Research Journal of Recent Sciences ISSN 2277-2502
Vol. **11(2),** 19-22, April **(2022)** *Res. J. Recent Sci.*

H_2O_2 assisted photocatalytic degradation of hazardous Colours using CaO

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Available online at: www.isca.in, www.isca.me
Received 30th December 2021, revised 3rd March 2022, accepted 25th March 2022

Abstract

Holi colours discharged into water bodies are a menace to the aquatic life. Photodegradation of a commercial orange holi colour using CaO photocatalyst and combination of CaO/H_2O_2 is attempted in the present investigation. The orange holi colour is a mixture of yellow and pink organic dyes. CaO photocatalyst synthesized by citrate gel method removes yellow dye of the sample but CaO/ H_2O_2, removes both dyes from orange colour within 15 minutes of exposure to sunlight. Huge load of organic carbon and proliferation of microbial colonies are observed in waters in which holi colour is discharged. Organic carbon in coloured water treated with CaO/H_2O_2 indicates that only chromophore responsible for colour is broken down and photodegradation is not complete. However CaO/H_2O_2 deactivates the micro-organisms in the treated water.

Keywords: Holi colour, Pollutant, Water bodies, Photodegradation, Photocatalyst, CaO/H_2O_2

Introduction

Environmental pollution is a matter of concern worldwide as it is increasing at an alarming rate. Water bodies are being polluted due to discharge of organic matter from sewage, industrial effluents and other sources. The conventional water treatments like slow filtration, sedimentation, adsorption, biological processes are not very effective in removal of these toxic materials. The advanced oxidation processes or photocatalysis which involve use of semiconductor oxides like ZnO, TiO_2 in natural sunlight are the present day methods to tackle these wastes without puting any more burden on the available resources.

CaO also called as quicklime is one of the widely used, cheap and easily available material. It is used as a sorbent for CO_2[1] and as a catalyst for transesterification of soyabean oil and production of biodiesel[2]. It is used as a photocatalyst in degradation of dyes like Rhodamine 6G, Methylene blue[3-5]. Calcium in its hydroxide form (chuna) is reported for dye degradation[6]. The band gap of CaO is reported as 7.7eV indicating that it is an insulator[7].

The CaO lattice is similar to NaCl lattice with one Ca^{+2} ion being surrounded by 6 Cl^- ions. One such environmental pollutant is the holi colour which is released in water bodies after the local festival. Research done on water samples after the discharge of holi colour shows an increase in parameters like COD, turbidity, conductivity of these contaminated waters bodies[8]. Also it is investigated that Holi colours can contain up to 80% of PM10 particles which are cytotoxic[9]. In the present investigation, photodegradation of a colour used in holi festivals is studied. So far no degradation of holi colours by any photocatalysts is reported.

Materials and methods

Preliminary characterization of holi colours: An orange coloured sample of holi colour collected from commercial market was used for study. Preliminary studies carried out on the sample include paper chromatography on Whatmann filter paper no. 1 using mixture of Ethyl acetate and Petroleum ether, SEM analysis on the instrument JEOL JSM-5800 in NIO, Goa, UV-Visible Absorbance spectroscopy on the instrument Shimadzu UV-2450. The colour sample was washed using distilled water to get coloured solution and white residue which was discarded. Stock solution of the colour 2.5g/250ml was prepared and stored in dark. River water was used to prepare the solutions. The dissolved oxygen of water was analysed before preparation of stock solution.

A blank sample colour was streaked on nutrient agar plates and incubated at 37°C for 24 hours for microbial growth. The colonies formed were counted. Gram staining test was done to identify gram positive and gram negative species. A colony from the nutrient agar plate was picked up and inoculated in saline. A loopful of the microbial suspension was taken and a smear was made on the clean grease free slide. The smear was dried by passing through the flame .To the slide 2-3 drops of crystal violet strain was added and was kept aside for 2-3 minutes and the strain was discarded. Later the smear was flooded with iodine and was kept aside for 1min. The iodine was washed with few drops of alcohol and the smear was stained with saffranine for 2mins, the slide was washed with water and air dried and was observed under oil immersion lens.

Synthesis and characterization of CaO: Citric acid (30g/50 ml) was added drop wise to $CaCl_2.2H_2O$ (7.34g/50ml) with continuous stirring. The solution was heated on burner till the quantity reduced to half of original amount and then heated

strongly to convert it to gel. Upon further heating the gel was ignited and burnt in air to give CaO.

Chemical analysis of calcium was done by standard gravimetric methods[10]. Phase formation was checked on the instrument Philips analytical PW1710, SEM analysis was done on the instrument JEOL JSM-5800 and UV-Visible Absorbance of the oxide was recorded on the instrument Shimadzu UV-2450.

Degradation of Holi colour using CaO: Stock solution (50 mL) was taken in a conical flask containing CaO (0.2g). The time of mixing and absorbance were noted down. The conical flask was exposed to sunlight with intermittent stirring. Another set of the solution with CaO/H_2O_2 and a blank solution was exposed to sunlight.

Analysis of decolourized sample: The decolourized solutions were analysed for total organic carbon (TOC analysis) and qualitative analysis of ions like NO_3^-, SO_4^{-2} to check for mineralization of the dye. In order to check the effect of these waters on river water flora, streaking and gram staining tests as explained earlier were performed.

Results and Discussion

Characterization of the holi colour: TLC of the orange holi colour show two spots suggesting that it is a mixture of two dyes, yellow and pink. SEM (Figure-1) images reveal that all particles are uneven shaped, irregular with particle size from 1.9 to 3.3µm. Since the particles have an aerodynamic diameter smaller than 10µm they are of serious concern. Literature reports suggest in vitro close association of such powders with human leukocytes. It is also reported that increase of particulates of diameter smaller than 10µm (PM10) concentrations in ambient air is associated higher cardiovascular and respiratory disorders[9]. The solid orange colour shows absorbance (Figure-2) in the multiple wavelength of 250nm, 370nm, 470nm and 560nm. The residue obtained during preparation of stock solution is indicative of addition of a base material/ filler like silica or asbestos in the holi colour. EDS analysis show that the colour sample is predominantly organic dyes with a ppm level concentration of inorganic coloured salts.

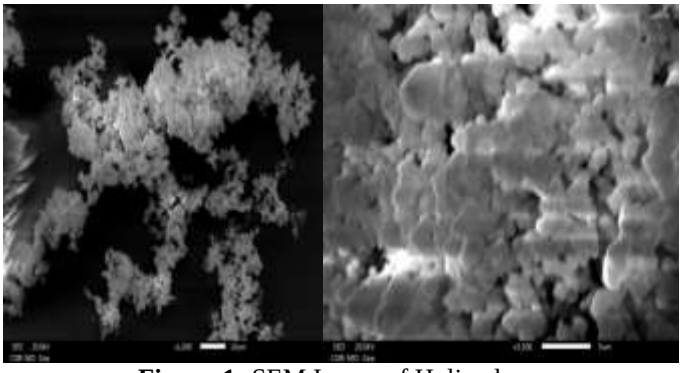

Figure-1: SEM Image of Holi colour.

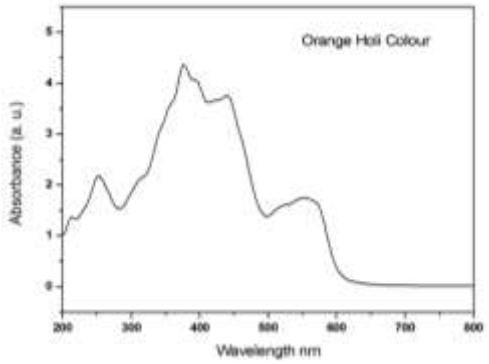

Figure-2: UV visible absorbance plot of holi colour sample.

Characterization of CaO: Gravimetric analysis show experimental percentage of Ca as 72.5% which is in agreement with theoretical percentage of 71.49%**.** Phase formation (Figure-3) of pure CaO in cubic form is confirmed by JCPDS Card NO 77-2376. The calculated particles size using Scherrer formula is 51.16nm. The UV–Visible spectrum of synthesized CaO (Figure-4) shows the band gap energies of CaO as (Table-1) 6.199, 4.959 and 3.542eV. The literature however reports varied band gap energies as 3.44eV[11] and 6.25eV[12] depending upon synthetic methods used. The SEM images (Figure-5) indicate spherical agglomerated particles of size 2.7 to 31.25µm.

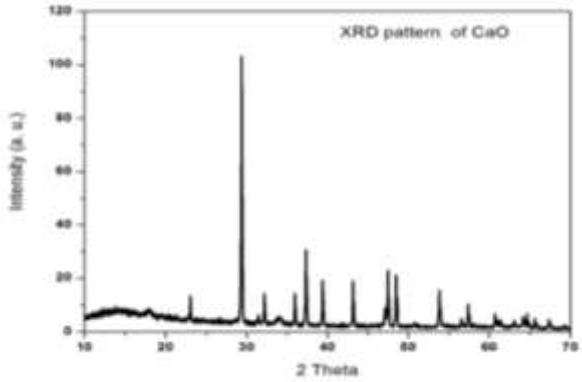

Figure-3: XRD pattern of synthesized CaO.

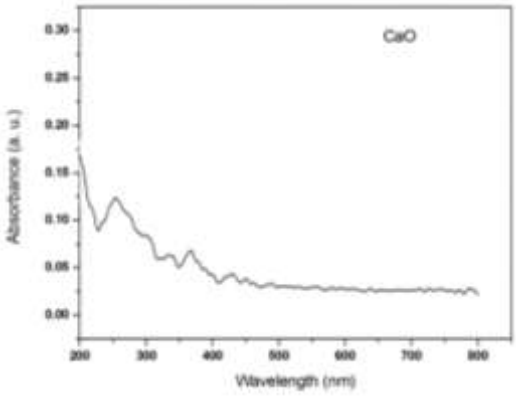

Figure-4: UV-Vis absorbance spectrum of synthesized CaO.

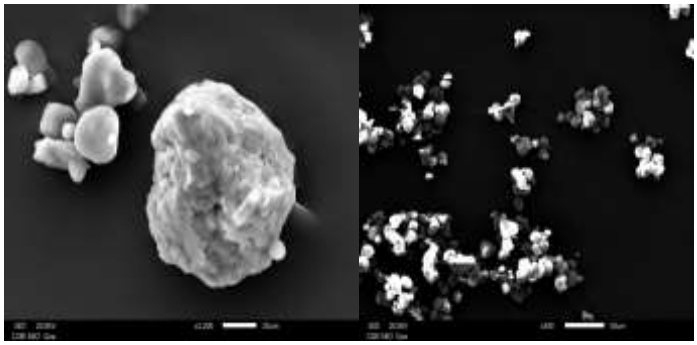

Figure-5: SEM image of synthesized CaO.

Table-1: Band gap of synthesized CaO.

Compound	Λmax	Band Gap
CaO	200	6.199
	250	4.9592
	350	3.5422

Table-2: TOC analysis of river water samples.

Sample	TOC (%)
River water with colour discharged	0.12
CaO/H_2O_2 treated river water	0.37
River water	0.054

Table-3: Results of streaking.

Water sample	Colonies formed after 24 hours
River water	28
CaO	2
Colour + river water	46

Photocatalytic degradation of Holi colour: The river water used for experiment was well aerated with dissolved oxygen of 8.0995mg/L. There was no change in dissolved oxygen of the river water upon addition of colour. During the photocatalysis, addition of CaO (the solution turned alkaline) yellow component of the colour was removed and solution appeared pink. The pink solution did not decolourize upon exposure to sunlight indicating the resistance of pink component to get degraded. The process was facilitated by H_2O_2. A synergistic action of CaO and H_2O_2 was observed. The solution decolourized within 15 minutes of addition of CaO and H_2O_2 and exposure to sunlight. This was due to release of $OH^{\cdot}$ radicals from H_2O_2 which facilitated the process. The blank solution did not decolourize upon exposure to sunlight.

TOC and mineral ions analysis: Disappearance of colour does not ensure complete degradation of organic matter. Hence total organic carbon in decolourized solutions was tested (Table-2). The river water in which the colour is mixed has a very low organic carbon i.e 0.054%. On addition of colour to this sample, TOC increases to 0.12%. Holi colour increases the total organic matter in the water bodies. The degraded sample show maximum TOC of 0.37% which is more than water in which colour was discharged indicating that the organic dye breaks down into fragments upon degradation.

The functional groups containing nitrogen and sulphur upon oxidation change to nitrates and sulphates. The colour solution degraded using CaO/H_2O_2 tests positive for nitrates indicating it breaks down the dye molecule upto the formation of ions like nitrates.

Streaking and gram staining: The results of streaking (Table-3) show that the river water contains variety of microorganism. These micro-organisms undergo proliferation upon discharge of holi colour into water due to increase in organic matter. The holi colour sample degraded using CaO/H_2O_2 shows the effect of photo produced hydroxide radicals on microbial colonies. The hydroxide radical raptures the cell wall and kill the micro-organisms resulting in depleted growth. The strong oxidizing species $OH^{\cdot}$ and O_2^{-} readily attacks the bacterial cell membrane resulting in the oxidation of polyunsaturated phospholipids leading to the destruction of the bacterial cell membrane and the exposure of the inner cellular components. These inner cellular components further undergo oxidation ultimately resulting in bacterial cell death. It is observed that the coloured river water degraded by CaO/H_2O_2 show presence of gram positive bacteria whereas other samples indicate presence of gram negative bacteria. This may be due to presence of thicker cell wall in gram positive bacteria which are more difficult to be attacked by photo-generated hydroxide radicals.

Conclusion

Photodegradation of orange holi colour was carried out using CaO and combination of CaO/H_2O_2.CaO photocatalyst was synthesized by citrate gel method and characterised by methods like chemical analysis, XRD, SEM and UV-visible spectroscopy which showed cubic CaO with spherical particles having varied particle size. It showed absorbance in UV as well as visible region with band gaps matching with reported. It was observed that advanced oxidation process using CaO removed only yellow component of the sample. When CaO was used in conjunction with H_2O_2, removal of both pigments took place. But removal of colour is not the removal of organic matter. Further analysis showed an increase in organic carbon content of the water and also the growth of colonies of micro-organisms due to presence of organic load when holi colours are discharged into water bodies. CaO/H_2O_2 degraded sample streaked on nutrient agar media showed less growth of micro-organisms due to $OH^{\cdot}$ radicals killing their cells.

Acknowledgement

The author would like to extend sincere gratitude to Mr Girish Prabhu, NIO, Goa XRD measurement, Mr Arif, NIO, Goa for SEM images and Dr Rahul Kulkarni, ICAR, Goa for TOC analysis.

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