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Chemical and Photocatalytic Degradation of Crystal Violet Dye by Indian Edible Chuna (Calcium Oxide/Hydroxide)

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Chemical (in dark) and photocatalytic (in presence of light) degradation of the crystal violet (CV) dye is studied using Indian edible chuna as a catalyst. Physico-chemical characterization of Indian edible chuna indicates that it is calcium oxide (in dry state) and/or calcium hydroxide (when dispersed in water/slurry form). It is observed that Indian edible chuna (calcium oxide/hydroxide) attacks crystal violet in dark and degrades it. This process (chemical degradation) is observed to be slow and gets activated in the presence of light (photocatalytic degradation). The ability of the calcium hydroxide to yield hydroxyl ions and the importance of the hydroxyl radicals in the photocatalysis process signify the importance of calcium oxide/hydroxide as a photocatalyst.

Keywords: Photocatalysis, Calcium Oxide, Calcium Hydroxide, Crystal Violet Dye.

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1. INTRODUCTION

Since the initial report by Fujishima and Honda,[1] extensive work has been carried out for application of photocatalysis process for water purification, air purification, splitting of water to generate hydrogen which can subsequently be used as fuel etc.[2–10] Simplicity of the process, availability of low cost and efficient photocatalyst materials like TiO_2, ZnO, etc., free and abundant availability of sunlight in a country like India—makes the technology attractive for large scale use for waste water treatment. TiO_2 and ZnO were widely studied as prototype photocatalyst materials, although, efforts were also directed towards developing visible light photocatalysts.[11]

As of today, TiO_2 remains unchallenged material in terms of its photocatalytic performance, cost, availability, environment friendly nature etc. Our accidental observation and subsequent studies on Indian edible chuna[12,13] stimulated our interest in using it for photocatalytic applications.

Physico-chemical characterization of the Indian edible chuna by us indicates that it is calcium oxide (in the dry state) and calcium hydroxide (when dispersed in water/slurry form). In India, it is used along with tobacco for chewing; in paan (Indian marathi word), Ayurvedic medicine etc. Since, it is directly consumed by humans, we call it as ‘edible chuna.’ Other impure variety is used for applications such as in construction (since it has cement-like property), paints etc. It is now known that calcium hydroxide $[Ca(OH)_2]$ is formed when calcium oxide (CaO) is added/reacts with water. This process is reversible. When the calcium hydroxide is dried/heated, transforms to calcium oxide and vice versa.

$$CaCO_3\ (solid) \xrightarrow{heating} CaO\ (solid) + CO_2\ (gas)\uparrow$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Calcium hydroxide (Molecular weight: 74.08) is a white odorless powder with low solubility in water (about 1.2 g/L at 25 °C), high pH (12.5–12.8), is insoluble in alcohol. It is classified as a strong base. It has many interesting properties and applications such as antibacterial property, medical applications like in dental applications etc. Many of the properties and applications of calcium hydroxide originate from its dissociation into calcium and hydroxyl ions and the subsequent action of these ions.

Lime ($CaCO_3$) is used in water purification from long time. However, there are very few reports on photocatalytic

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property of $CaO/Ca(OH)_2$.[14, 15] In general, the mechanism of photocatalysis involves photo-generation of radicals and their action on the organic pollutants. Before performing the present experiment, we strongly felt that the property of calcium hydroxide $[Ca(OH)_2]$ to dissociate itself into calcium and hydroxyl ions might be very useful in realizing the photocatalytic degradation of dyes and organic materials, particularly, crystal violet (CV) dye. Indeed, very interesting results are observed and are presented here.

In the present work, we observed that Indian edible chuna (calcium oxide/hydroxide) attacks CV dye in dark and degrades it. This process (chemical degradation) is observed to be slow and gets activated in the presence of light (photocatalytic degradation). We strongly believe that calcium oxide/hydroxide is an excellent photocatalyst due to its ability to give hydroxyl ions/radicals which plays important role in photocatalytic degradation of the organic pollutants. More experiments are underway to know the exact nature and mechanism of the process.

2. MATERIALS AND METHODS

Crystal Violet $[C(C_6H_4N(CH_3)_2)_3]Cl$ is a cationic dye. Stock solution of CV dye in distilled water (DW) is made having a concentration of 2.6×10^{-5} M and was used for further studies. The sketch of the chemical structure of CV dye is shown in Figure 1.

Indian edible chuna is obtained from the local market and used as it is (without any further purification) as a photocatalyst. For the experimental evaluation purpose, paste of Indian edible chuna is dried and the dried powder is used in the subsequent studies like for X-ray diffraction (XRD), energy dispersive X-ray analysis (EDAX) etc. 0.5 gm of Indian edible Chuna (calcium oxide—in dry state) is dispersed in 500 ml stock solution of CV in distilled water (DW). Solution was illuminated with direct sunlight with constant stirring. Sampling was done at a regular interval of time for studying the visible light optical absorption spectra and optical density at λ_{max}. Reduction of optical density at λ_{max} is taken as a direct measure for photocatalytic degradation of the CV dye—since color of the dye is directed related to its structure.

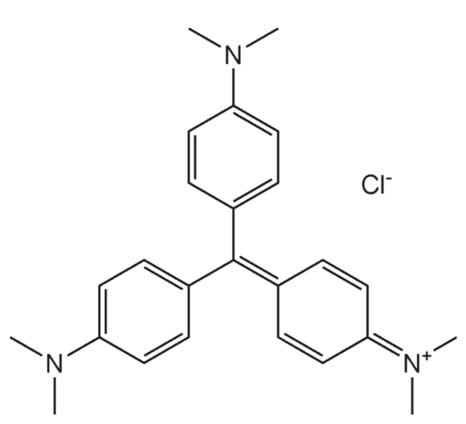

Fig. 1. Molecular structure of the crystal violet dye (sketch).

3. RESULTS AND DISCUSSION

Detailed physico-chemical characterization of Indian edible chuna is presented in our earlier published reports.[12, 13] For completeness of the present report, it is discussed in brief here. SEM observation indicates that Indian edible chuna was made of aggregated nanoparticles of size between 500 nm to 1 μm. Elemental composition as obtained from the energy dispersive X-ray analysis (EDAX) indicates presence of only calcium (45.12 at.%) and oxygen (54.88 at.%) as its constituents, indicating high purity of the material. In X-ray diffraction (XRD) spectra of Indian edible chuna, major X-ray diffraction peaks were observed at 29° $[Ca(OH)_2]$, 29.5°, 34° $[Ca(OH)_2]$, 47.5° $[Ca(OH)_2]$, 51° $[Ca(OH)_2]$, 54° (CaO), 63°, 64° (CaO)—2θ values. X-ray diffraction spectra of Indian edible chuna was identified as a mixture of calcium oxide (CaO) and calcium hydroxide $[Ca(OH)_2]$. This was as per our expectation.[12, 13]

It is well known and accepted fact that when calcium oxide is exposed to air environment, absorbs moisture (water) from the surrounding atmosphere and partly gets converted to calcium hydroxide. Indian edible chuna was identified as calcium oxide (in the dry state) and calcium hydroxide (in the dispersed form/paste form).[12, 13]

Figure 2 shows the visible light absorption spectras of the CV dye solution taken at different intervals of time after adding the Indian edible chuna $(CaO/[Ca(OH)_2])$—in dark. It should be noted here that the solution was protected from external light (i.e., No photocatalysis process). From the decrease in the optical density at λ_{max} and overall absorption peak centered at 600 nm. It is observable that CV dye degrades as the time progress—even in dark, in presence of Indian edible chuna $(CaO/[Ca(OH)_2])$. This is identified as chemical degradation of the CV dye due to

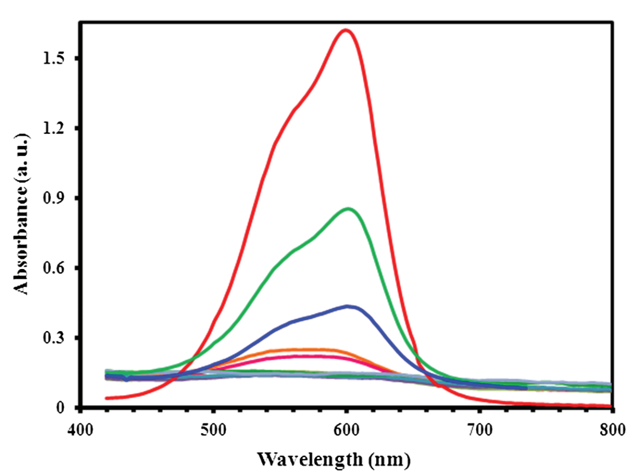

Fig. 2. Visible light absorption spectra of the crystal violet dye solution during chemical degradation by Indian edible chuna in dark.

Indian edible chuna. Further, No new peaks are observed indicating no complex formation between the two materials. No shift in the absorption peak position of the dye is observed indicating no electronic coupling/interaction between the two materials. It is to be noted here that complete discoloration of the dye solution was not observed—even after 18–20 hours in dark. This process of chemical degradation of the dye is observed to be slow compared to that under illumination (i.e., photocatalytic degradation).

Figure 3 shows the visible light absorption spectra of the CV dye solution taken at different intervals of time after adding the Indian edible chuna ($CaO/[Ca(OH)_2]$)—in presence of sunlight. From the decrease in the optical density at λ_{max} and overall absorption peak centered at 582 nm. It is observable that Indian edible chuna bring out photocatalytic degradation of the CV dye. This process is observed to be faster than that of chemical degradation in dark. Complete discoloration of the dye solution was observed in about 40 min time. This indicates that Indian edible chuna ($CaO/[Ca(OH)_2]$) acts as a photocatalyst.

Figure 4 displays the variation of optical density at 582 nm for chemical and photocatalytic degradation of the CV dye using Indian edible chuna ($CaO/[Ca(OH)_2]$) as a photocatalyst. Comparison indicates that chemical degradation of the CV dye which occurs within first 15 min. after addition of the Indian edible chuna is very fast. This process becomes faster in presence of light—indicating photochemical degradation of the dye. Complete discoloration of the dye solution was observed as a result of photocatalytic degradation within 40 min. In dark, the degradation of the dye is due to chemical degradation process; while under illumination the degradation of the dye is due to a combined action of chemical, photochemical and photocatalytic degradation process. A combination of these phenomena makes this process very interesting.

We speculate the process for chemical and photocatalytic degradation of the CV dye due to Indian edible chuna ($CaO/[Ca(OH)_2]$) here. In the dry state, Indian edible chuna can be considered as calcium oxide (CaO); while in the dispersed (in water) form it is calcium hydroxide [$Ca(OH)_2$]. Calcium hydroxide is a strong base and has the ability to yield hydroxyl (OH^-) ions. When in strongly basic condition, CV dye is known to get converted into triphenylmethanol—which is colorless. We believe that

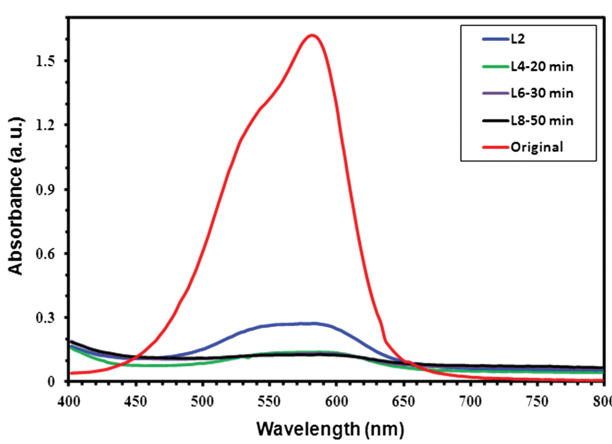

Fig. 3. Visible light absorption spectra of the crystal violet dye solution during photocatalytic degradation due to Indian edible chuna.

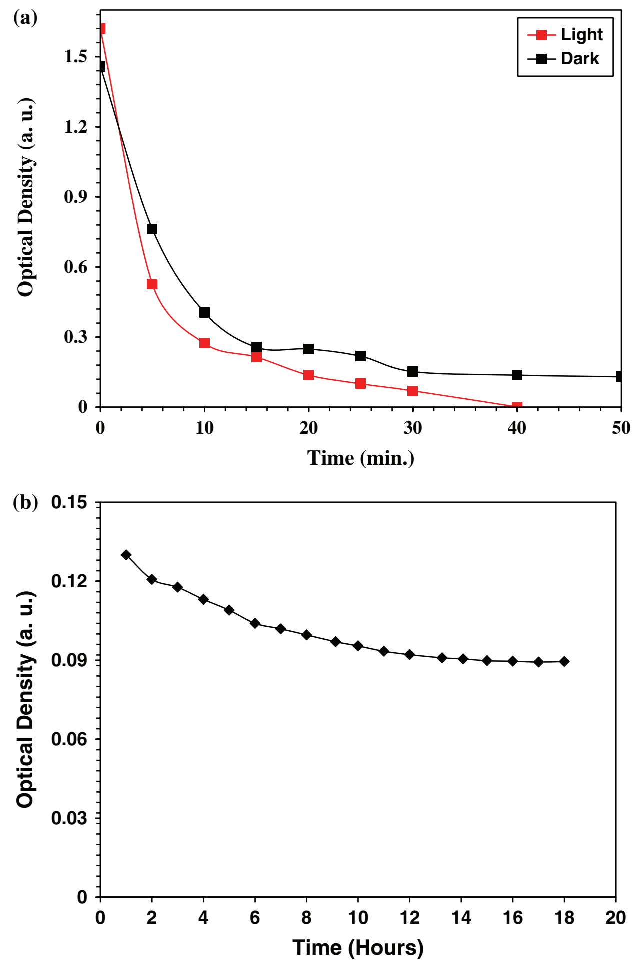

Fig. 4. (a) Variation of optical density at 582 nm for degradation of crystal violet dye in dark and light with Indian edible chuna as photocatalyst. (b) Variation of optical density at 582 nm for crystal violet dye degradation in dark (chemical degradation process) using Indian edible chuna.

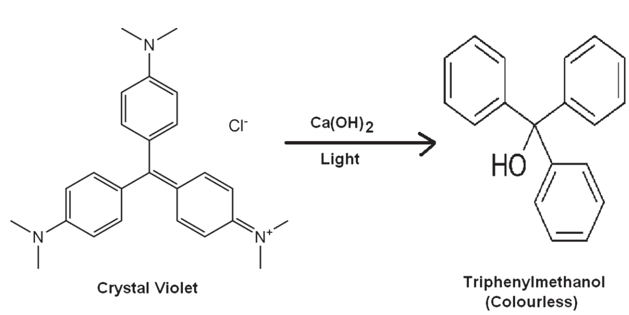

Fig. 5. Possible mechanism for chemical/photocatalytic degradation of crystal violet dye due to Indian edible chuna.

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even in dark, calcium hydroxide yields hydroxyl (OH^-) ions and presents strongly basic condition to the dye—resulting in degradation of the dye (i.e., chemical degradation of the dye). Under the action of light, Indian edible chuna ($CaO/[Ca(OH)_2]$) acts as a photocatalyst, abundantly providing hydroxyl ions/radicals to degrade the dye. This process is schematically represented in Figure 5.

4. CONCLUSIONS

Physico-chemical characterization of the Indian edible chuna indicates its composition as calcium oxide (in dry state) and calcium hydroxide (in slurry/dispersed from in water). Calcium hydroxide is observed to degrade crystal violet dye by chemical (in dark) as well as by photocatalytic (in presence of light) route. The process of chemical degradation of the dye is observed to be fast and occurs in about 15 min. The process of chemical degradation of the dye gets activated in presence of light. Process of photocatalytic degradation is observed to be relatively slow (as compared to that of chemical degradation process) and brings complete discoloration to the dye solution—suggesting complete degradation of the dye in about 40 min time. The ability of the calcium hydroxide to yield hydroxyl ions and the importance of the hydroxyl radicals in the photocatalysis process indicates the importance of calcium oxide/hydroxide as a photocatalyst.

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