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Efficiency of Photodegradation Properties of Nickel Calciate Nanoparticle Synthesized by solution combustion method

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Abstract- In the present work, With the intention of removal of colour from Coomassie Brilliant Blue R (CBBR), a triphenylmethane azo dye using the synthesized Nickel Calciate nanoparticles ($NiCaO_2$) in presence of natural sunlight. The nanoparticles were synthesized by using solution combustion method and characterisation was done by Scanning Electron Micrograph (SEM), X-Ray Diffraction (XRD), Energy Dispersive X-ray (EDX), Brunauer Emmett-Teller surface area determination and point zero charge determined by pH drift method. The band gap was determined by using UV-absorption spectroscopy. The rate of degradation efficiency was studied by varying different parameters such as catalyst concentration, solution pH dye concentration. The rate of degradation is highly efficient in 5×10^{-4} mol/dm^3 dye concentration with pH 6 and constant catalyst concentration 0.027g/50ml. Pseudo first-order rate constants and initial rates were determined and the photocatalytic mechanism was proposed. The result proves that $NiCaO_2$ can be used for removal of dyes from CBBR.

Keywords- *Catalyst, Coomassie Brilliant Blue R, Nanoparticles, $NiCaO_2$, Photodegradation*

I. INTRODUCTION

Water is the vital and basic need of life. Water is highly polluted by the many ways, majorly by the industries. Dyes and pigments are widely used in textiles, paper, plastics, leather, food and cosmetic industry to colour products [1]. Approximately 10,000 different types of dyes and pigments are utilized worldwide, around 10-15% of the dyes are remained in effluent throughout the course of dying process [2]. The various types of dyes used in textile industry, such as direct dyes, reactive dyes, vat dyes sulphur dyes, disperse dyes and naphthol dyes, which are both soluble and insoluble in water and involves a variety of organic chemicals [3]. Dyes and their substitute's products have found to be dangerous to aquatic life, mutagenic/carcinogenic and genotoxic [4],[5],[6],[7],[8].

The Coomassie brilliant blue belongs to the class of triphenylmethane azo dyes family and shows greater solubility in water in the form of its sodium salt [9]. Coomassie brilliant blue R-250 (CBBR-250) widely used in the biological staining, printing and dyeing leather, ink, lithography, *etc*. Exposure to these dyes can cause irritation to nose, throat and upper respiratory tract, chemical conjunctivitis to eyes and on chronic exposure it may cause skin dermatitis and show some mutagenic effects in the living organisms [10]. Other researchers have investigated the degradation of CBBR-250 by different nanoparticles like Fe_3O_4, [11] ZnO, [10] α-chitin nanoparticles [12] and Copper modified iron oxide nanoparticles [13]. Altikatoglu and Celebi [14] decolourize the CBBR-250 by Dextran Aldehyde-modified Horseradish Peroxidase. Sankar *et al.*, [15] degrade the CBBR-250 by green synthesized copper oxide nanoparticles.

The treatment through the biological methods is efficient to remove COD but not remove colour because of their complex aromatic molecular structures that resist degradation. Chemical and physical treatment is not harmful, but it can transfer pollutants from one phase to another, hence evolving new treatment technologies for eliminating contaminants from wastewater.[16],[17]. More recently, "Advanced Oxidation Process" (AOPs) use chemical procedures based on the use of catalysts or photochemical compounds which generate highly reactive transient species as the hydroxyl radical which possesses high affectivity for the oxidation of organic compounds [18].

Advanced Oxidation Processes (AOP) has been proposed as a substitute method for water purification of dyes and many other organics in wastewater and effluents. These processes usually, imply UV/H_2O_2, UV/O_3 or UV/Fenton's reagent for

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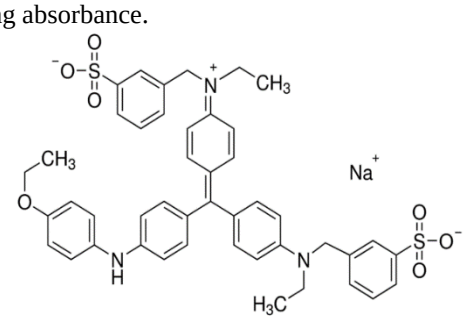
the oxidative degradation of contaminants [19],[20]. Semiconductor photocatalysis is another developed AOP, which has significant among AOP as a predicting tool for enforcing to the large-scale purification of wastewaters at low cost [21].

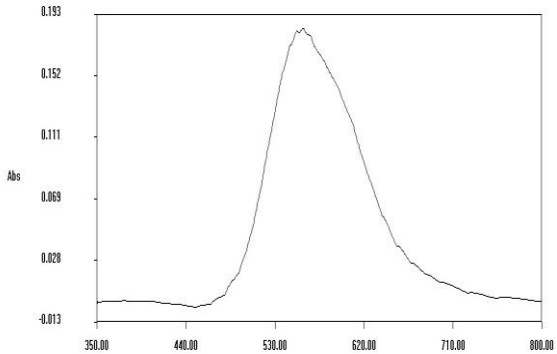
As per the research works carried out by many researchers in the past, the present work was carried out with the intention of providing a solution to the aquatic pollution and their effects. Here, the nanoparticle will act as a solar catalyst and through photocatalytic activity will remove the colour from the dye solution and controls the pollution. With different parameters like dosage, pH, and dye concentration were examined and studied in the present work.

II. MATERIAL AND METHODS

The commercially available water soluble dyes Coomassie Brilliant Blue R (λ_{max} 557nm) were obtained from Sisco Research Laboratory Pvt. Ltd. Maharashtra (Figure 1). The chemicals like Nickel Nitrate ($Ni(NO_3)_2.6H_2O$) (99% A. R.), are obtained from Sisco Research Laboratory Pvt. Ltd. Maharashtra Calcium Nitrate ($Ca(NO_3)_2.4H_2O$) (99%, A. R.), and Urea (NH_2CONH_2) (99.5%), were obtained from Hi-Media Chemicals, Mumbai and used as received without any further purification. The UV-VIS single beam spectrophotometer-119 (Systronics) has been used for recording absorbance.



(a)



(b)

Figure 1: (a) Chemical Structure of CBBR (b) Absorption Spectra of CBBR

2.1 SYNTHESIS OF NANOPARTICLES

The Nickel Calciate nanoparticle was prepared by solution combustion method using Nickel Nitrate, Calcium Nitrate, and Urea as fuel. Stoichiometric compositions of Nickel Nitrate (5.48g), Calcium Nitrate (7.08g), and were dissolved in minimum quantity of water along with Urea (6.05g) was taken in a silica crucible (with volume of 100 cm^3) using distilled water. Crucible was then introduced into the muffle furnace for calcination which was preheated to 600°C. According to propellant chemistry the reaction is as follows.

$3Ni(NO_3)_2 + 3Ca(NO_3)_2 + 10NH_2CONH_2$ ------- $3NiCaO_2 + 10CO_2 + 20H_2O + 16N_2$ – (1)

The solution boils and undergoes dehydration followed by decomposition along with the release of certain amounts of gases it froths and swells forming foam which ruptures with a flame and glows to incandescence. The product obtained after calcination is crushed in a mortar to make it amorphous and further used for the photocatalytic degradation study of CBBR aqueous suspensions.

2.2 CHARACTERIZATION OF SYNTHESIZED NANOPARTICLES

Powder X-ray diffraction (XRD) was performed by (Rigaku diffractrometer) using Cu-Kα radiation (1.5406 Å) in a θ-2θ configuration. Specific surface areas (SSA) of all photocatalysts were evaluated at 77 K by Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption (NOVA-1000 version 3.70 Instrument). Scanning electron microscope (SEM) image was taken with a JEOL (JSM-840A). The UV-visible spectra of the photocatalysts were carried out using a UV-visible spectrophotometer in the λ range from 200 to 1200 nm. The confirmatory presence of elements was carried out using Energy Dispersive X-ray (EDAX).

2.3 POINT OF ZERO CHARGE:

Point of zero charge or isoelectric point is the pH of the solution at which the total charge on the surface of the nanoparticles becomes zero (neutral). The point of zero charge of $NiCaO_2$ was measured by pH drift method, 50ml of Nacl 0.01M was taken in six separate beakers and bubbled it with Nitrogen gas to expel the dissolved CO_2 for few minutes at room temperature till it gets a stable pH reading. The pH of the solution in each beaker was adjusted between 2 to 12 by adding 0.1N Hcl and 0.1N NaoH after which 50mg of $NiCaO_2$ nanoparticles were added. This system was kept at room temperature until concurrent pH measured, this was kept for 92hrs for the stabilization of pH. The graph was plot against final pH v/s initial pH, the point which this curve crosses the initial pH=final pH straight line is the point of zero charge.

2.4 PHOTOCATALYTIC EXPERIMENT

A Stock solution of CBBR was prepared by dissolving 0.0412 g of triphenylmethane azo dye with 50mL double

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distilled water using a 50ml volumetric flask. The photocatalytic degradation of the triphenylmethane azo dye was conducted the batch study under solar light irradiation. Experiments were conducted in 100ml beakers, which were placed on a magnetic stirrer which continuously agitate the solution until the whole experiment was complete. In each experiment, an appropriate amount of triphenylmethane azo dye from stock solution was diluted to 50 ml with double distilled water. The pH of the dye solution was adjusted by adding 0.1N NaOH or 0.1N HCl. In all the experiments, the dye solution of appropriate concentration was taken in the 100ml glass beaker and covered with a glass plate to avoid evaporation of dye solution in the sunlight. Experiments were conducted for 240 min, and 05 mL of samples were taken from beakers with time intervals 30min. The whole experimental set-up was placed in sunlight between 11 a.m. and 4 p.m. and the average intensity of sunlight during this period is 889×100 lux unit using lux meter. The progress of photocatalytic degradation of the brilliant blue R was monitored by withdrawing a definite quantity of aliquot at regular intervals and measuring the absorbance in UV-vis spectrophotometer.

2.6 KINETIC STUDIES

The photodegradation of CBBR dye containing $NiCaO_2$ obeys pseudo-first order kinetics. The rate expression is given by

Rate = - (dC/dt) = kC (2)

Where C the concentration of dye (milligrams per liter), t the irradiation time, k the reaction rate constant (milligrams per liter hour), and k is the adsorption coefficient of the reactant (liters per milligram). As the initial concentration (Co) of dye is low, the equation can be simplified to an apparent first-order expression.

$\ln(Co/C) = k't,$ (3)

Where Co is the equilibrium concentration of the dye and C the concentration at time 't'. When a plot of ln (Co/C) versus time results in a straight line; its slope is the pseudo-first-order decolourization rate constant (k_{app}).

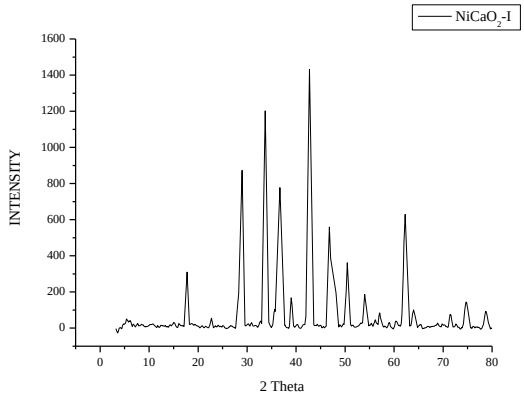

Figure 2: XRD of the synthesized $NiCaO_2$ Nanoparticles

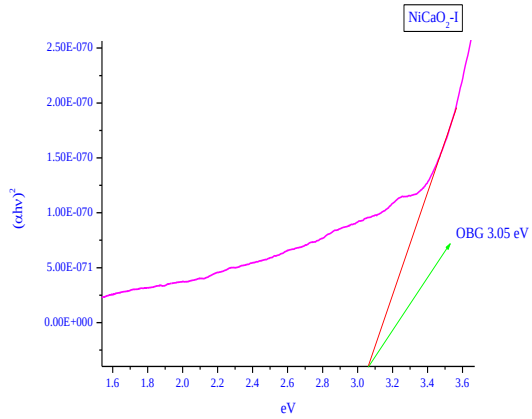

Figure 3: UV-absorption spectra of synthesized $NiCaO_2$ Nanoparticles

Figure 4: Scanning Electron Micrographs of synthesized NiCaO2 Nanoparticles

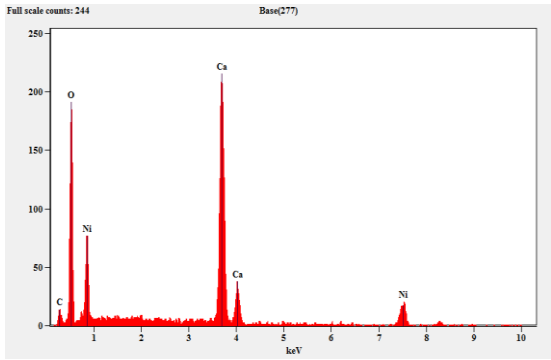

Figure 5: Energy Dispersive X-ray of synthesized $NiCaO_2$ Nanoparticles

III. RESULT AND DISCUSSION

3.1 CHARACTERIZATION OF THE NANOPARTICLES

Figure 2 shows, the XRD patterns of $NiCaO_2$ nanoparticles reveal that, the presence of Rhombo Hedral structure and the 2θ peaks were observed which related to Nickel oxide, (36.67°, 42.72°, 54.00°, 62.26°) (JCPDS card No.01-089-3080) Caliate (28.97°, 39.02°, 46.78°) (JCPDS card No.00-003-0569) and the XRD was performed by powder X-ray diffraction (Rigaku diffractrometer) using Cu-Kα radiation (1.5406 Å) in a θ-2θ configuration. The pattern obtained from the XRD analysis of the prepared $NiCaO_2$ nanoparticles is presented in figure 2.

According to the Debye Scherrer's formula: $D=K\lambda/\beta \cos\theta$ (4)

In the present work, the powdered sample of newly synthesized $NiCaO_2$ nanoparticle was examined by XRD studies and found that $NiCaO_2$ nanoparticle size varies from 8 nm to 18 nm and henceforth the average crystallite size was found to be 14 nm. Figure 3 illustrated that, the optical absorption is an important tool to obtain the optical energy band gap of crystalline and amorphous materials. The fundamental absorption corresponds to the electron excitation from the valence band to the conduction band can be used to determine the nature and value of the optical band gap. The absorption spectrum reveals that the $NaCaO_2$ nanoparticle absorption in the visible light region with a wavelength above 400 nm. The optical energy band gap Eg is calculated from the relation

$$(\alpha h\upsilon)=B(h\upsilon-Eg)^n \quad (5)$$

Where, 'hυ' is the photon energy, 'B' is the constant and 'n' is the power factor and that takes 1/2, 2, 3/2 and 3 allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. The optical band gap of the $NaCaO_2$ nanoparticle found to be 3.05eV [22].

Figure 4 reveals that, the structural morphology of the nanoparticles looks like agglomeration, cluster, and foamy in nature [23]. Figure 5 confirms the presence of nickel, calcium, carbon and oxygen signals of the nickel calciate Nanoparticles. The vertical axis displays the number of x-ray counts although the horizontal axis displays energy in KeV (Figure 5). The weight and atomic percentage of carbon, Oxygen, calcium, and Nickel were found to be 7.79, 51.80, 25.74, 14.67 and 13.57, 67.76, 13.44, 5.23 for $NiCaO_2$ nanoparticles, these corresponds, the spectrum without impurities peaks. [23-24].

3.2 BET SURFACE AREA ANALYSIS

The catalytic activity of the nanoparticles is nearly related to their porous structure helping for contact with the pollutant which favors positively to the photocatalytic activity. Using the BET surface area analysis, the specific surface area and pore volumes obtained for the nanoparticles are reported in table 1. The surface area for $NiCaO_2$ is 2.44m^2/g. This value is analogues to the other nanoparticles [25],[26],[27]. The obtained surface area for $NiCaO_2$ is suitable to carry out for the photocatalytic activity, as the efficiency of photoelectric conversion is directly proportional to the surface area available [22],[28]

Table 1: Surface properties of the nanoparticles

Catalyst	Surface area	Pore volume	Average pore diameter
$NiCaO_2$ (urea)	2.4416 m^2/g	0.01013 cc/g	165.87Å

3.3 NATURE OF POINT OF ZERO CHARGE

It is important to determine the iso-electric point or point zero charge of the nanoparticles. For the determination of PZC of $NiCaO_2$. $NiCaO_2$ nanoparticle graph of initial pH against final pH was plotted and the values of $pH_{(pzc)}$ was found to be 11.5 (Figure 6). Below this $pH_{(pzc)}$ the surface is acidic in nature, positively charged and above this surface is basic in nature and negatively charged. The pH of CBBR is below the $pH_{(pzc)}$, which favors the adsorption of anionic Brilliant Blue R and thus the suitable for Photocatalysis [28],[29].

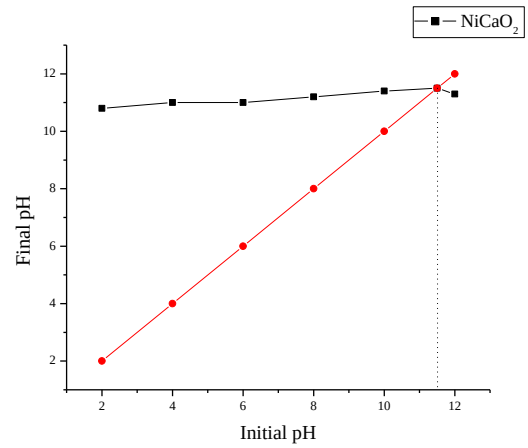

Figure 6: Point zero charge of $NiCaO_2$ nanoparticles

3.4 EFFECT OF CONTACT TIME

The effect of contact time on the adsorption of BBR was studied to determine the time taken by $NiCaO_2$ nanoparticles to remove 3×10^{-4} mol/dm^3 to 7×10^{-4} mol/dm^3 CBBR solution at pH 6. A 0.027g of $NiCaO_2$ nanoparticles were added into a 50mL of CBBR solution. Absorbance of the solution at 557nm with time was determined to monitor the CBBR concentration. The results are shown in figure 7. The CBBR concentration decrease with time is due to its adsorption on $NiCaO_2$ nanoparticles. It can be seen that in about 60 min, almost all the BBR became adsorbed. Agitation time of 60min was selected for succeeding experiments.

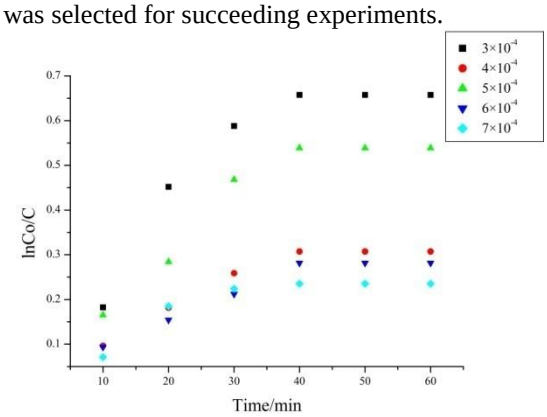

Figure 7: Effect of contact time on different dye concentration

3.5 MECHANISM OF THE PHOTOCATALYTIC DEGRADATION

The mechanism of photocatalytic activity of nanoparticles can be predicted. Nanoparticles when exposed to sunlight, molecules get activated and transfer electrons from valence bond to conduction band. Molecular oxygen reduces

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electron present in the conduction band to generate the super oxide radical. The surface of the photocatalyst was adsorb the molecular oxygen to prevent the hole-electron pair recombinant process [30],[31]. Photocatalytic degradation decreases by combining the hole-electron pair. In presence of oxygen and organic molecule may generate the hydrogen peroxide or organic peroxide and hydrogen peroxide can be generated in another way. Hydroxyl radicals are powerful oxidizing agents forms by the hydrogen peroxide and these radicals are capable to degrade the dye molecules.

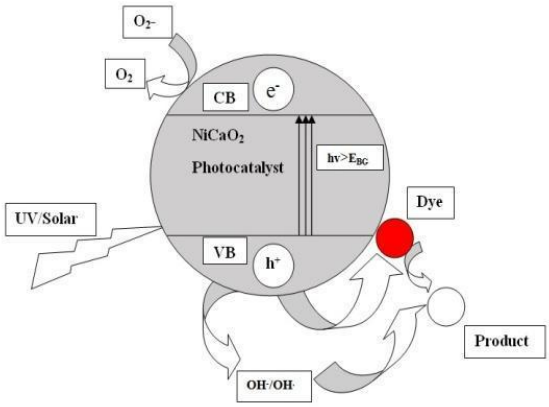

Figure 8: Mechanism of Photodegradation of CBBR dye

3.6 EFFECT OF INITIAL DYE CONCENTRATION

The effect of initial dye concentration on the rate of degradation of CBBR by varying the dye concentration from 3×10^{-4} mol/dm^3 to 7×10^{-4} mol/dm^3 with pH 6, constant catalyst loading 0.027g/50ml and the results are present in table 2 and figure 9 shows the relationship between the dye concentration and $NiCaO_2$ nanoparticles with respect to the irradiation time on photocatalytic degradation of CBBR dye. The results depict that, the rate of degradation increases with increase in the dye concentration up to 5×10^{-4} mol/dm^3 and gradually decreases and due to the equilibrium adsorption of the dye on the catalyst surface which results in the decrease in the active sites of the $NiCaO_2$ nanoparticles and the generation of the hydroxyl radicals are constant. The decolourization rate relates to the formation of •OH radical, critical species in the decolourization process. Reactions of hydroxyl radicals decrease by increasing the dye concentration [32]. Similarly, this kind of study reported in [33],[34]. Hence k can be expressed as follows

$k = k_o P^{\cdot}_{OH} P_{dye}$

Dye Concentration	k	r
3×10^{-4}	1.5	1.1
4×10^{-4}	2.2	1.4
5×10^{-4}	3.4	2.9
6×10^{-4}	2.3	1.8
7×10^{-4}	1.7	1.9

Table 2: Effect of Initial dye concentration on the degradation of CBBR, *k* pseudo first-order rate constant ($\times10^2$, mol/dm^3), catalyst amount= 0.027g/50ml, pH=6, *R*-Initial, rate constant ($\times10^7$, mol/dm^3).

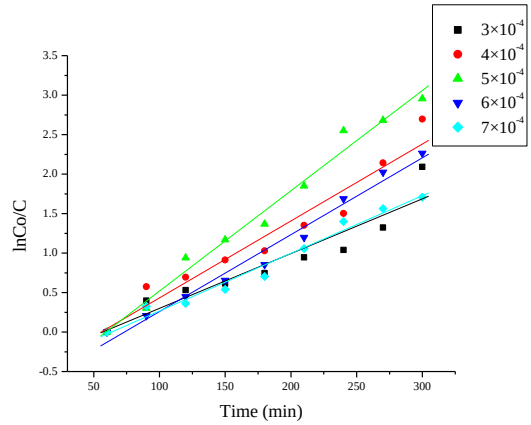

Figure 9: Effect of Initial dye concentration on the degradation of CBBR using $NiCaO_2$ catalyst, catalyst amount= 0.027g/50ml, pH=6.

Where k is the overall rate constant, k_o is the reaction rate constant, $P^{\cdot}_{OH}$ is the probability of generation of the $^{\cdot}$OH radicals on the catalyst surface, P_{dye} is the probability of the $^{\cdot}$OH radicals reacting with dye molecules. The reaction rate constant k_o is independent of the initial dye concentration by $P^{\cdot}_{OH}$ and P_{dye} will depend on the dye concentration implicitly. The previous work shows that, the photocatalytic aromatic compound is through hydroxylation of hydroxyl radicals [34]. Sakthivel et al. (2003) [34] point out the rate-determining reaction may be the formation of $^{\cdot}$OH since they react with aromatic ring compounds. Thus, the formation of hydroxyl radicals by the reaction of holes with adsorbed OH^- and H_2O. If we accept the adsorbed OH^- places are replaced by dye ions (dye$^-$) which are produce from the dissociation of the sodium salt of dye molecules,

(Dye-Na) → (dye$^-$) +Na^+ then the production of $^{\cdot}$OH will be reduces the active surfaces for producing $^{\cdot}$OH radicals. Therefore, $P_{.OH}$ is adversely affected by the catalyst site, coverage fraction of dye and its oxidation intermediates. Hence the photon passes through the solution decreases by the increase in dye concentration, and reduces the light penetration resulting in lower production of O_2- species and hydroxyl radicals in low concentration the reverse effect is observed [35],[36],[37]. From this study, it is concluded that as the initial concentration of dye increases, the amount of dye adsorbed on the catalyst surface increased up to optimum dye concentration and further increase in the dye concentration there is a decrease in photons passes through the solution. Since illumination time and optimum catalyst concentration remains constant, the attacking of OH and O_2^{2-} species molecules decreases by increasing the dye concentration [38],[39].

3.7 EFFECT OF PH

The release of industrial effluents had varied pH. In this study, the effect of pH is a very significant parameter in the photodegradation of dyes and also characteristics of

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wastewater. In this study pH was varying from the 2 to 10 with constant loading of catalyst (0.027g/50ml) and constant dye concentration 5×10^{-4} mol/dm^3, the results are shown in table 3 and figure 10. The result illustrated that, the rate of degradation is increasing with increase in pH and shows maximum degradation at pH 6 and increase in pH the rate of degradation was gradually decreased in alkaline pH. Many researchers have reported this kind of work reported in [39],[40],[41]. The rate of degradation depends on the dye adsorbed on the surface of the catalyst. The adsorption was highly influenced by pH of the solution. So it can be suggested that, the dye adsorbed on $NiCaO_2$ nanoparticles influences the photocatalytic activity [42].

pH	k	r
2	1.7	1.2
4	1.9	2.0
6	3.4	2.9
8	2.3	2.3
10	1.7	2.0

Table 3: Influence of pH on the rate of degradation of CBBR, *k* pseudo first-order rate constant ($\times10^2$, mol/dm^3), CBBR= 5×10^{-4} catalyst amount = 0.027g/50ml, *R*-Initial, rate constant ($\times10^7$, mol/dm^3).

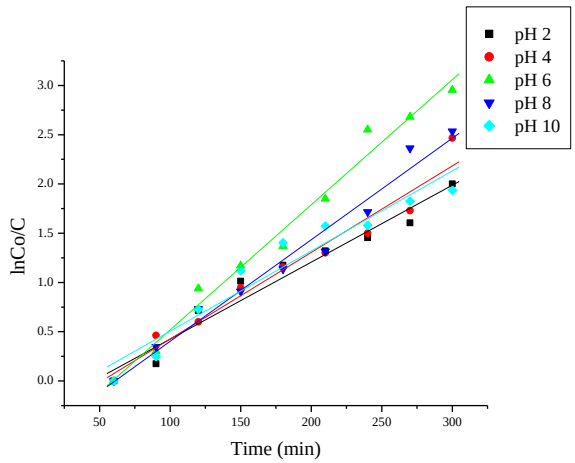

Figure 10: Influence of pH on the rate of degradation of CBBR using $NiCaO_2$. CBBR= 5×10^{-4}, catalyst amount= 0.027g/50ml.

The effect of pH can be explained on the basis of zero point charge (ZPC) of $NiCaO_2$ nanoparticles, where zero point charge of $NiCaO_2$ was 11.5 shown in figure 6. $NiCaO_2$ nanoparticles surface is positively charged with below the 11.5 pH. The CBBR is an anionic in nature, it can easily combine with cationic charged nanoparticles and forms ionic bonds and it gets easily degraded. When the solution containing dye and nanoparticles expose to sunlight its hydroxyl anions increases the production of hydroxyl radicals. The result table 3 and figure 10 illustrated that, the rate of degradation shows higher in the acidic pH and adsorption of dye molecules was low at the alkaline pH. Increase in the hydroxyl radicals, they combine with the hole of the semiconductor and the $^{\cdot}OH$ radicals are critical oxidizing species responsible for photodegradation on the greater the optimum pH [43],[44]. The decrease in the rate of degradation explained in terms of amphoteric nature of the catalyst, because the catalyst surface becomes negatively charged for the higher pH value, which causes the electrostatic repulsion between the catalyst and negatively charged dyes [35].

3.8 EFFECT OF CATALYST CONCENTRATION

A series of the experiment was carried out to assess the optimum catalyst loading by varying the amount of catalyst from 0.020g to 0.050g with constant dye concentration 5×10^{-4} mol/dm^3 and constant pH 6. The rate of degradation is shown in table 3 and figure 11. Increase in the amount of photocatalyst, there is an increase in the number of active sites on the surface of the $NiCaO_2$ nanoparticle which turns to increases the number of $OH^{\bullet}$ and $OH_2\bullet$ radicals [45]. The table 4 and Figure 11 illustrated that, the increase in the photocatalyst loading up to 0.027g/50ml the rate of degradation also increase, further the increase in the catalyst loading the rate of degradation was decreases due to excess loading of catalyst leads to turbidity of the solution and reduces the light penetration through the solution [46].

Dosage	k	r
0.020g	1.1	1.4
0.025g	1.7	1.9
0.027g	3.4	2.9
0.030g	1.9	1.8
0.040g	1.7	1.5
0.050g	1.3	1.2

Table 4: Effect of catalyst loading on the degradation of CBBR, *k* pseudo first-order rate constant ($\times10^2$, mol/dm^3), CBBR= 5×10^{-4} pH=6, *R*-Initial, rate constant ($\times10^7$, mol/dm^3).

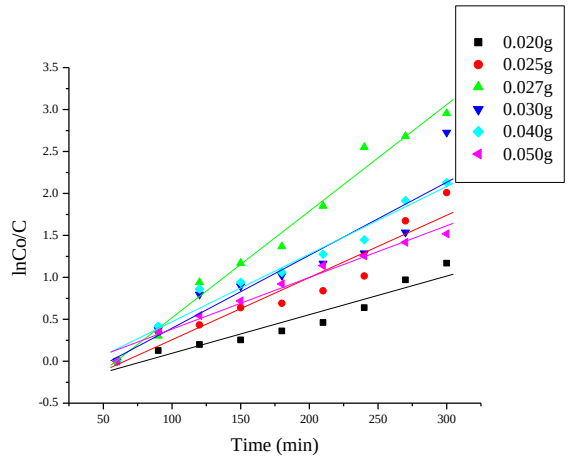

Figure 11: Effect of catalyst loading on the degradation of CBBR using $NiCaO_2$. CBBR= 5×10^{-4}, pH=6.

Many authors have investigated the reaction rate as a function of catalyst loading under different experimental conditions [32],[47],[48]. The rate of degradation may decrease due to the loss of active sites on the surface area due to the overlapping of surface and adsorption sites, hence it requires a number active surface area [49],[50]. While

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below the level, it assumes that the catalyst surface and adsorption of the light by the catalyst are limiting factor [51],[52].

3.9 REUSE OF CATALYST

The $NiCaO_2$ nanoparticle was used to test the reusability under similar condition solar light irradiation, the efficiency of $NiCaO_2$ nanoparticle gets decreases first and second reuse. The efficiency decreased from 86% and 77% respectively due to the surface leaching of nanoparticles during separation [22],[28],[53],[54].

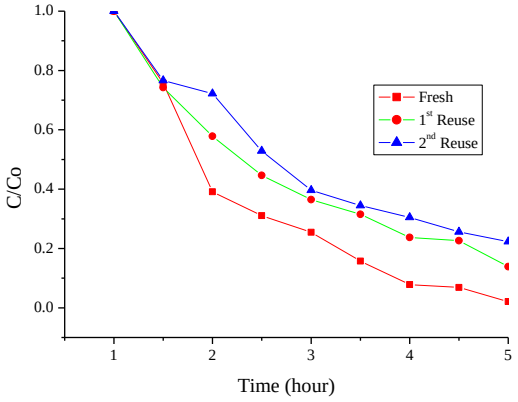

Figure 12: Reusability of $NiCaO_2$ nanoparticles against CBBR dye

IV. CONCLUSION

In the present work, as per the result, the synthesized nanoparticles have proved to be more consistent and efficient photocatalysts. The maximum degradation was achieved at 5×10^{-4} mol/dm^3 dye concentration with constant catalyst concentration (0.027g/50ml) and constant pH 6. The photodegradation of the dye with $NiCaO_2$ nanoparticles obeyed pseudo-first-order kinetics and it is recommended for industrial application. Hence, further research work can be carried out in a bigger scale and can be applied at industrial sectors to control aquatic pollution. Also, there is a scope for further improvement in the quality of the nanoparticles.

REFERENCES

[1]. M. Ghaedi, S. Heidarpour, S.N. S.R. Kokhdan, A. Daneshfar B. Brazesh, "Comparison of silver and palladium nanoparticles loaded on activated carbon for efficient removal of Methylene blue : Kinetic and isotherm study of removal process", Powder Technology, Vol. 228, pp. 18–25, 2012. Doi.org/10.1016/j.powtec.2012.04.030

[2]. S, Padmavathy, S. Sandhya, K. Swaminathan, Y.V. Subrahmanyam, T. Chakrabarti, S.N. Kaul, "Aerobic Decolorization of Reactive Azo Dyes in Presence of Various Cosubstrates", Chem. Biochem. Eng. Q, Vol. 17, No. 2, pp. 147–151, 2003.

[3]. Subramanyam, M.K.V. Subba-Rao, "Photocatalytic degradation of textile dyes using TiO_2 based catalyst", Indian journal of environmental protection, Vol. 18, No. 2, pp. 266-272, 1997

[4]. C. Guillard, H. Lachheb, A. Houas, M. Ksibi, E. Elaloui, J.M. Herrmann, "Influence of chemical structure of dyes, of pH and of inorganic salts on their photocatalytic degradation by TiO_2 comparison of the efficiency of powder and supported TiO_2", Journal of Photochemistry and Photobiology A: Chemistry, Vol. 158, pp. 27–36, 2003.

[5]. S. Alahiane, S. Qourzal, M.E. Ouardi, A. Abaamrane, A. Assabbane, "Factors Influencing the Photocatalytic Degradation of Reactive Yellow 145 by TiO_2-Coated Non-Woven Fibers", American Journal of Analytical Chemistry, Vol. 5, pp. 445-454, 2014.

[6]. A.A. Essawy, A.E. Ali, M.S.A. Abdel-mottaleb, "Application of novel copolymer-TiO_2 membranes for some textile dyes adsorptive removal from aqueous solution and photocatalytic decolorization", Journal of Hazardous Materials, Vol. 157, pp. 547–552, 2008.

[7]. N. Daneshvar, M.H. Rasoulifard, A.R. Khataee, F. Hosseinzadeh, "Removal of C. I. Acid Orange 7 from aqueous solution by UV irradiation in the presence of ZnO nanopowder", Journal of Hazardous Materials, Vol. 143, pp. 95–101, 2007.

[8]. H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard, J. Herrmann, "Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo red, Methylene Blue) in water by UV-irradiated titania", Applied Catalysis B: Environmental, Vol. 39, pp. 75–90, 2002.

[9]. M. Qadri, S. Nisar, N. Fatima, "Photokinetics of the oxidation of Coomassie Brilliant Blue by Potassium dichromate in acidic medium", International Journal of Advanced Research, Vol. 3, No. 2, pp. 888-898, 2015.

[10]. G.R. Chaudhary, P. Saharan, A. Umar, S.K Mehta, S. Mor, "Well-Crystalline ZnO Nanostructures for the Removal of Acridine Orange and Coomassie Brilliant Blue R-250 Hazardous Dyes", Science of Advanced Materials, Vol. 5, pp. 1886–1894, 2013.

[11]. G.R. Chaudhary, P. Saharan, A. Kumar, S.K. Mehta, S. Mor, A. Umar, "Adsorption Studies of Cationic, Anionic and Azo-Dyes via Monodispersed Fe_3O_4 Nanoparticles", Journal of Nanoscience and Nanotechnology, Vol. 13, pp. 3240–3245, 2013.

[12]. S. Dhananasekaran, R. Palanivel, S. Pappu, "Adsorption of Methylene Blue, Bromophenol Blue, and Coomassie Brilliant Blue by a-chitin nanoparticles", Journal of Advanced Research, Vol. 7, pp. 113–124, 2016.

[13]. N. Ameta, J. Sharma, S. Sharma S. Kumar, P.B. Punjabi, "Copper modified iron oxide as heterogeneous photo-Fenton reagent for the degradation of coomassie brilliant blue R-250", Indian journal of chemistry, Vol. 51, No. A, pp. 943-948, 2012.

[14]. M. Altikatoglu, M. Celebi, "Enhanced Stability and Decolourization of Coomassie Brilliant Blue R-250 by Dextran Aldehyde-modified Horseradish Peroxidase", Artificial Cells, Blood Substitutes, and Biotechnology, 1–6, 2010.

[15]. R. Sankar, P. Manikandan, V. Malarvizhi, T. Fathima, K.S. Shivashangari, V. Ravikumar, Green synthesis of colloidal copper oxide nanoparticles using Carica papaya and its application in photocatalytic dye degradation", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Vol. 121, pp. 746–750, 2014.

[16]. A. Mahyar, M.A. Behnajady, N. Modirshahla, "Enhanced Photocatalytic Degradation of C.I. Basic Violet 2 using TiO_2–SiO_2 Composite Nanoparticles", Photochemistry and Photobiology, Vol. 87, No. 4, pp. 795-801, 2011.

[17]. H.P. Shivaraju, "Removal of Organic Pollutants in the Municipal Sewage Water by TiO_2 based Heterogeneous Photocatalysis", International Journal of Environmental Science, Vol. 1, No. 5, pp. 911-923, 2011.

[18]. M.C. Cotto-maldonado, T. Campo, E. Elizalde, A. Gómez-martínez, C. Morant, F. Márquez, "Photocatalytic Degradation of

© 2018, IJSRPAS All Rights Reserved

Rhodamine-B under UV-Visible Light Irradiation Using Different Nanostructured Catalysts", American Chemical Science Journal, Vol. 3, No. 3, pp. 178–202, 2013.

[19]. M.A. Lazar, S. Varghese, S.S. Nair, "Photocatalytic Water Treatment by Titanium Dioxide: Recent Updates", Catalysts, Vol. 2, pp. 572–601, 2012.

[20]. K. Zhang, W. Chun-Oh, "Effect of Heat-Treated Temperature on Surface Crystal Structure and Catalytic Activity of ACF/ZnO Composite under Ultraviolet Irradiation and Ultrasonication", Journal of the Korean Ceramic Society, Vol. 47, No. 2, pp. 136–141, 2010.

[21]. R. Comparelli, E. Fanizza, M.L. Curri, P.D. Cozzoli, G. Mascolo, A. Agostiano, "UV-induced photocatalytic degradation of azo dyes by organic-capped ZnO nanocrystals immobilized onto substrates", Applied Catalysis B: Environmental, Vol. 60, pp. 1–11, 2005.

[22]. A.M. Santhosh, K. Yogendra, K.M. Mahadevan, N. Madhusudhana, "Application of Nickel Calciate Nanoparticles in the Degradation of direct green 6 Dye", International Research Journal of Environmental Sciences, Vol. 7, No. 6, pp. 12-18, 2018.

[23]. A.M. Santhosh, K. Yogendra, K.M. Mahadevan, N. Madhusudhana, "Photodegradation of Congo red azo dye, a Carcinogenic Textile dye by using synthesized Nickel Calciate Nanoparticles", International Journal of Advance Research in Science and Engineering, Vol. 6, No. 7, pp. 51-64, 2017.

[24]. C. Parthibana, N. Sundaramurthy, "Biosynthesis, Characterization of ZnO Nanoparticles by Using Pyrus Pyrifolia Leaf Extract and Their Photocatalytic Activity", International Journal of Innovative Research in Science, Engineering and Technology, Vol. 4, No. 10, pp. 9710-9718, 2015.

[25]. M. Ge, N. Zhu, Y. Zhao, J. Li, L. Liu, "Sunlight-Assisted Degradation of Dye Pollutants in Ag_3PO_4 Suspension", Industrial and Engineering Chemistry research, Vol. 51, pp. 5167−5173, 2012.

[26]. X. Meng, L. Zhang, H. Dai, Z. Zhao, R. Zhang, Y. Liu, "Surfactant-assisted hydrothermal fabrication and visible-light-driven photocatalytic degradation of methylene blue over multiple morphological $BiVO_4$ single-crystallites", Materials Chemistry and Physics, Vol. 125, pp. 59–65, 2011.

[27]. T. K. Ghorai, N. Biswas, "Photodegradation of rhodamine 6G in aqueous solution via $SrCrO_4$ and TiO_2 nano-sphere mixed oxides", Journal of Materials Science and Technology, Vol. 2, No. 1, pp. 10-17, 2013.

[28]. S.D. Kulkarni, S. Kumbar, S.G. Menon, K.S. Choudhari, C. Santhosh, "Magnetically separable core–shell $ZnFe_2O_4$@ZnO nanoparticles for visible light photodegradation of methyl orange", Materials Research Bulletin, Vol. 77:, pp. 70–77, 2016.

[29]. W.F. Khalik, L.N. HO, S.A. Ong, Y.S. Wong, N.A. Yusoff, F. Ridwan,. "Decolorization and Mineralization of Batik Wastewater through Solar Photocatalytic Process", Sains Malaysiana, Vol. 44, No. 4, pp. 607–612, 2015.

[30]. F. Shahbaa, Bdewi, M. Ayad, Abdulrazaka, K.A. Bakhtyar, "Catalytic Photodegradation of Methyl orange using MgO nanoparticles prepared by molten salt method", Asian Transactions on Engineering, Vol. 5, No. 6, 1-5, 2015.

[31]. G. Shilpa, K. Yogendra, K.M. Mahadevan, N. Madhusudhana, and A.M. Santhosh, "A Comparative Study over Degradation of Direct Green 6 by using Synthesized Magnesium Aluminate and Magnesium Zincate Nanoparticles", IOSR Journal of Applied Chemistry (IOSR-JAC), Vol. 11, No. 5, pp. 01-08, 2018. DOI: 10.9790/5736-1105010108

[32]. K. Selvam, M. Muruganandham, N. Sobana, M. Swaminathan, "Enhancement of UV-assisted photo-Fenton degradation of reactive orange 4 using TiO_2 -P25 nanoparticles", Separation and Purification Technology, Vol. 54, pp. 241–247, 2007.

[33]. B. Pare, V. Singh, P. More, T.R. Thapak, "Visible Light Induced Degradation of Acridine Orange dye over $BaCrO_4$ Photocatalyst, Int. J. Chem. Sci, Vol. 9, No. 2, pp. 537-544, 2011.

[34]. S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, "Solar Photocatalytic Degradation of Azo Dye : Comparison of Photocatalytic Efficiency of ZnO and TiO_2", Solar Energy Materials & Solar Cells", Vol. 77, pp. 65–82, 2003.

[35]. N. Mohammad, M. Arami, "Degradation and toxicity reduction of textile wastewater using immobilized titania nanophotocatalysis', Journal of Photochemistry & Photobiology, B: Biology, Vol. 94, No. 1, pp. 20–24, 2009.

[36]. N.U. Sangari, P. Velusamy, "Photocatalytic Decoloration Efficiencies of ZnO and TiO_2 : A Comparative Study", Journal of Environmental Science and Pollution Research, Vol. 2, No. 1, pp. 42–45, 2016.

[37]. A.V. Rupa, D. Manikandan, D. Divakar, T. Sivakumar, "Effect of deposition of Ag on TiO_2 nanoparticles on the photodegradation of Reactive Yellow-17", Journal of Hazardous Materials, Vol. 147, pp. 906–913, 2007.

[38]. V. Murugesan, S. Sakthivel, "Photocatalytic degradation of leather dyes in aqueous solution using solar/UV illuminated TiO_2 /ZnO", Proceedings of International Symposium on Environmental Pollution Control and Waste Management, Tunis, pp. 654-659, 2002

[39]. N. Sobana, K. Selvam, M. Swaminathan, "Optimization of photocatalytic degradation conditions of Direct Red 23 using nano-Ag doped TiO_2", Separation and Purification Technology, Vol. 62, pp. 648–653, 2008.

[40]. L.G. Devi, K.M. and Reddy, "Enhanced photocatalytic activity of silver metallized TiO_2 particles in the degradation of an azo dye methyl orange: Characterization and activity at different pH values", Applied Surface Science, Vol. 256, pp. 3116–3121, 2010.

[41]. A. Afkhami, R. Moosavi, "Adsorptive removal of Congo Red, a carcinogenic textile dye, from aqueous solutions by maghemite nanoparticles", Journal of Hazardous Material, Vol. 174, pp. 398-403, 2010.

[42]. B. Subash, B. Krishnakumar, M. Swaminathan, M. Shanthi, "Solar-light-assisted photocatalytic degradation of NBB dye on Zr-codoped Ag–ZnO catalyst", Research on Chemical Intermidiate, Vol. 39.No. 7. pp. 3181–3197, 2012. doi.org/10.1007/s11164-012-0831-3.

[43]. X. Li, X. Mao, X. Zhang, Y. Wang, Y. Wang, Zhang, X. Hao, C. Fan, "Citric acid-assisted synthesis of nano-Ag / BiOBr with enhanced photocatalytic activity", Science China Chemistry, Vol. 58, No. 3, pp. 457–466, 2015.

[44]. P. Jayamadhava, A. Sudhakara, S. Ramesha, G. Nataraja, "Synthesise of ZnO nano particle as an alternative catalyst for Photocatalytic degradation of brilliant red azo dye", American Journal of Environmental Protection, Vol. 3, No. 6, pp. 318–322, 2014.

[45]. B.N. Patil, D.B. Naik, V.S. Shrivastava, "Photocatalytic degradation of hazardous Ponceau-S dye from industrial wastewater using nanosized niobium pentoxide with carbon", Desalination, Vol. 269, pp. 276–283, 2011.

[46]. F. Buazar, S. Alipouryan, F. Kroushawi, S.A. Hossieni, "Photodegradation of odorous 2-mercaptobenzoxazole through zinc oxide/ hydroxyapatite nanocomposite", Applied nanoscience, Vol. 5, pp. 719-729, 2014. Doi.org/10.1007/s13204-014-0368-4.

[47]. B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, "Solar light induced and TiO_2 assisted degradation of textile dye reactive blue 4", Chemosphere, Vol. 46, pp. 1173–1181, 2002.

[48]. P.K. Boruah, P. Borthakur, G. Darabdhara, C.K. Kamaja, I. Karbhal, M.V. Shelke, P. Phukan, D. Saikiad, M.R. Das,

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"Advances Sunlight assisted degradation of dye molecules and reduction of toxic Cr (VI) in aqueous medium using magnetically recoverable Fe_3O_4/ reduced graphene oxide nanocomposite", RSC Advances, Vol. 6, pp. 11049–11063, 2016.

[49]. A. Habib, M. Muslim, M.T. Shahadat, M.N. Islam, I. Mohmmad, I.M.I. Ismail, T.S.A. Islam, A.J. Mahmood, "Photocatalytic decolourization of crystal violet in aqueous nano-ZnO suspension under visible light irradiation", International Nano Letters, Vol. 3, No. 5, pp. 1-8, 2013.

[50]. A.K. Subramani, K. Byrappa, S. Ananda, K.M. Lokanatha Rai, C. Ranganathaiah, M. Yoshimura, "Photocatalytic degradation of indigo carmine dye using TiO_2 impregnated activated carbon", Bulletin of materials science, Vol. 30, pp. 37-41, 2007.

[51]. H. Wang, C. Xie, W. Zhang, S. Cai, Z. Yang, Y. Gui, "Comparison of dye degradation efficiency using ZnO powders with various size scales", Journal of Hazardous Materials, Vol. 141, pp. 645–652, 2007.

[52]. A. Akyol, H.C. Yatmaz, M. Bayramoglu, "Photocatalytic decolourization of Remazol Red RR in aqueous ZnO suspensions", Applied Catalysis B: Environmental, Vol. 54, pp. 19–24, 2004.

[53]. A. Khanna, V.K. Shetty, "Solar light induced photocatalytic degradation of Reactive Blue 220 (RB-220) dye with highly efficient Ag@TiO_2 core–shell nanoparticles: A comparison with UV Photocatalysis", Solar Energy, Vol. 99, pp. 67–76, 2014. Doi.org/10.1016/j.solener.2013.10.032.

[54]. A.M. Santhosh, K. Yogendra, K.M. Mahadevan, I.H. Mallikarjuna, N. Madhusudhana, "A Comparative Study in Photocatalytic Degradation of Coomassie Brilliant Blue G Dye by using Nickel Calciate Nanoparticles", Journal of Emerging Technologies and Innovative Research, Vol. 5, No 6, pp. 155-164, 2018.

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