Original Article

Photocatalytic Degradation of Methyl Violet Dye Using Calcium Carbonate Nanoparticles Synthesized by Precipitation Method

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Abstract

Background: The problem associated with the textile industries are the direct discharge of coloring chemicals into water body that causes threat to the aquatic lives.

Objectives: Photocatalytic degradation of methyl violet dye has been studied by employing inexpensive calcium carbonate nanoparticles ($CaCO_3$ Nps) prepared by a simple precipitation method.

Materials and Methods: As prepared $CaCO_3$ Nps are characterized using XRD, FESEM, UV-visible analysis, etc.

Results: The XRD pattern exhibits a well resolved peaks characteristic to rhombohedral crystal phase with crystallite size of 82 nm. FESEM image reveals about the morphology of $CaCO_3$ Nps which is in irregular shape with size ranges from 100 to 200 nm. Photocatalytic activity of $CaCO_3$ Nps has been checked by degrading aqueous methyl violet dye solution as model organic pollutant exposing to sunlight.

Conclusions: Degradation of methyl violet dye has been followed spectro photometrically at a wavelength of λ_{max} = 579 nm. Complete degradation of organic dye is noticed at a shorter duration of 40 min.

Key words : Calcium carbonate nanoparticles; Precipitation technique; Photocatalytic degradation; UV-Vis analysis.

Introduction

The present decade is considered as the nanotechnology era, since nano material-based devices had been extensively used in nano-electronics, textile industries, agriculture, catalysis, coating, etc.[1-5] One of the problem associated with the textile industries are the direct discharge of coloring chemicals like dyes and pigments into natural water resources. It is a major threat and endangers the aquatic lives. The color present in the effluent blocks the sunlight and cause disturbance to the natural growth cycles of many aquatic organisms.[6, 7] The heavy metals, organic and inorganic complexes used in making of pigments and dyes are highly toxic and their deposition influences severe health risk.[8, 9] Obviously, the dye effluents from the textile and other industries have been considered as major pollutants that disturb the ecosystem and affects quality of the environment.[10, 11] Majority of the effluents is discharged during the production and application process in the dye industries and therefore has to receive attention. Among the various kinds of dyes, azo dyes are popular dyes that are most commonly used in the textile industries.[12, 13] However, regarding its disposal after usage, industries have adopted various physical techniques such as coagulation by chemical agents, usage of ion exchange, activated carbon, ultrafiltration, reverse osmosis, etc.[14, 15] Although, these techniques convert the organic compounds present in the water into a secondary pollutant like sludge, needs further treatment. Furthermore, such additional techniques required to treat the secondary pollutants enhances the cost of remediation.[16, 17]

Photocatalysis is a method used to degrade organic compounds found in waste water by mineralizing them into simplest compounds like H_2O, CO_2, etc. Nano photocatalysts have been studied extensively since they have favorable combination of electronic structure, light absorption properties; charge

transport characteristics, etc.[18, 19] Among the different kinds of photocatalysts, the prominent nanocatalysts extensively used are TiO_2, ZnO, SnO_2, etc.[20-23] However, reports about the usage of $CaCO_3$ Nps as photocatalyst against the degra- dation of organic pollutant are scarce. Pei et al.[23] prepared calcium carbonate micro rods using hydrothermal method and used as an effective photo-catalyst to degrade methyl violet dye with degradation efficiency of 72.29 % at an exposure time of 4 h. Besides, other types of carbonate- based particles of micron size are also used as photocatalyst in the degradation studies of organic pollutants.[25-27] Though all these literatures dealt with the photo-catalytic activity of micron-sized carbonate, the micron sized carbonate particles exhibit photo-catalytic behavior and its influence of nano size effect is not yet reported. If the photo-catalytic carbonates are in nano size, the overall surface area of the photo-catalyst increases resulting in the inclination of surface-active sites. Therefore, the specific site for photo-catalytic degradation process increases drastically that might enhance the rate of degradation of the pollutant.

In this context, $CaCO_3$ Nps prepared by a simple precipitation technique is used as a photo-catalyst to degrade methyl violet dye in aqueous condition. Like traditional photo-catalyst (TiO_2, ZnO, SnO_2, etc.), $CaCO_3$ Nps also displays excellent photocata- lytic activity towards the degradation of organic pollutant within a short span of time.

Experimental procedure

Preparation of CaCO³ Nps

Calcium chloride (1.47 g, 0.01 M) is dissolved in 50 ml of distilled water. To this solution 1.06 g (0.01 M) of sodium carbonate dissolved in 50 ml of water is gradually added with continuous stirring. Instantly, a white precipitate of $CaCO_3$ is formed. Addition of sodium carbonate solution is continued for a period of 30 mins with constant stirring. Formed white precipitate is separated by filtration and washed thoroughly with distilled water to remove unreacted salts. White $CaCO_3$ Nps particles are dried in hot air oven at 105°C for 1 hr. The dried powder is collected and stored in vacuum.

Photocatalytic degradation of methyl violet

1 mg of crystal violet is weighed accurately and dissolved in 100 ml of distilled water. 0.1 g of as obtained $CaCO_3$ Nps is mixed with 100 ml of distilled water and then sonicated for 10 mins using probe type sonicator (SONICS, US). Nanoparticles dispersed solution appeared like a turbid solution, since $CaCO_3$ Nps are uniformly distributed. To this solution, aqueous methyl violet solution is added, stirred thoroughly and mixture is exposed to sunlight. Once in 10 mins, an aliquot of the exposed

mixture is collected and its optical absorption is recorded using UV-Vis absorption spectrometer (Perkin Elmer, Lambda 25, USA) at λ_{max} = 579 nm, whereby it is possible to evaluate the reduction in concentration of methyl violet dye.

Results and discussion

The XRD pattern obtained for CaCO3 Nps is shown in Fig. 1. All reflection peaks in Fig. 1 can be readily indexed to pure rhombohedral phase of CaCO3 Nps. The diffraction peaks found at 2θ = 23.08°, 29.35°, 35.93°, 39.36°, 43.10°, 47.12°, 47.45°, 48.44°, 56.52°, 57.39°, 60.69°, 63.03°, 64.65°, 65.59°, 70.21°, 72.98°, and 77.17° are labeled to (012), (104), (110), (113), (202), (024), (018), (116), (211), (122), (214), (125), (300), (0012), (0210), (128), and (1112) planes respectively is well resembled with the JCPDS No. 85-1108.[28]

The crystallite size (D) of $CaCO_3$ Nps has been calcu- lated using the Scherrer equation,

$$D= k\lambda/\beta\cos\theta \qquad (1)$$

where β = FWHM (full-width at half-maximum or half-width) is in radian, θ is the position of the diffraction peak, k is the so-called shape factor, which usually takes a value of about 0.9, and λ is the wavelength of X-ray used (1.5406 Å for Cu Kα). The average crystallite size of $CaCO_3$ Nps has been calculated as 82 nm.

FESEM analysis

FESEM image of $CaCO_3$ Nps recorded using Carl Zeiss SUPRA-55 is depicted in Fig. 2a-b. The micro- graphs are taken in different magnifications like 60,000× and 1, 20,000× respectively at a working distance of 10.8 mm. The operating voltage used for retrieving the image is 24 kV. The $CaCO_3$ Nps shows irregular shaped structures with size ranges from 100 nm to 200 nm. The nanoparticles are found agglomerated and fused together with each other.
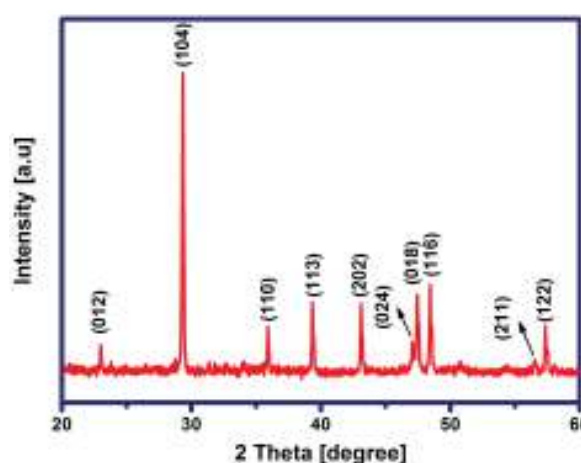
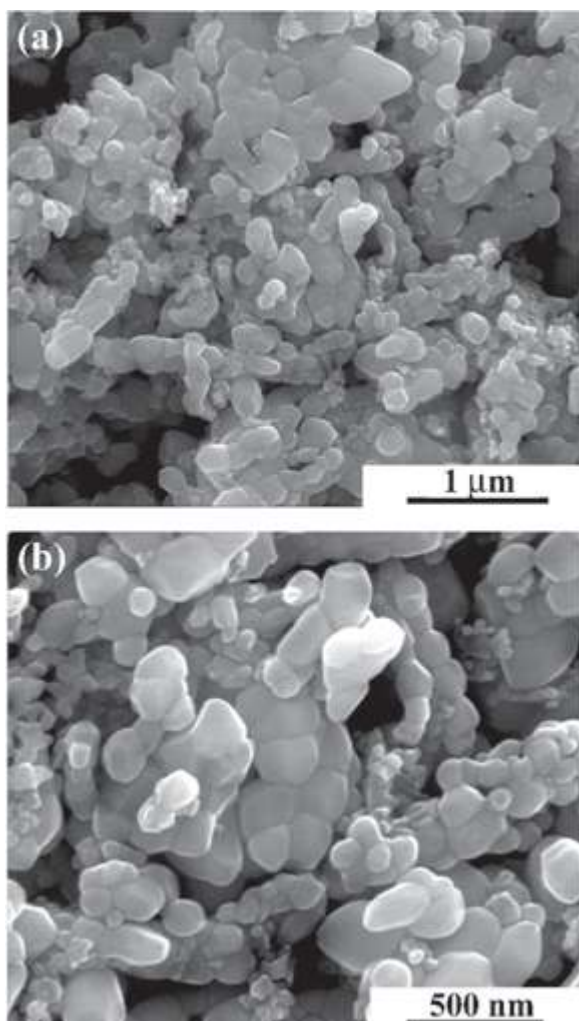

Figure 1: XRD pattern of calcium carbonate nanoparticles

Figure 2 a-b: FESEM images of CaCO3 Nps recorded at different magnifications
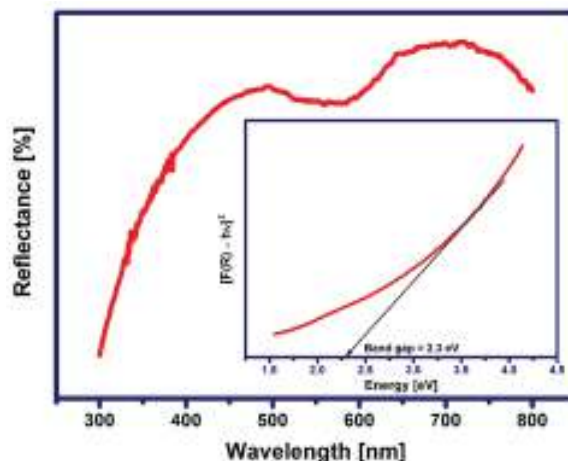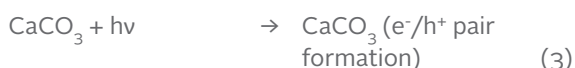

Figure 3: Reflectance spectra and [inset] band gap determination of CaCO3 Nps

part of the graph gives the band gap energy of the $CaCO_3$ Nps is equal to 2.3 eV.

Photodegradation of methyl violet dye

Experimentally, the photodegradation of methyl violet dye catalyzed by $CaCO_3$ Nps has been followed through UV-Vis spectrometer. The mixture containing $CaCO_3$ Nps and methyl violet dye prepared by taking 1 mg of dye dissolved in 100 ml of distilled water and 100 ml of $CaCO_3$ Nps (0.1 g dispersed in 100 ml water) dispersion exposed to sunlight (around 12.00 pm). Till the disappearance of violet color, the contents are kept at sunlight. Periodically, the change in color of the dye is recorded spectroscopically. Violet color ($\lambda = 579$ nm) of the chosen azo dye is characterized to azo bonds linked with chromophores and auxo- chromes. Azo bonds are active bonds that can degrade into colorless fragments by reactive species generated in the solution in an in-situ manner while exposing to sunlight. Hydroxyl radical, e-/h+ pair, O_2- species, etc. are responsible for the cleavage of azo bonds that leads to the degradation of organic network.[29] The degrada- tion of MV by exposing to sunlight in the presence of $CaCO_3$ Nps is described below,

UV-Vis analysis

UV-Vis reflectance spectrum of $CaCO_3$ Nps recorded in the range of 300 nm to 800 nm using UV–Vis spectrophotometer, Shimadzu, UV-2450, Japan is shown in Fig. 3. From the plot, it is found that the $CaCO_3$ Nps has an absorption band edge near UV region and therefore there is a possibility of excitation to occur at the characteristic wavelength.

The energy band gap exist between the conduction band and valence band of $CaCO_3$ Nps can be deter- mined from the data obtained from reflectance spectra using Kubelka-Munk function $F(R\infty)$, which is expressed as,

$$F(R) = (1-R)^2/2R \qquad (2)$$

Where, R is the reflectance value and $F(R)$ is equiva- lent to the absorption coefficient. For determining the band gap of the prepared nano particles, a graph is plotted with $[F(R)*h\upsilon]^2$ along Y-axis and $h\upsilon$(eV) along X-axis [inset image given in Fig. 3]. Intercept made at X-axis by drawing a tangent from the linear

$CaCO_3 + h\upsilon$	$\rightarrow$	$CaCO_3$ (e^-/h^+ pair formation) (3)
$e^- + O_2$	$\rightarrow$	$O_2\bullet-$ (4)
$H_2O + O_2\bullet-$	$\rightarrow$	$OOH^\bullet + OH^-$ (5)
$2OOH\bullet$	$\rightarrow$	$O_2 + H_2O_2$ (6)
$OOH\bullet + H_2O + e-$	$\rightarrow$	$H_2O_2 + OH^-$ (7)
$H_2O_2 + e-$	$\rightarrow$	$OH^\bullet + OH^-$ (8)
$H_2O_2 + O_2\bullet-$	$\rightarrow$	$OH^\bullet + OH^- + O_2$ (9)
e^-/h^+ pair/$OH^\bullet$ / $O_2{}^{\bullet-}$/ $CaCO_3\bullet$+dye	$\rightarrow$	Dye degradation (10)

In sunlight, $CaCO_3$ Nps get excited; transfer an electron to the conduction band [Eq. (3)]. The excitation of e- causes effective charge separation
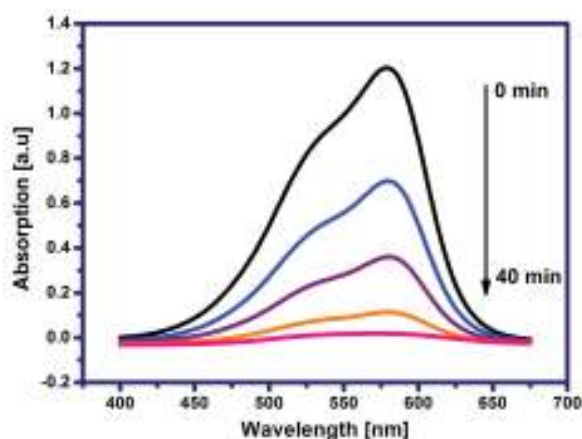
Figure 4a: Photo-catalytic degradation of MV using $CaCO_3$ Nps

Figure 4c: ln (Co/Ct) vs irradiation time for determining rate constant

and leads to the production of e^-/h^+ pair, which is a key step for the photo-catalytic degradation process.[29] e^- found on the conduction band of $CaCO_3$ Nps reacts with the dissolved oxygen present in water and produces super oxide radical [Eq. (4)]. These radicals further react with oxygen and organic molecules produces hydrogen peroxide [Eq. (5-7)]. Hydrogen peroxide further generates hydroxyl radicals which are powerful oxidizing agents [Eq. (8, 9)], capable of attacking dye molecules and degrade them [Eq. (10)].

The spectroscopic investigation of photo-catalytic degradation of MV at an interval of 10 mins is recorded using UV-Vis spectrometer is depicted in Fig. 4a. From the spectra, it is visualized that the intensity at λ_{max} = 579 nm found decreases with increase in exposure time. This indicates that the concentration of the dye gets reduced with respect to exposure time. The absorption peak at λ_{max} = 579 nm almost reaches to zero when the irradiation time is about 40 mins. The remarkable performance of $CaCO_3$ Nps is due to the efficient charge separation process and the reduction in recombination process as described.
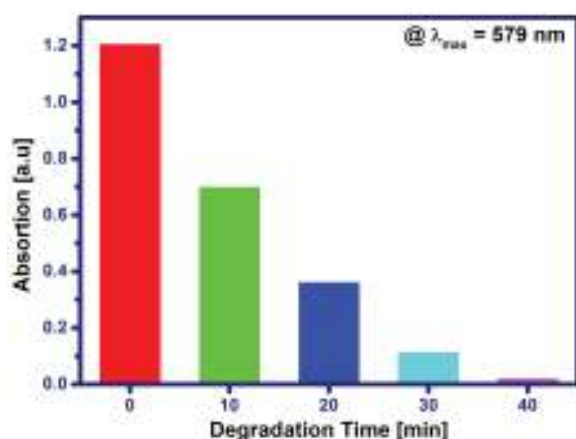
Fig. 4b indicates about the reduction in optical density at λ_{max} = 579 nm while exposing to sunlight. From the graph, it is inferred that the optical density gets changed with increase in exposure time and almost equal to zero at about 40 mins of exposure time. From these data, the degradation efficiency of $CaCO_3$ Nps against methyl violet is evaluated and found as 98.5 %. However, there is no reduction in dye concentration when MV solution is exposed to sunlight without the presence of $CaCO_3$ Nps. These results clearly indicate that the photo-catalytic degradation occurs more efficiently in presence of sunlight along with the catalyst only.

Kinetics of the degradation process is evaluated for low dye concentration that obeys first-order-kinetic reactions. The Langmuir – Hinshelwood relation provides the data for the steady state reaction process is represented as,[30]

$$dC/dt = -K_c C \qquad (11)$$

$$\ln (C_o/C_t) = K_c t \qquad (12)$$

Where, Kc is the rate constant, Co and Ct is the initial concentration and final concentration of dye after exposing to sunlight at time t respectively. Rate constant of the reaction is calculated by plotting ln (C_o/C_t) vs. the degradation time [Fig. 4c]. Slope obtained from the graph gives the rate constant Kc, is found to be 0.10212. Such a high rate constant confirms the degradation of organic dye at faster rate.

Conclusion

Present study revealed about the preparation of $CaCO_3$ Nps by simple precipitation method. As obtained $CaCO_3$ Nps are characterized using XRD, FTIR, FESEM, UV-Vis analysis, etc. Photocatalytic activity of $CaCO_3$ Nps is studied by degrading aqueous methyl violet solution exposing to sunlight. The prepared nano particle displayed higher

Figure 4b: Change in absorption intensity at λ_{max}=579 nm with respect to irradiation time

photo-catalytic activity with a degradation efficiency of 98.5 % within 40 mins. The rate constant of the degradation process is calculated as 0.10212 using Langmuir – Hinshelwood relation. All these results confirmed that the as obtained $CaCO_3$ Nps possess excellent photocatalytic degradation efficiency towards organic methyl violet dye.

Acknowledgments

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