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Photodegradation of Congo red azo dye, a Carcinogenic Textile dye by using synthesized Nickel Calciate Nanoparticles

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ABSTRACT

The photodegradation of Congo Red (CR) by using nickel calciate nanoparticles (NiCaO₂) was investigated. The Nickel calciate nanoparticles (NiCaO₂) were prepared by solution combustion method using urea and acetamide as fuels and they were characterized by Scanning Electron Micrograph (SEM), X-Ray Diffraction (XRD), Energy Dispersive X-ray (EDX), Brunauer Emmett-Teller surface area determination and band gap was determined by using UV-absorption spectroscopy. Point zero charge determined by pH drift method. All experiments were carried out under natural sun light. Examined the percentage of degradation of these nanoparticles on Congo Red by varying the dye concentration, pH and catalyst loading. The percentage of degradation was highly efficient in 20ppm dye concentration with pH 4 and constant catalyst concentration 0.4g/100ml for both nanoparticles. This proves that, synthesized nickel calciate nanoparticles are efficient in removing the Congo Red from the waste water.

Keyword: Congo red, Nickel Calciate, Nanoparticles, Photodegradation

I. INTRODUCTION

Azo dyes are majorly used in the textile industries and also used in paper making, pharmacy, textile, cosmetics and food processing [3]. These azo dyes are known to be largely non-biodegradable, because which characterized by one or more azo groups (-N=N-) and the release of these azo compounds into water streams is undesirable, it can cause toxic or mutagenic to the living organisms by not only the colour, due to their breakdown products of many azo dyes [4,5]. Under aerobic conditions and their stability is proportional to the structural complexity of their molecular structures [6]. Azo dyes resistant to aerobic degradation but under anaerobic conditions they can be reduced to potentially carcinogenic aromatic amines [7].

Congo red widely used in textile, printing and dyeing, paper, rubber and plastic industries and banned in, many countries because of health concerns. Synthetic dyes, such as CR, are difficult to biodegrade due to their stable compounds and complex aromatic structures and affects carcinogen and mutagen [8-12]. Various physical and chemical treatment methods are employed for the removal of azo dyes from the aqueous solution such as, chemical precipitation, activated carbon, ultra-filtration, adsorption, coagulation, membrane filtration, biological

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degradation, and oxidation via ozonation. But, these methods are costly, ineffective non-destructive, simply they can transfer the pollutant from one phase to another phase and produce secondary pollutants waste products that need further disposal [4,7,13,14]. In recent years an alternative to conventional methods, *i.e.* "Advanced Oxidation Processes" (AOPs), based on the generation of reactive species (hydroxyl radicals), mainly hydroxyl radicals by using solar, chemical or other forms of energy, that strongly oxidizing radical allows the destruction ofbroad range of organic pollutants [13,15,16].

Other researcher has investigated the degradation of CR in presence of different catalysts [8, 17-23]. In this study newly synthesized nickel calciate nanoparticles were applied to degrade the CR azo dye by varying the different parameters such as, initial dye concentration, pH, catalyst loading and in different conditions with respect to UV light and dark conditions.

II. MATERIALS AND METHODS

The commercially available water soluble dyes Congo Red (λ_{max} 496nm) were obtained from Sisco Research Laboratory Pvt. Ltd. Maharashtra (Figure 1). The chemicals Nickel Nitrate (Ni(NO₃)₂.6H₂O) (99% A. R.), obtained from Sisco Research Laboratory Pvt. Ltd. Maharastra Calcium Nitrate (Ca(NO₃)₂.4H₂O) (99%, A. R.), Urea (NH₂CONH₂) (99.5%), Acetamide (CH₃CONH₂) (99%, A.R.), were obtained from Hi-Media Chemicals, Mumbai. The visible spectrophotometer (Elico, SL 177) has been used for recording absorbance at λ_{max} . Later the absorbance was recorded in visible spectrophotometer (Elico, SL 177).



Fig 1: Chemical structure of CR

2.1 Synthesis and Characterization of Nanoparticles

The synthesis of nickel claciate nanoparticles were prepared by solution combustion method by using urea and acetamide as a fuel. The ratios were taken according to stochiometric equation and reaction as follows. The solution taken in crucible was inserted in preheated 600°C muffle furnace and the synthesized nanoparticles was crushed in a mortar to make it amorphous and used for further characterization and application to photocatalytic degradation study of CR dye

$$3 \operatorname{Ni}(\operatorname{NO}_3)_2 + 3\operatorname{Ca}(\operatorname{NO}_3)_2 + 10\operatorname{NH}_2\operatorname{CONH}_2 \rightarrow 3\operatorname{Ni}\operatorname{CaO}_2 + 10\operatorname{CO}_2 + 20\operatorname{H}_2\operatorname{O} + 16\operatorname{N}_2$$
(Eq. 1)

11 Ni $(NO_3)_2$ +11Ca $(NO_3)_2$ +20CH₃CONH₂ \rightarrow 11NiCaO₂+50CO₂+40H₂O+32N₂ (Eq. 2)

Characterization of nanoparticles by Powder X-ray diffraction (XRD) was performed by powder X-ray diffraction (Rigaku diffractrometer) using Cu-K α radiation (1.5406 Å) in a θ -2 θ configuration. 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 (EDX) spectrometer. Specific surface areas (SSA) of all photocatalysts were measured at 77 K by Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption (NOVA-1000 version 3.70 Instrument).

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www.ijarse.com 2.2 Point of Zero Charge

Point of zero charge (pzc) or isoelectric point is the pH of the solution at which the total charge on the surface of the nanoparticles becomes zero (neutral). The pzc of NiCaO₂ were measured by pH drift method, 50ml of Nacl 0.01M was taken in six separate beaker sand bubbled it with Nitrogen gas to expel the dissolved CO₂ for few minutes at room temperature till it get 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 NiCaO₂ 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.

2.3 Experiment Procedure

Photocatalytic experiments were conducted under direct sunlight. The CR solution was prepared by dissolving 0.02 g of azo dye with 1000mL double distilled water using a 1000ml volumetric flask and degradation in the presence of Nickel Calciate nanoparticles at different catalyst dosages pH levels and initial dye concentration. Initially, 100ml of 20ppm of dye samples were tested with different catalyst dosage (from 0. 1g to 1g), by varying pH (from 2pH to 11pH), dye concentration (20ppm to 50ppm) and different conditions with respect to U.V and dark. Except U.V and dark conditions all experiments carried out in the presence of direct sunlight. The whole experimental set-up was placed under sunlight between 11 a.m. and 2 p.m. and the average intensity of sunlight during this period is 834×100 lux unit using lux meter. After the photocatalytic degradation, the extent of degradation was estimated by recording absorbance of the dye solution using spectrophotometer (Elico, SL 177) in order to get the optimum catalyst dose.

The percentage was calculated by equation,

$$\mathbf{D} = (\mathbf{C}_0 - \mathbf{C}_t / \mathbf{C}_0 \times 100)$$
 (Eq. 3)

Where, C_0 is the initial absorbance of the dye solution C_t is absorbance at time interval 't' *i.e.*, after 120 minutes.

III. RESULT AND DISCUSSION

3.1 Characterization of the Nanoparticles

The structural morphology of the nanoparticles looks like foamy in nature [24] (Fig 2a and 2b). In Fig 3 shows the powdered sample of newly synthesized NiCaO₂-I and NiCaO₂-II nanoparticles were examined by XRD studies and the average crystallite size of NiCaO₂-I and NiCaO₂-II was found to be 14nm and 19nm respectively. The pattern obtained from the XRD analysis of the prepared NiCaO₂ nanoparticles is presented in Fig 3a and 3b and calculated average size of nanoparticles by using Debye Scherrer's formula equation.

$$D = (K \lambda / (\beta \cos \theta))$$
 (Eq.4)

Fig 4 shows that, the band gap energy of the $NiCaO_2$ nanoparticles was calculated using the following simple conversion equation. The band gap equation is calculated using the Planck's equation as follows.

$$E = h C / \lambda$$
 (Eq. 5)

The band gap energy of nanoparticles was found to be 3.3eV for both NiCaO₂ I and NiCaO₂ II. The UVabsorbance spectra of synthesized NiCaO₂ are presented in Figure 4a and 4b. Figure 5 confirms the presence of Nickel, Calcium, Carbon and Oxygen in Nickel Calciate Nanoparticles. The vertical axis displays the number of

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x-ray counts although the horizontal axis displays energy in KeV (Fig. 5a and 5b). The weight and atomic percentage of Carbon, Oxygen, Calcium, and Nickel was found to be 7.79, 51.80, 25.74, 14.67 and 13.57, 67.76, 13.44, 5.23 for NiCaO₂-I and NiCaO₂-II found to be 20.57, 46.88, 17.85, 14.69 and 32.08, 54.88, 8.344.69 these corresponds, the spectrum without impurities peaks [25].



(b)







Fig 3: XRD of the synthesized Nanoparticles (a) NiCaO₂-I (b) NiCaO₂-II



(b) (a)



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Fig 5: Energy Dispersive X-ray of synthesized Nanoparticles (a) NiCaO₂-I (b) NiCaO₂-II

3.2 Bet Surface Area Analysis

The catalytic activity of the nanoparticles is closely related to their porous structure facilitating the contact with the pollutant which favours positively to the photocatalytic activity. Using the BET surface area analysis, the specific surface area, pore volume and average pore diameter for NiCaO₂ nanoparticles are depicted in table 1. This value is analogues to the other nanoparticles [26-29]. The obtained surface area for NiCaO₂ nanoparticles is suitable to carry out the photocatalysis as the photoelectric conversion efficiency is directly proportional to the surface area available [30].

Catalyst	Surface area	Pore volume	Average pore
			diameter
NiCaO ₂ (urea)	2.4416 m ² /g	0.01013 cc/g	165.87Å
NiCaO ₂	2.3778 m ² /g	0.00265 cc/g	44.578Å
(acetamide)			

Table 1: Surface properties of the nanoparticles

3.3 Nature of Point of Zero Charge

In order to understand the behaviour of adsorption or photocatalysts with respect to pH it is important to determine the isoelectric point or point zero charge of the nanoparticles. For the determination of pzc of NiCaO₂ nanoparticles, graph of initial pH against final pH was plotted and the values of $pH_{(pzc)}$ were found to be 11.5 and 11.7 (Fig 6). Below this $pH_{(pzc)}$ the surface is positively charged and above this surface negatively charged. The pH of CR is below the $pH_{(pzc)}$, which favours the degradation of anionic CR and thus the suitable for photocatalysis [30]

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3.4 Mechanism of Photodegradation

NiCaO₂ photocatalyst was found to be photo-excited under solar irradiation. When sunlight strikes on the nanoparticle surface, an electron from its valance band (vb) jumps to the conduction band (cb) leaving behind positively charged hole (h^+_{vb}). The negative charge is increased in the conduction band (e^-_{cb}) and photocatalytic active centers are formed on the surface of NiCaO₂nanoparticles. The valence band holes react with the chemisorbed H₂O molecules to form reactive species such as ·OH radicals, which subsequently react with dye molecules to cause their complete degradation. The e^-_{cb} and h^+_{vb} can be trapped in surface states where they may react with species adsorbed or close to the surface of the particle. The e^-_{cb} can react with an acceptor, such as dissolved O₂, which consequently is transformed into a super oxide radical anion (O₂⁻⁻) which leads to the formation of additional H₂O. On the other hand, h^+_{vb} could interact with donors, such as OH⁻ and H₂O⁺, to form 'OH radicals. These radicals also attack the CR. Hence, these radicals will attack the dye molecules and degrade them [31].



Fig 7: Mechanism of photocatalytic degradation

3.5 Effect of Catalyst Loading

A series of experiment were carried out to assess the optimum catalyst loading by varying the amount of catalyst from 0.1g to 1g/100ml in neutral pH. The percentage of degradation of dye has shown appreciable results. Where, NiCaO₂-I (Fig. 8) (Photo 1a) showed maximum of 97.67 % at 0.4g/100ml, NiCaO₂-II (Fig. 8) (Photo 1b) showed 97.19% at 0.4g/100ml in 120 minutes. The photodegradation rate of the CR was found to increases with increase in the catalyst loading, then decrease with the increase in the catalyst concentration (Fig. 3), a general characteristic of heterogeneous photocatalyst, and our results are good agreement with the earlier reports



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in the literature [32-34] further the increase in the catalyst loading the rate of degradation was decreases due to excess loading of catalyst leads to reduced the light penetration through the solution [35] and decrease in the number of active sites on the surface area due to the aggregation of NiCaO₂ particle at high concentration, hence it requires a number active surface area [36]. While below the level, it assumed that the catalyst surface and adsorption of the light by the catalyst are limiting factor [37,38].



Fig 8: Effect of catalyst concentration on dye solution at 120 minutes=20ppm, pH=7, (a) = NiCaO₂-I, (b) = NiCaO₂-II.



Photo 1: Effect of catalyst concentration on CR dye at 120 minutes=20ppm, pH=7, (a) = NiCaO₂-I, (b) = NiCaO₂-II.

3.6 Effect of ph

The pH plays a major role in the treatment of waste water and also generation of hydroxyl radicals. The degradation of CR dye was investigated varying pH ranging from 2 to11. The percentage of degradation on CR dye for NiCaO₂-I (Fig.9) (Photo 2a) increased from 95.06% to 98.06% from pH 2 to pH 4 and decreased to 86.75% at pH 11 in 120 minutes for 0.4g/100ml. For NiCaO₂-II (Fig. 9) (Photo 2b) the degradation of the CR increased from 94.58% to 97.48% from pH 2 to pH 4 and decreased 84.33% at pH 11 in 120 minutes for 0.4g/100ml. The maximum percentage of degradation for the two different nanoparticles was achieved at pH 4. Similar kind of work reported in the previous work [39,40].

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The effect of pH in the photodegradation of dye in presence of NiCaO₂ can be explained on the basis of zero point charge (pH_{zpc}) of the nanoparticles. The pH_{zpc} of the NiCaO₂ nanoparticle was 11.5 and 11.7 (fig 6). Thus, the surface of the catalyst is positively charged below the zpc and negatively charged above the zpc. The interaction of CR dyes on the surface of the catalyst increasing the generation of OH' radicals. These OH' ions will generate more 'OH radicals by combining with the hole of the semiconductor and the OH' radicals are the main oxidizing species responsible for photocatalytic degradation







Photo 2: Effect of pH on dye at 120 minutes=20ppm, (a) pH=4 NiCaO₂-I, (b) pH=4 NiCaO₂-II

The experimental data revealed that higher degradation of CR was observed in acidic medium. Since, the photocatalytic activity, below the pzc electrostatic interaction between positive charged surface NiCaO₂ and CR anions leads to the strong adsorption and in greater the zpc the reverse effect is observed [41]. After the optimum pH (above pH 5) the degradation efficiency was decreased, can be explained on the basis of amphoteric nature of the catalyst [42].

3.7 Effect of Initial Concentration of Dye

Dye concentration is an very important parameter in treatment of waste water. The effect of initial concentration of dye on the degradation was performed by varying the initial dye concentration from 20ppm to 50ppm with constant catalyst loading and pH (0.4g/100ml/4). The results obtained for NiCaO₂-I (Fig. 10) (Photo 3a) was 98.06% for 20ppm, 97.19% for 30ppm, 72.84% for 40ppm and 60.12% for 50ppm. And for NiCaO₂-II (Fig. 10)

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(Photo 3b) is 97.48% for 20ppm, 96.21% for 30ppm, 86.64% for 40ppm and 72.61% for 50ppm, these experiments illustrated that the degradation efficiency was directly affected by the concentration.

The results, showed that, the percentage of degradation decrease as the dye concentration increases. Similar results have been reported for the photocatalytic oxidation of other dyes [36,43,44]. When the concentration of the dye solution increases, this leads to the amount of dye adsorbed on the catalyst surface increases and affects the photocatalytic activity of the NiCaO₂ nanoparticles, this also decreases the path length of photons entering into the dye solution. The degradation is mainly related to the formation of OH radicals, these OH radicals are the main critical species in the degradation process.



Fig 10: Effect of initial dye concentration on the photocatalytic degradation of CR ($a = NiCaO_2$ -I g/pH=0.3/6, b = NiCaO₂-II g/pH=0.4/3

Important point for this behaviour is that as the initial concentration of dye increases, the more and more number of dye molecules are adsorbed on the surface of the NiCaO₂ nanoparticles are decreases, consequently attacking of OH radicals to the dye molecules are decreased [45] and competence between dye and OH⁻ ion adsorption on the surface of catalyst [37]. The path length of photons entering the solution decreases, and in low concentration the reverse effect is observed, the number of photon absorption by the surface of catalyst in lower concentration when increase the dye concentration. [43]. Hence, the rate of degradation decreases with increase in the dye concentration.



Photo 3: Effect of initial dye concentration on the photocatalytic degradation of CR (a = NiCaO₂-I g/pH=0.4/4, $b = NiCaO_2$ -II g/pH=0.4/4)

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3.8 Effect of Different Conditions

The photocatalytic degradation of CR dye (20ppm) under three different experimental conditions were examined, *i.e.*, through, dye/dark/catalyst, dye/UV/catalyst and dye/sunlight/catalyst for the catalyst. CR dye solution when exposed directly to the sunlight without the catalyst, the degradation was found to be nil during the entire experiments. The degradation rate was found to be increase with increase in irradiation time, for dye/sunlight/ NiCaO₂-I showed 98.06%, dye/UV/ NiCaO₂-I found to be 67.98% and for dye/dark/ NiCaO₂-I 44.77% was recorded (Fig. 11) (Photo 4a).Similarly for CR dye (20mg/L) for dye/sunlight/ NiCaO₂-II showed 97.48%, dye/UV/ NiCaO₂-II found to be 55.89% and for dye/dark/ NiCaO₂-II 37.04% was recorded (Fig. 11) (Photo 4b). These results clearly indicate that, photodegradation occurs most efficiently in the presence of sunlight. Under sunlight, excitation of electrons from the catalyst surface takes place more rapidly than in the absence of light. Similar observations have been reported for photocatalytic degradation of dyes [46].



Fig 11: Effect of sunlight irradiation with respect to Dark condition and UV condition on photocatalytic degradation of CR in 120 minutes.



Photo 4: Effect of sunlight irradiation with respect to Dark condition and UV condition on photocatalytic degradation of CR in 120 minutes (a = NiCaO₂-I g/pH=0.4/4, b = NiCaO₂-II g/pH=0.4/4)

IV. CONCLUSION

Photocatalysis is a very effective method for the degradation of industrial or textile dyes. In this study, NiCaO₂ nanoparticles were synthesized and characterized by XRD, SEM, EDX, BET and UV-Vis reflectance. It was observed that the synthesized NiCaO₂-I (average particle size 14 nm) and NiCaO₂-II (average particle size

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19nm) are photosensitive and effective in degrading selected azo dye (CR) completely in a short interval of time (120 minutes). From this experiment, we can conclude that the NiCaO₂ did in fact degrade the dye over short interval of time with the help of sunlight. Even though the result was achieved more than 97%, we still believe that if this experiment was done over a longer period of time that the concentration of the dyes would have been zero. This protocol developed may be employed effectively in the treatment of textile dye effluents which are hazardous to the environment.

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