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Indian Edible Chuna (Calcium Oxide/Hydroxide) as a Green Photocatalyst

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Photocatalytic degradation of Methylene blue dye is studied using Indian Edible Chuna as a photocatalyst. Physico-chemical characterization of Indian Edible Chuna indicates that it is calcium oxide (in dry state) or calcium hydroxide (in paste form/dispersed in water). Our results indicate that Indian Edible Chuna (Calcium oxide/hydroxide) acts as an excellent photocatalyst for degradation of Methylene blue and has added advantages of low cost, easy availability and environment friendly nature—making it a Green photocatalyst.

Keywords: Indian Edible Chuna, Calcium Oxide, Calcium Hydroxide, Photocatalysis, Methylene Blue.

RESEARCH ARTICLE

1. INTRODUCTION

Since the first report of Fujishima and Honda,[1] lots of work has been carried out for utilizing the photocatalysis process for water purification.[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 of waste water treatment. TiO_2 and ZnO are the most studied photocatalytic materials; although, efforts are also directed towards developing visible light photocatalytic materials.[11]

Indian edible chuna is used as a Photocatalyst in our present studies. It is usually a paste made from calcium oxide [CaO, which is in turn obtained from combustion of lime—i.e., Calcium Carbonate—$CaCO_3$]. In India, it is used along with tobacco for chewing; in Paan (Indian word). Since, it is directly consumed by humans, we call it as ‘Edible Chuna.’ Other impure variety can be called as ‘Chuna’ which is used for variety of applications as in construction (since it has cement-like property); paints etc. Impure chuna is of lower cost and is used for bulk applications. 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.

$$CaCO_3\ (solid) \xrightarrow{heating} CaO(solid) + CO2(gas) \uparrow$$

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

Calcium hydroxide (Molecular weight: 74.08) is a white odorless powder. It has low solubility in water (about 1.2 g/L at 25 °C), high pH (12.5–12.8), 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.

Although, lime ($CaCO_3$) is used in water purification from ages, there are very few reports on photocatalytic property of $CaO/Ca(OH)_2$.[12] The mechanism of photocatalysis involves photo-generation of radicals and their action on the organic pollutants. Before doing the experiments, 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 using it. Indeed, very interesting results are observed and are under publication, including this.

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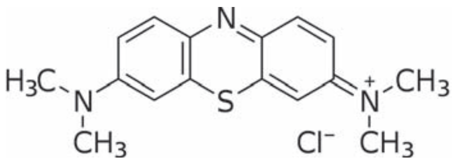

Fig. 1. Molecular structure of methylene blue dye.

2. EXPERIMENTAL DETAILS

Methylene blue is a cationic (thiazine) dye. Stock solution of Methylene Blue dye in distilled water (DW) was made having a concentration of 2.6×10^{-5} M and is used for further studies. The sketch of the chemical structure of Methylene Blue dye is shown in Figure 1.

Indian edible chuna [paste form] is used as a Photocatalyst. For the experimental evaluation purpose, such paste of Indian edible chuna is dried and the dried powder is used in the subsequent studies like for XRD, EDAX etc. Indian edible chuna was purchased from the local market and used as it is (without any further purification). 0.5 gm of Indian edible Chuna (dry Calcium Oxide) is dispersed in 500 ml stock solution of Methylene Blue in distilled water (DW). Solutions were illuminated with direct sunlight with constant stirring. Light intensity is measured with Lux meter. Sample (3 ml) was collected 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 methylene blue dye—since color of the dye is directed related to its structure. Dye looses its color if its structure is broken down.

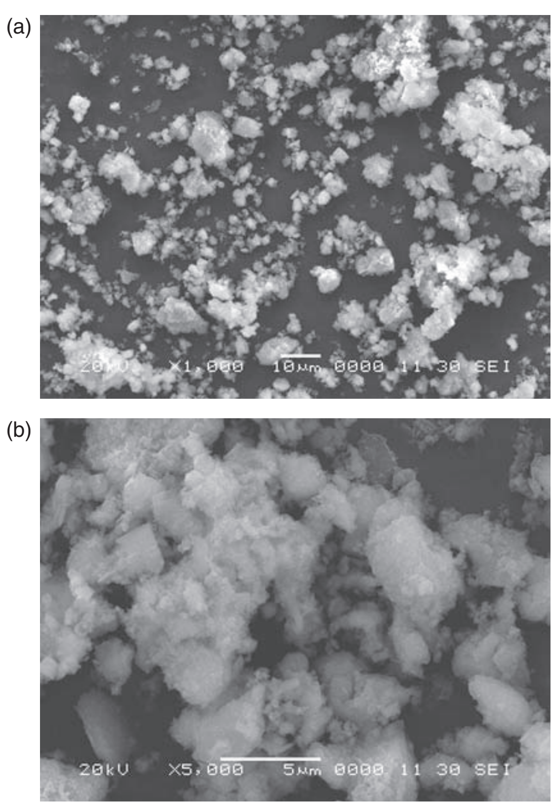

Fig. 2. SEM photograph of the photocatalyst (Indian edible Chuna).

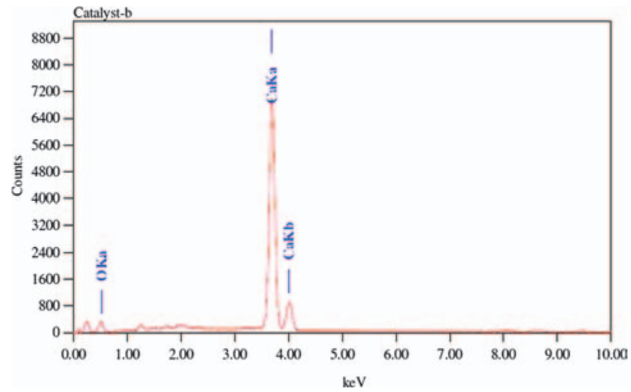

Fig. 3. EDAX spectra of the photocatalyst (Indian edible chuna).

3. RESULTS AND DISCUSSION

Figure 2 shows the scanning electron micrograph (SEM) of the Indian edible chuna (dry form). It should be remembered here that Indian Edible Chuna in the dry form is Calcium Oxide (CaO), and in the slurry/dispersed form in water is Calcium hydroxide [$Ca(OH)_2$]. SEM shows particle size in microns with strong aggregation of particles. Shapes of the particles are irregular.

Elemental composition as obtained from the Energy Dispersive X-ray Analysis (EDAX, shown in Fig. 3) indicates presence of only Calcium (45.12 at.%) and Oxygen (54.88 at.%) as its constituents. This indicates that the constituent of Indian Edible Chuna is CaO (in the dry state). Absence of any other elements in the EDAX spectra indicates its highly pure nature.

Powder X-ray diffraction (XRD) spectra of Indian edible chuna is shown in Figure 4. Major X-ray diffraction peaks are 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

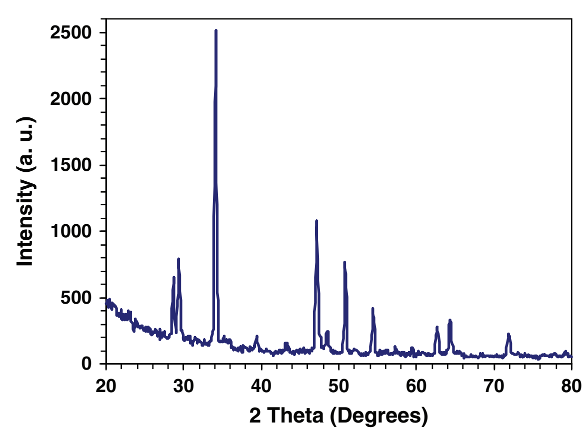

Fig. 4. XRD of the photocatalyst (Indian edible chuna).

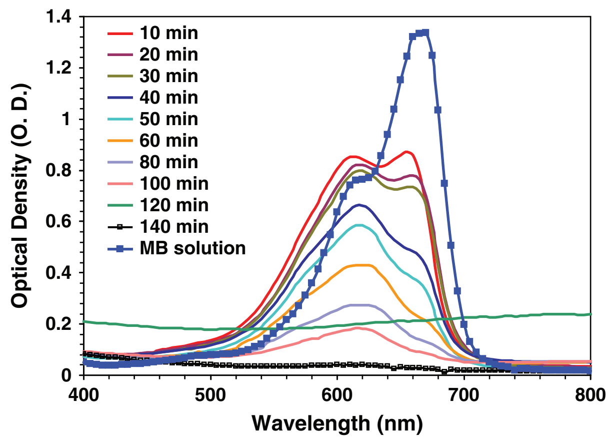

Fig. 5. Visible region absorption spectra of the methylene blue dye solution with different photocatalytic degradation time.

Indian Edible Chuna is identified as a mixture of calcium oxide (CaO) and calcium hydroxide [$Ca(OH)_2$]. This is as per our expectation. It is well known and accepted fact that when calcium oxide is exposed to air environment, absorbs moisture (water) from the surrounding atmosphere and a part of it gets converted to calcium hydroxide.

Figure 5 shows the visible light absorption spectra of the methylene blue dye solution (in distilled water) sample taken out at different intervals of time during photocatalytic degradation process. Concentration of original methylene blue solution at the start of the experiment was 2.6×10^{-5} M. Amount of photocatalyst used was 0.5 gm. It is observable that Methylene blue absorptions spectra show a prominent absorption peak at 665 nm (λ_{max}) and a shoulder at 615 nm. No appreciable shift in the peak positions have been found. No new peaks have been observed. From Figure 5, it is observable that the optical density (at λ_{max}) decreases as the photocatalysis process proceeds.

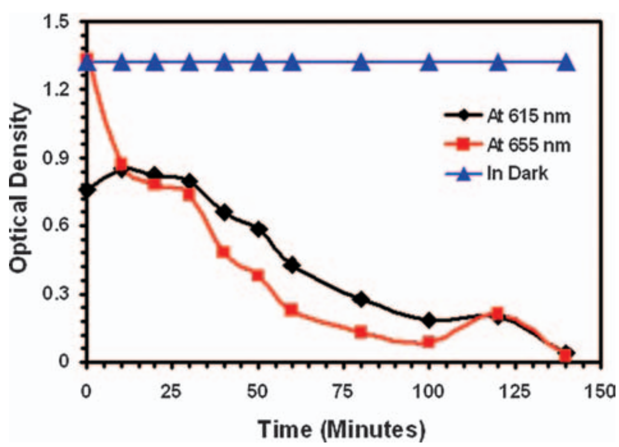

Fig. 6. Variation of optical density of the methylene blue dye solution with respect to photocatalytic degradation time at 615 nm and 655 nm wavelengths. Amount of photocatalyst used was 0.5 gm. In dark, the optical density of the methylene blue solution remains practically constant indicating no degradation in dark.

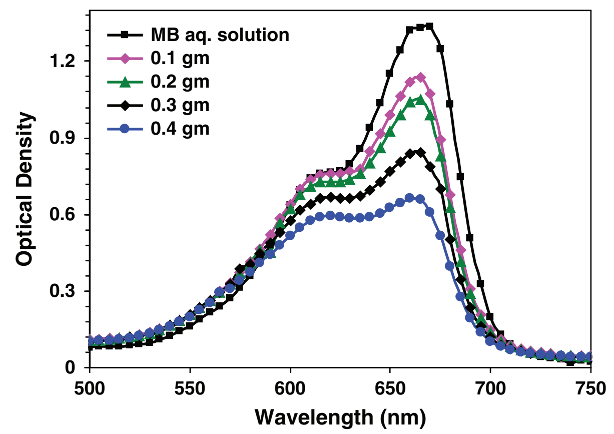

Fig. 7. Visible region absorption spectra of methylene blue dye solution with varying amount of photocatalyst, after 30 min exposure to light.

It is also observable that the optical density of the peak at 665 nm decrease very rapidly compared to that of the shoulder at 615 nm. Hence for most of the spectra taken for the samples collected at different time intervals during photocatalysis process, intensity (optical density) of peak at 665 nm and 615 nm could be found comparable; or even more for the peak at 615 nm. Methylene blue solution becomes colorless/transparent after about 140 min. time.

Figure 6 shows the variation of optical density at 655 nm and 615 nm with photocatalytic degradation time. It is observable that the optical density at 615 nm decreases rather slowly compared to that at 655 nm peak position. No change in the optical density (either at 655 nm or 615 nm) was observed when the sample was kept in dark indicating that in dark—No degradation of Methylene blue dye occurs due to the presence of Indian Edible Chuna. This further confirms that Indian Edible Chuna acts as a photocatalyst and brings out photocatalytic degradation of the methylene blue dye.

In order to know how amount of photocatalyst affects the degradation process; experiment was carried out by keeping all other parameters constant (MB concentration =

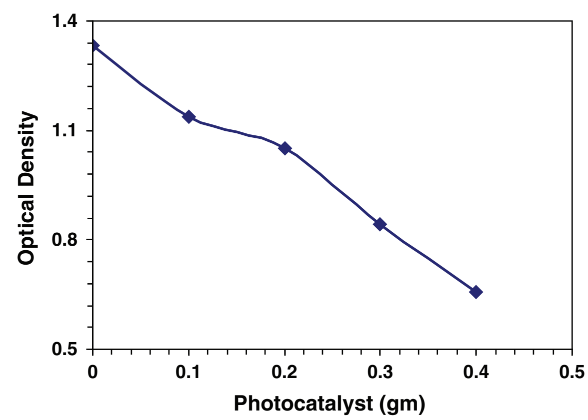

Fig. 8. Optical density (O. D.) at 655 nm after 30 min of photocatalytic action in sunlight with variation of photocatalyst amount. Almost linear relation is seen.

Fig. 9. Photograph of the variation of colors with photocatalytic action.

2.6×10^{-5} M, Illumination time = 30 min.), except varying the amount of photocatalyst. Figure 7 shows the visible light absorption spectra of the methylene blue dye solution with varying amount of photocatalyst used. Figure 8 shows variation of optical density at 655 nm versus amount of photocatalyst. It is observable that the optical density decreases as the amount of photocatalyst increases—almost linearly, within the experimental parameters studied. Figure 9 displays the photograph showing the variation in the color of the dye solution as the photocatalytic process proceeds.

It is to be noted here that Indian Edible Chuna was successfully recovered from the (dye) solutions by filtration and drying—after the first use of it as a photocatalyst. Such recovered photocatalyst is observed to show photocatalytic degradation effect multiple times (3 times studied by us)—confirming the fact that Indian Edible Chuna acts as a photocatalyst.

4. CONCLUSIONS

Physico-chemical characterization of the Indian Edible Chuna indicates that it is Calcium Oxide (in dry state)/Calcium Hydroxide (when dispersed in water/in slurry form). Indian Edible Chuna is observed to act as excellent photocatalyst and degrades methylene blue dye completely in about 140 min time. Low cost, easy availability and environment friendly nature of the Indian Edible Chuna (Calcium Oxide/Hydroxide) suggests that it can be a novel, Eco-friendly (Green) photocatalyst. More detailed experiments are underway to know the photocatalytic degradation process in detail.

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