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Application of Nickel Calciate Nanoparticles in the Photodegradation of direct green 6 Dye

Santhosh A.M.[1], Yogendra K.[1*], Mahadevan K.M.[2], Mallikarjuna I.H.[3] and Madhusudhana N.[1]
[1]Dept. of P.G. Studies and Research in Envi. Science, Kuvempu University, Jnana Sahyadri, Shankaraghatta, Shivamogga, Karnataka, India
[2]Department of P.G. Studies and Research in Chemistry, Kadur P.G Center, Kuvempu University, Kadur, Karnataka, India
[3]Department of Chemistry, Government Science College, Hassan, Karnataka, India
yogendraku@gmail.com

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Abstract

Dyes are components associated with major water pollution and results in several health issues, so that alternative technologies are required in the treatment of dye effluent. In study mainly focused on photodegradation on Direct Green 6 (DG6) a textile dye by using synthesized Nickel Calciate ($NiCaO_2$) nanoparticles and these nanoparticles were prepared by economically viable method by using acetamide as a fuel. The characterization was done by X-ray diffraction (XRD), scanning electron microscope (SEM), Energy Dispersive X-ray (EDX), Brunauer Emmett-Teller surface area determination and UV-absorption spectroscopy. The results suggested that that, the band gap was found to be 3.3eV and also point zero charge was found to be 11.7, it is determined by pH drift method. Photocatalytic degradation was determined against DG6, with respect to parameters such as catalyst concentration, pH, dye concentration and in different conditions. From these experimental results we came to know that, the optimum catalyst concentration and pH was found to be 0.3g/100ml at pH 8. The maximum degradation was found to be 91.80%. Hence, the efficiency of photodegradation of DG6 dye by using $NiCaO_2$ nanoparticles was ascertained.

Keywords: Direct Green 6, $NiCaO_2$¸ Nanoparticles, Photodegradation.

Introduction

Textile effluents contributes a major contents of dye molecules, during dyeing process[1],which effects to the local water bodies, decrease in light penetration effects in photosynthesis[2] and these dye molecules are non-biodegradable, carcinogenic and mutagenic. Dyes are highly stable and complex aromatic structure[1]. In the recent years, emerging technology leading heterogeneous photocatalytic degradation is easy way to colour from effluents due to their strong oxidation ability[3,4]. In heterogeneous photocatalytic process, the UV/visible radiation cause photo-excitation in a semiconductor catalyst within the presence of oxygen.

Under these circumstances, photocatalytic degradation supported the powerful oxidizing species, either certain hydroxyl radicals or free holes are generated. Applying photocatalysts, organic pollutants are often fully mineralized by reacting with the oxidizers to create CO_2, water has mineral acids. The method is heterogeneous as a result of there is 2 active phases, solid and liquid[5,6].

The factor influencing photocatalytic degradation of dyes are, dye concentration, pH, and catalyst concentration, irradiation time and light intensity. In continuation of our work[7-11], we synthesized $NiCaO_2$ nanoparticles and studied for the colour removal of DG6 dye under natural sunlight. Hence, experiments were conducted with $NiCaO_2$ nanoparticles by varying dye concentration, pH, catalyst loading and different conditions with respect to dark and UV conditions.

Materials and methods

Easily available dye in the market DG6 (λ_{max}592nm) was obtained from Mysore Paper Mill, Bhadravathi, Shivamogga, Karnataka (Figure-1). The chemicals Nickel Nitrate ($Ni(NO_3)_2.6H_2O$) (99% A.R.), Calcium Nitrate ($Ca(NO_3)_2.4H_2O$) (99%, A.R.), Acetamide (CH_3CONH_2) (99.5%), were procured from Hi-Media Chemicals, Mumbai. Through visible spectro-photometer (Elico, SL 177) the absorbance were recorded at λ_{max}.

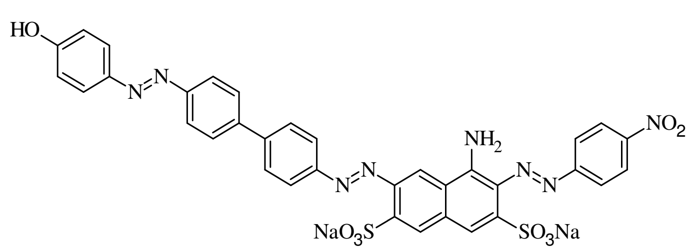

Figure-1: Chemical structure of DG6.

Synthesis of Nanoparticles: The nickel calciate nanoparticles have been synthesized by solution combustion method[9], and were subjected to photocatalytic degradation study against DG6 dye.

$$11Ni\,(NO_3)_2+11Ca\,(NO_3)_2+20CH_3CONH_2\rightarrow 11NiCaO_2+50CO_2+40H_2O+32N_2 \quad (1)$$

Characterization of Synthesized Nanoparticle: X-Ray Diffraction: The X-ray diffraction patterns of $NiCaO_2$ nanoparticles reveal that, the presence of Rhombo Hedral structure and the 2θ peaks were related to Nickel oxide, (37.29°, 43.30°, 62.87°, 75.40°, 79.33°) (JCPDS card No.01-089-3080) Calciate (23.13°, 29.48°, 39.48, 48.59°, 57.48°) (JCPDS card No.00-024-0027) and the XRD was performed by powder X-ray diffraction (Rigaku diffractometer) using Cu-Kα radiation (1.5406Å) in a θ-2θ configuration (Figure-2). According to the Debye Scherrer's formula:

$$D=K\lambda/\beta\, \mathrm{Cos}\theta \quad (2)$$

In the present work, the powdered sample of newly synthesized $NiCaO_2$ nanoparticles were examined by XRD studies and found that, the found to be varied from 10nm to 24 nm and its average size was achieved on 19nm respectively.

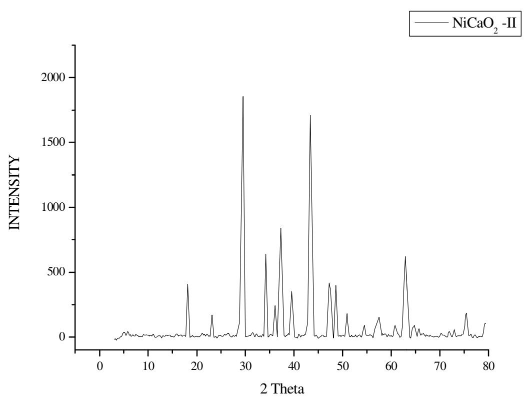

Figure-2: XRD of the synthesized $NiCaO_2$ (acetamide) Nanoparticles.

Scanning electron micrograph: The SEM pictures shows a cluster and foamy like structures. The enlarged image shows the uneven texture of the different nanoparticles, and also shows strong bonding of nanoparticles over one another (Figure-3)[12].

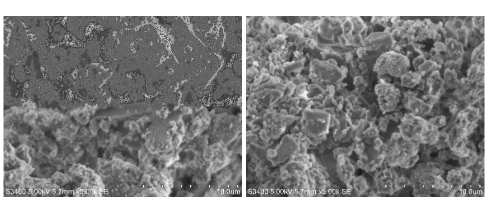

Figure-3: Scanning Electron Micrographs of synthesized $NiCaO_2$ (acetamide) Nanoparticles.

UV-Vis Absorption Spectroscopy: The optical absorption is a significant tool to get optical energy band gap of crystalline and amorphous materials. The elemental absorption corresponds to the electron jumps from valence band to the conductivity band are often wont to verify the character and price of the optical band gap (OBG).

The spectrum reveals that, the $NaCaO_2$ nanoparticles absorption in the visible radiation with an above wavelength 400 nm. The OBG Eg is calculated from the relation:

$$(\alpha h\upsilon)=B(h\upsilon-Eg)^n \quad (3)$$

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 OBG of the $NaCaO_2$ nanoparticle found to be 2.86eV.

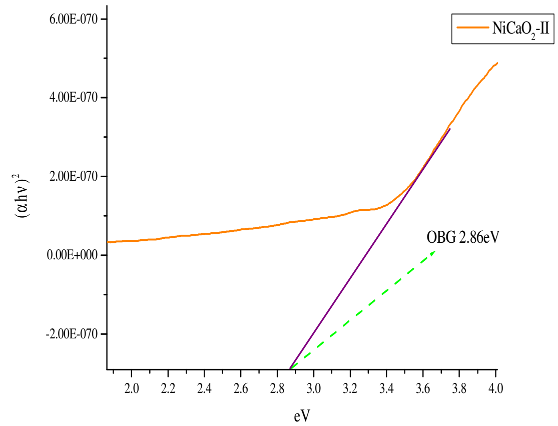

Figure-4: UV-absorption spectra of synthesized $NiCaO_2$ (acetamide) Nanoparticles.

Energy Dispersive X-ray: The confirmatory presence of elements was carried out using EDX spectrometer. The presence of Nickel, Calcium, Carbon and Oxygen signals of the $NiCaO_2$ nanoparticles. The vertical axis displays the amount 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 was found to be 20.56, 46.88, 17.85, 14.69 and 32.08, 54.88, 8.34, 4.69 these corresponds, the spectrum without impurities peaks[9].

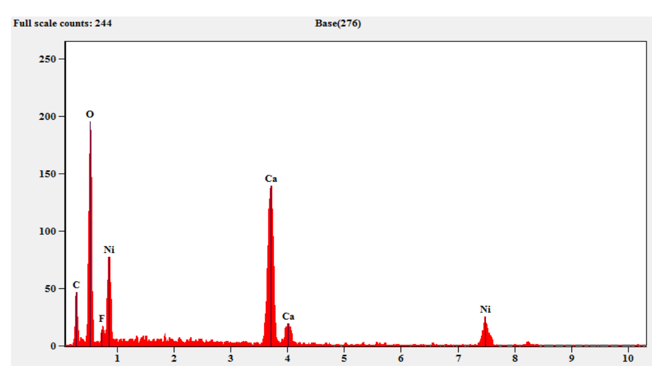

Figure-5: Energy Dispersive X-ray of synthesized $NiCaO_2$ (acetamide) Nanoparticles.

BET Surface area analysis: A specific surface area (SSA) of photocatalyst was measured at 77 K by Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption (NOVA-1000 version 3.70 Instrument). The BET surface area analysis, the SSA, pore volume and average pore diameter for $NiCaO_2$ nanoparticles shown in Table-1. This value is analogues to the other nanoparticles[13,14]. The surface area obtained for $NiCaO_2$ nanoparticles was efficient to carry out the photocatalysis, which was directly proportional to the surface area available[15].

Table-1: Surface properties of the nanoparticles.

Catalyst	Surface area	Pore volume	Average pore diameter
$NiCaO_2$ (acetamide)	2.3778 m^2/g	0.00265 cc/g	44.578Å

Experimental Procedure: The experiments were conducted in presence of direct sunlight. Prepare known concentration of solution by dissolving 0.02g of DG6 dye in 1000ml double distilled water and decolourization was investigated in presence of $NiCaO_2$ nanoparticle at different catalyst dosages, pH levels and different experimental conditions. After the exposure, decolourization of the dye was recorded by visible spectrophotometer (Elico, SL 177) to know the optimum catalyst concentration. Hence, the experiments were repeats for different pH levels for the same standard dye solutions with the optimum concentration of catalyst.

$$D = A_o - A_t / A_o \times 100$$

Where: A_o is the initial absorbance of the dye solution, A_t is absorbance at time interval 't' i.e., after 120 min.

Results and discussion

Point of zero charge: Point of zero charge (PZC) or iso-electric point was the pH of the solution at which, the charge on the surface of the nanoparticles turns zero (neutral). The PZC of $NiCaO_2$ were carried out by pH drift method, 50ml of Nacl 0.01M were taken in 6 different beakers and bubbled it with Nitrogen gas to expel the dissolved CO_2 for few minutes at room temperature till it get a stable pH reading. To each one of the beakers was adjust between 2-12 pH by adding 0.1N NaOH and HCl and by adding 50mg of $NiCaO_2$ nanoparticles kept in 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, point which crosses the curve of initial and final pH and plot the straight line is PZC. To understand the adsorption behaviour or photocatalysts affecting pH, PZC of $NiCaO_2$ nanoparticles was found to be 11.7 (Figure-6). Below this $pH_{(pzc)}$ the surface becomes positive in nature and above this $pH_{(pzc)}$ the surface is negative in nature. The pH of $NiCaO_2$ is below the pH(pzc), which favours the degradation of DG6 and thus the suitable for photocatalysis[15].

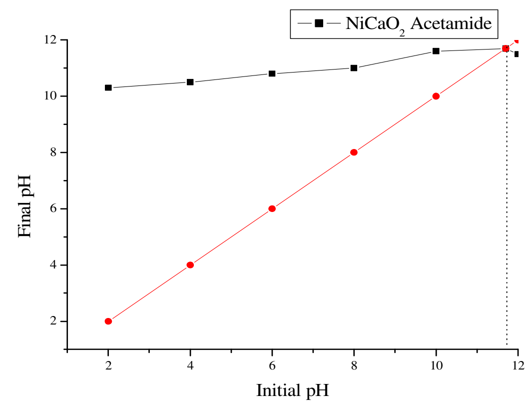

Figure-6: PZC of $NiCaO_2$ nanoparticles.

Mechanism of photocatalytic degradation

Nanoparticles + hν → ($e^-_{CB} + h^+_{VB}$) (4)

Step-1: When sunlight falls on the nanoparticles, it gets exited and the electrons gets transfered from valance band to conduction band.

$e^-_{CB} + O_2 \rightarrow O_2^{\bullet-}$ (5)

Step-2: It can reduce molecular oxygen and super oxide radicals were produced.

$H_2O + O_2^{\bullet-} \rightarrow OOH^{\bullet} + OH^-$ (6)

$2OOH^{\bullet} \rightarrow O_2 + H_2O_2$ (7)

$O_2^{\bullet-}$ + Direct Green 6 → Direct Green 6 -$OO^{\bullet}$ (8)

Step-3: The adsorbed molecular oxygen on the photocatalytic surface prevents the hole-electron pair recombination process[8] and decrease photodegradation and this can be produced by hydrogen peroxide or organic peroxide in front of oxygen and organic molecule.

$O\ OH^{\bullet} + H_2O + e^-_{CB} \rightarrow H_2O_2 + OH^-$ (9)

Step-4: From the other path Hydrogen peroxide can be generated.

$H_2O_2 + e^-_{CB} \rightarrow OH^{\bullet} + OH^-$ (10)

$H_2O_2 + O_2^{\bullet-} \rightarrow OH^{\bullet} + OH^- + O_2$ (11)

Step-5: The powerful oxidizing agent hydroxyl radicals produced by the hydrogen peroxide.

$OH^{\bullet}$ / $O_2^{\bullet-}$/ Nano-particles$^{\bullet+}$+ Direct Green 6 → Direct Green 6 degradation (12)

Step-6: The produced hydroxyl radicals are more efficient in degrading the dye molecules.

Effect of catalyst loading: The effect of concentration $NiCaO_2$ photocatalyst on the photodegradation was examined over a range of 0.1 to 1g/100ml for DG6. The prepared nanoparticles have shows satisfactory results. The $NiCaO_2$ (acetamide) with the nanoparticle size 19 nm has shown 90.16 % degradation. Since, the photodegradation was very efficient at 0.3g/100ml in 120 minutes for $NiCaO_2$ nanoparticles concentration showed in (Figure-7) (Photo-1). The degradation increasing proportional to catalyst loading upto 0.3g/100ml since, more number of active sites are exposed, resulting dye molecule adsorb on the surface of the nanoparticles[16,17] and further decrease (0.4g to 1g) in degradation due to more number of active sites present on the surface of the catalyst and block penetration of sunlight to the solution. The over loading of catalyst tends to the overcrowding, leads to turbidity of the solution and blocking the photons entering into the solution. Further, experiments were continued with same dosages[18-20].

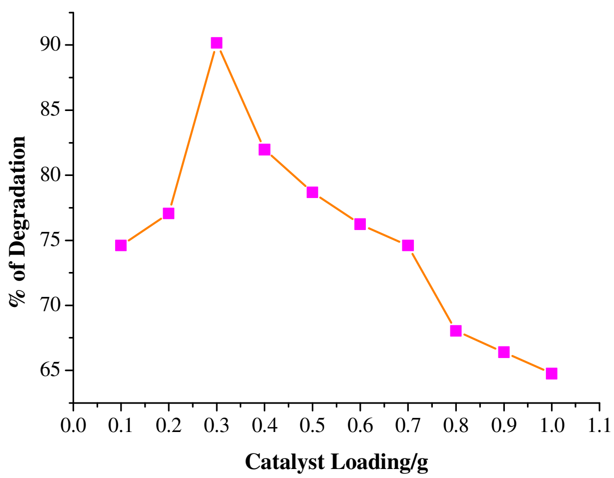

Figure-7: Effect of catalyst concentration on DG6 at 120 minutes [DG6=20 ppm, pH=7, $NiCaO_2$ (acetamide)].

Effect of pH: The effect of pH is the only factor depends on the degradation; the experiments were carried out at pH varying from 2 to11. The percentage of degradation of DG6 for $NiCaO_2$ nanoparticles was obtained from 61.47% to 91.80% from pH 2 to 8, similarly the degradation decreases to 59.83% at pH 11in 120 minutes for 0.3g/100ml. From the result we know that pH is affecting the efficiency of degradation (Figure-8) (Photo-2).

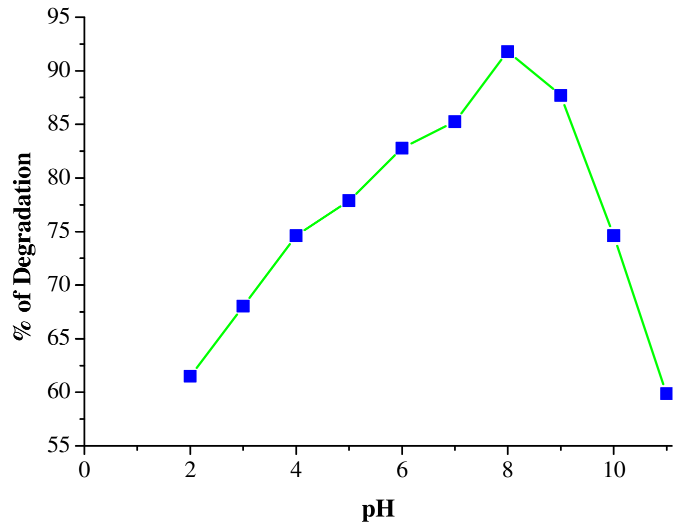

Figure-8: Effect of pH on DG6 at 120 minutes [DG6=20 ppm, $NiCaO_2$ (acetamide)].

The highest degradation was found at pH 8. However, the pH of the solution was increases the degradation also increases upto 8 and further decreases the degradation. Photocatalytic activity explains on the basis of PZC of the nanoparticle was found to be 11.7 (Figure-6). The below the pzc of the surface is positive in nature and above the pzc of the surface is negative in nature. The experimental results show that, the degradation was effectively in pH 8 due to the interaction between the dye and nanoparticles leads to generation of $OH^{\bullet}$ in the alkaline medium and main oxidizing species $OH^{\bullet}$ radicals are responsible for the photodegradation.

Above the pH 9 the degradation is decrease due to amphoteric nature of the catalyst and electrostatic repulsion between negatively charged dye molecules and the catalyst[21-23]. Thus, the adsorption is mainly depends on the pH of the solution[16].

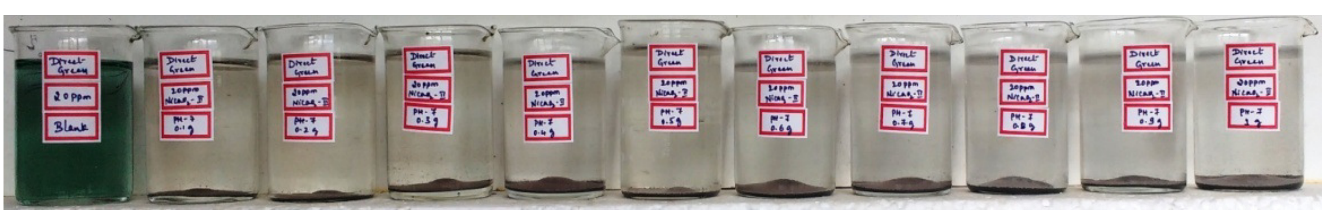

Photo-1: Effect of catalyst concentration on DG6 at 120 minutes [DG6=20 ppm, pH=7, $NiCaO_2$ (acetamide)].

Photo-2: Effect of pH on DG6 at 120 minutes [DG6=20 ppm, $NiCaO_2$ (acetamide)].

Effect of initial dye concentration: The present work was carried out to study the effect of initial concentration of the dye by varying the DG6 concentration from 20, 30, 40, and 50 ppm respectively (Photo-3). The results obtained for $NiCaO_2$ is 91.80% for 20ppm, 87.70% for 30ppm, 79.50% for 40ppm and 54.09% for 50ppm respectively (Figure-9). As the dye concentration increases the capability of degradation decreases[24-26] and the dye concentration increased the colour gets deeper, decrease the photons penetration to the solution, surface of the catalyst affected by the photons interception[26,27] and this experiment clearly shows that, the interaction of dye and catalyst should be in optimum range[28].

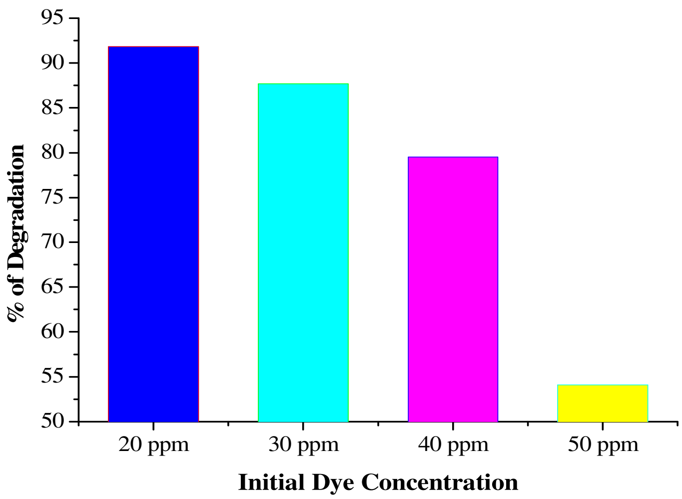

Figure-9: Effect of initial dye concentration on the photodegradation of DG6 [$NiCaO_2$ (acetamide) g/pH=0.3/8 and DG6= (20, 30, 40 and 50) ppm].

Photo-3: Effect of initial dye concentration on the photodegradation of DG6 [$NiCaO_2$ (acetamide) g/pH=0.3/8 and DG6= (20, 30, 40 and 50) ppm].

Effect of sunlight irradiation: The degradation of DG6 dye (20mg/L) were examined under 3 different conditions, *i.e.,* through, dye/dark/catalyst, dye/UV/catalyst and dye/sunlight/catalyst for the catalyst. The degradation of the dye was found to be nil throughout the experiment when exposed to sunlight due to absence of catalyst.

The percentage of degradation was increased with increase in irradiation time, for dye/sunlight/$NiCaO_2$ showed 91.80%, for dye/dark/ $NiCaO_2$ 35.24% and for dye/UV/catalyst 73.77% was recorded (Figure-10). From this result we know that, the degradation efficient in sunlight is more when compared to UV and dark conditions (Photo-4)[8,29,30].

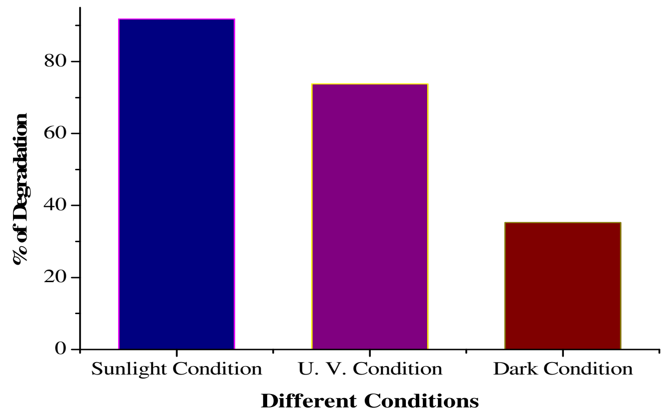

Figure-10: Effect of sunlight irradiation with respect to Dark and UV conditions on photodegradation of DG6 in 120 minutes.

Photo-4: Effect of sunlight irradiation with respect to Dark and UV conditions on photodegradation of DG6 in 120 minutes.

Conclusion

This study, mainly focused on the photodegradation of DG6 dye by $NiCaO_2$ nanoparticles. These nanoparticles were characterized by XRD, SEM, EDX, BET and UV-Vis reflectance. The pzc was found to be 11.7. These nanoparticles achieved maximum degradation (91.80%) at 0.3g/100ml for pH 8 in a very short span of time (120 min). For dark condition 35.24% and UV 73.77% were recorded. So here, the efficiency of $NiCaO_2$ nanoparticles were examined on DG6 and positive results were observed. Hence, $NiCaO_2$ nanoparticles can be effectively used in the process of photodegradation in a wider range in industries and environmental related issues.

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