect of concentration variation in decolorization of proclor red mx -5B dye

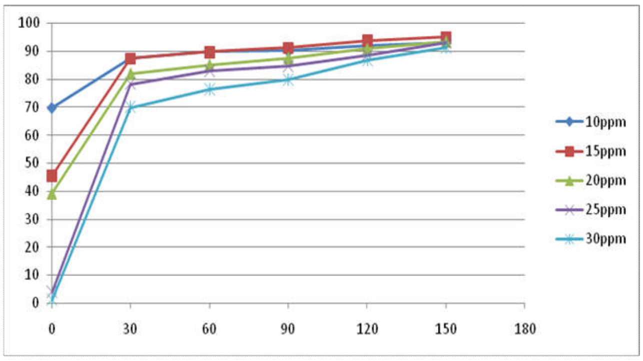

Figure 17: Effect of concentration variation in decolorization of 2 mix dye

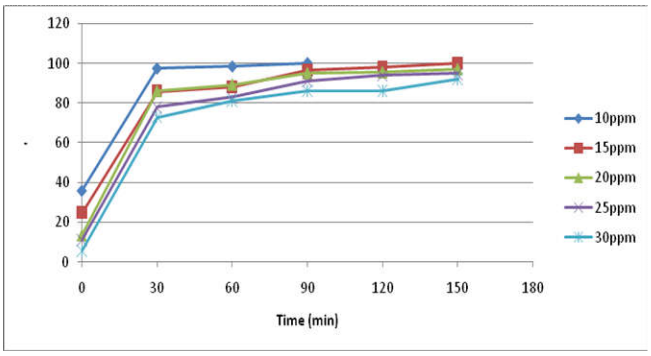

Figure 18. Effect of concentration variation in decolorization of 3 mix dye

Table 1: Percentage removal of COD in catalyst loading rate of brilliant yellow dye

Catalyst Dosage (g/L)	Initial COD mg/L	Final COD mg/L	% Removal
4	279.14	47.90	82.84
8	279.14	39.01	86.03
12	279.14	41.50	85.13
16	279.14	51.97	81.38
20	279.14	60.26	78.41

Table 2. Percentage removal of COD in catalyst loading rate of brilliant blue dye

Catalyst Dosage (g/L)	Initial COD mg/L	Final COD mg/L	% Removal
4	171.56	50.47	70.58
8	171.56	41.50	75.81
12	171.56	35.75	79.16
16	171.56	40.86	76.18
20	171.56	42.08	75.47

Table 3. Percentage removal of COD in catalyst loading rate of rhodamine B dye

Catalyst Dosage (g/L)	Initial COD mg/L	Final COD mg/L	% Removal
4	384.81	89.23	76.81
8	384.81	54.23	78.11
12	384.81	74.61	80.61
16	384.81	80.11	79.18
20	384.81	93.73	75.64

Table 4. Percentage removal of COD in catalyst loading rate of proclor red mx 5B dye

Catalyst Dosage (g/L)	Initial COD mg/L	Final COD mg/L	% Removal
4	384.18	156.8	59.18
8	384.18	123.43	67.87
12	384.18	122.28	68.17
16	384.18	122.28	68.17
20	384.18	119.82	65.81

Table 5: percentage removal of COD in catalyst loading rate of 2mix dye

Catalyst loading in (g/L)	Initial COD mg/L	Final COD mg/L	% Removal
4	627.70	129.49	79.37
8	627.70	113.11	81.98
12	627.70	118.38	81.14
16	627.70	131.12	79.11
20	627.70	156.86	75.01

Table 6. Percentage removal of COD in catalyst loading rate of 3-mix dye

Catalyst loading in (g/L)	Initial COD mg/L	Final COD mg/L	% Removal
4	863.85	208.96	75.81
8	863.85	148.75	82.78
12	863.85	171.81	80.11
16	863.85	210.95	75.58
20	863.85	221.81	74.32

Table 7: percentage removal of COD in concentration variation of brilliant yellow dye

Concentration of dye in ppm	Initial COD in mg/L	Final COD in mg/L	%Removal
10	188.16	21.63	88.5
15	279.14	36.42	86.95
20	362.63	57.40	84.17
25	440.7	89.73	79.48
30	586.44	172.17	70.64

Table 8. Percentage removal of COD in concentration variation of brilliant blue dye

Concentration of dye in ppm	Initial COD in mg/L	Final COD in mg/L	% Removal
10	116.78	20.10	82.78
15	171.56	33.09	80.71
20	221.43	51.21	76.87
25	328.78	82.81	74.81
30	467.11	140.88	69.84

Table 9. Percentage removal of COD in concentration variation of rhodamine B dye

Concentration of dye in ppm	Initial COD in mg/L	Final COD in mg/L	%Removal
10	250.11	42.06	83.18
15	384.81	72.49	81.16
20	521.48	111.96	78.53
25	632.79	163.89	74.10
30	778.11	227.13	70.81

Table 10: Percentage removal of COD in concentration variation of proclor red mx 5B dye

Concentration of dye in ppm	Initial COD in mg/L	Final COD in mg/L	%Removal
10	260.78	47.35	81.84
15	384.18	82.06	78.64
20	523.31	121.35	76.81
25	785.69	216.37	72.46
30	1104.35	350.74	68.24

Table 11. Percentage removal of COD in concentration variation of 2 mix dye

Concentration of dye in ppm	Initial COD mg/L	Final COD mg/L	%Removal
10	417.87	59.96	85.65
15	627.70	107.90	82.81
20	842.47	175.52	79.11
25	1051.64	254.70	75.78
30	1250.36	312.71	74.99

Table 12. Percentage removal of COD in concentration variation of 3 mix dye

Concentration of dye in ppm	Initial COD mg/L	Final COD mg/L	%Removal
10	564.48	80.26	85.78
15	863.85	142.79	83.47
20	1162.89	235.13	79.78
25	1378.91	338.93	75.42
30	1644.93	498.08	69.72

organics in the solution and decrease of cod reflects the degree of mineralization at the end of Photocatalytic process. COD disappearance of brilliant blue, brilliant yellow, rhodamine b, proclor Red Mx 5B dye, two mixed dye (rhodamine b and proclor red Mx 5B dye) and three mixed dye (brilliant blue, brilliant yellow and rhodamine b Dye) of catalyst variation (Table 1, 2, 3, 4, 5 and 6) and concentration variation (Table 7, 8, 9, 10, 11, 12) has been depicted in the table. Complete removal of COD was not achieved because it is difficult to destroy aromatic structure and halides group that are attached to the chromopore structure in dye molecule which is revealed from the result.

Conclusion

Ru^+ doped ZnO nanoparticles are deposited homogeneously on the surface of calcium aluminum silicate beads under solvothermal condition. It was observed that, Ru^+ doped ZnO profound effect on its optical response in the visible length range due to reduction in band gap and hence the as synthesized Ru^+ doped ZnO coated on Calcium aluminum silicate beads was found to be effective catalyst both in decolorization as well as destruction of dye stuff. The abundant supply of oxygen from natural atmosphere lead to increase in Photocatalytic rate due to reduction in electron and hole recombination because dissolved oxygen presents as an opposite effect, enhancing Photocatalytic activity, by acting as electron scavenger, resulting in improved parting of electron hole and allowing for more proficient movement of the charge carriers into the photo reaction sites. The rate and extent of Photocatalytic degradation is based on catalyst load, light source and initial dye concentration in aqueous medium. The reduction in percent transmission of dye solution indicated complete decolorization of dye in aqueous solution. Complete removal of COD was not achieved because it is difficult to destroy aromatic structure and halides group that are attached to the chromopore structure in dye molecule which is revealed from the result.

REFERENCES

Al-kaim, A, F., Ahmed, L, M., Mashkour, M, S., and Hussein F, H. 2011. Zinc oxide assisted Photocatalytic decolorization of reactive red 2 dye. *Int.J. Chem.Sci*, 9(3), 969-979.

Amini, M., and Ashrafi, M (2016) Photocatalytic degradation of some organic dyes under solar light irradiation using TiO_2 and ZnO nanoparticles. *Winter and spring* 1(1), 79-86.

Ananda, S., Byrappa, K., Kumar, V., Pakamard, S., Rungnapa, T., and Shivaraju, H. P. 2010. Hydrothermal coating of ZnO onto calcium alumino silicate beads and their application in photodegradation of amaranth dye. *Material Research innovation* 14 73-79.

Baruah, S., Dutta, J., and Pal, S, K (2012) Nanostructured Zinc oxide for water treatment. *Nanoscinence and technology*. 2, 90-102.

Bojja, S., Thota S., and Tirukkovalluri, s, R. 2014. visible light induced photocatalytic degradation of methyl red with codoped titania. *Journal of catalyst* 1-7.

Chen, L, L., Ding, J., Hong, R, Y., Li, J, H., Liu, D, Q., Li, H, Z., and Zheng, Y. 2009. synthesis, surface modification and photocatalytic property of ZnO nanoparticles. *Powder technology* 189, 426-432.

Das, A, K., Ferdous, T., Karim, M, M., Islam, A.S.M.A., and Masum, S.M. 2015. Photocatalytic degradation of direct brown RN dye in the presence of ZnO nanoparticles. *Bangladesh.J.Sci.ind.Res.* 50(1), 1-6.

Fahim, Y., Hadi, S., Jawad, A., Sadoon, A., and Salih A. 2014. Photocatalytic decolorization of methylene blue dye by Zinc oxide powder. *Journal of Babylon University/pure and applied sciences,* 9(22), 2508-2515.

Gao, W., Han , J., Liu Y., singhal N., and wang, l. 2012. Comparitve Photocatalytic degradation of estrone in water by ZnO and TiO_2 under artificial UVA and Solar irradiation. *Chemical engineering journal,* 213, 150-162.

Kalita, C., Malakar B., Miah A, T., and Saikia, P. 2015. structural evaluation and photocatalytic performance of chemically synthesized ZnO nanoparticles. *Chemical Science and transaction* 4(3), 788-798.

Kuzhalosai, V., and Shanthi, M. 2012. Photocatalytic degradation of azo dye, acid red 27, in aqueous solution using nano ZnO. *Indian journal of chemistry* 51, 428-434.

Mohabansi, N, P., Patil, V, B., and Yenkie, N. 2011. A comparative study on photodegradation of methylene blue dye effluent by advanced oxidation process by using TiO_2/ZnO Photocatalyst. *Rasayan J. chem,* 4(4), 814-819.

Mondal, K. and Sharma, A. Photocatalytic oxidation of pollutant dyes in wastewater TiO_2 and ZnO nanomaterials- A mini review. *Department of chemical engineering, Indian institute of technology, Kanpur, India.*

Rabbani, M., Rahimi, R., and Shokrayian J., Photocatalytic removing of methylene blue by using Cu-doped ZnO, Ag doped ZnO and Cu, Ag-codoped ZnO nanostructures. *Department of Chemistry, Iran university of Science and technology.*

****