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ARTICLE

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Synthesis and characterization of $CuGeO_3$ photocatalyst using Green Chemistry and its application for the degradation of direct black dye

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In this paper, we report synthesis of $CuGeO_3$ photocatalyst by mechanochemical, solid state synthesis, method with green chemistry approach. The product obtained was characterized by various investigative techniques like UV-Diffuse Reflectance Spectroscopy, Fourier Transform Infrared Spectroscopy, X-ray Diffraction, Scanning Electron Microscopy, with Energy Dispersive X-ray Spectroscopy, and BET Surface area. The study confirm orthorhombic pervoskite crystal structure of photocatalyst with band gap 3.7 eV. The photocatalytic activity of the catalysts $CuGeO_3$ was evaluated by photochemical bleaching of Direct black dye, under sun light.

Keywords : Photocatalysis, $CuGeO_3$, Direct black dye

1. Introduction : There is no world possible without water. For all living being, water is one of the prime essential requirements of existence. Wrong adulteration of chemical substances makes it unfit for human consumption. Speedy industrialization has provided much more ease to human life. However, its horrible adverse effects have appeared in the shape of environmental collapse. The domestic use and industrial activity both produces a large amount of wastewater, which then disposed into natural channels leading high pollution risk. Synthetic dyes are toxic refractory chemicals, which generates murky color to the water and are hazardous to the environment. The dyes were detected in dissolved state in wastewater [1]. Most of these dyes are toxic and carcinogenic in nature [2].

Various methods have been suggested for purification of polluted water, these includes; surface adsorption [3, 4], and bio-degradation [5, 6] use of membrane [7]. The light induced photocatalytic process has received considerable attention in the last few decades. The advantages of semiconductor photocatalyst are their non toxicity, high activity, large stability, and low cost. The photocatalytic reactions on semiconductors have been utilized for many applications, such as air cleaners [8], self-cleaning materials [9], and antibacterial materials [10] degradation of fungicide [11].

In photocatalysis, light used to activate a substance that alters the rate of a chemical reaction without involvement of itself. The great significance of photocatalysis process is that, it can degrade and/or detoxify various complex organic chemicals, which has not tackled by other methods of purification. Furthermore, it increases the chance of reuse of water. Generally, the reaction recognized as phenomena originating from electrons and holes excited by absorption of photons with energy greater than the band gap energy of the semiconductors. The holes have a strong potential to draw electrons out of organic and inorganic contaminants, resulting in the decomposition of hazardous materials, such as dyes, [12, 13] pesticides [14] and insecticides [15], and many organic pollutant.

Among the photocatalyst, TiO_2 is widely studied and demonstrated its photocatalytic activity [16]. The ZnO is another broadly studied photocatalyst for the dye degradation [17]. Few reports are available on the studies related to the photocatalytic activity of coupled semiconductor photocatalyst, such as TiO_2-

CeO_2 [18], TiO_2-WO_3 [19], TiO_2-SnO_2 [20] and ZnO-SnO_2 [21].

Considering ugly head of pollution and the importance of photocatalysis for its control, there is a need to synthesize some innovative material that can be useful for environmental cleaning purpose. In this study, we report the synthesis of the $CuGeO_3$ photocatalyst by simple one-pot mechanochemical method using a green chemistry approach. The structural properties of the synthesized $CuGeO_3$ photocatalyst was approved by the various analytical techniques The $CuGeO_3$ photocatalyst is applied for the degradation of Direct black as a representative dyes.

2. Experimental :

2.1 Synthesis of $CuGeO_3$: A green chemistry approach, with mechanochemical solid state synthesis method was adopted for the synthesis of $CuGeO_3$ photocatalyst. There are certain advantages of the solid-state, mechanochemical synthesis method over other synthesis method like; it is an environmentally friendly, easy, and low cost method. Also, no special additives are required for the synthesis of the compound. It is fast and ecologically pure. The chemical stability of the catalyst produced is moderately high. For this A.R. grade equimolar amount of GeO_2 (CAS No-1310-53-8, Lot 10148683, Lancaster, UK.) CuO (CAS No- 1317-38-0, Batch No-92730804, India) was mixed thoroughly and calcinated at 500 ^oC for 3 h. The mixture was grinded with mortar and pestle to acquire fine powder. Again the obtained powder was further calcinated at 800 ^oC following milling after each interval of three-hour of time. The calcination was continued for next twenty hours with milling. Afterwards, at the end mixture was heated up to the terminal temperature. The product $CuGeO_3$, thus obtained, was used for characterization and photocatalytic degradation.

2.2 Characterization of $CuGeO_3$: The vibrational frequency of the synthesized catalyst was studied by FTIR, 8400S-Shimadzu, in the range of 400 - 4000 cm^{-1}. The optical property of the synthesized product was studied by using Perkin Elmer-λ-950, UV–Visible spectrophotometer. The structural properties of the material was studied by using X-ray diffractometer, Rigaku-D/MAX-2500 with Cu-Kα radiation, having λ =1.5406 A°. The surface morphology and chemical compositions of the synthesized catalyst was analyzed by using a scanning electron microscope JEOL, JED-2300LA, coupled with an energy dispersive spectrometer-JED-2300LA. The Surface area, Pore volume and Pore diameter was evaluated by Quntachrome Autosorb automated Gas sorption System, Autosorb-1 NOVA-1200 and Mercury Porositymeter Autosoeb-IC. Thermal stability of the catalyst was evaluated by thermogravimetric analysis on Perkin Elmer-TG, Thermogravimetric analyzer.

2.3 Photocatalytic activity : The photocatalytic activity of the $CuGeO_3$ was evaluated by photodegradation of direct black dye under sun light radiation. During the experiment, three types of the observation ware recorded. In one set of experiment, 20 ppm of a dye solution (50 ml) was irradiated with 0.2 g $CuGeO_3$ photocatalyst. Similar second set was kept in dark. In third set, only a dye solution was exposed directly to the sun light. Decrease in the color due to photodegradation was monitored by UV-Visible spectrophotometer after every 30 min. The variation sun light intensity during experimental progress was monitored by Lux-meter.

2.4 Reusability of the photocatalyst : The reusability of photocatalyst was investigated in order to study the stability and degree of photodegradation. After first photocatalysis degraded dye solution containing photocatalyst mixture was filtered, and recovered photocatalyst was washed five times with deionized water and dried at 250°C in an oven for 3 h. The activated photocatalyst was reused for degradation process. This process was repeated subsequently three times.

3 Results and discussion :

3.1 Characterization : The infrared absorption spectrum of the synthesized $CuGeO_3$ catalyst is shown in Figure (1). The vibrational frequency band at 425, 535, 518, 621, and 1178 cm^{-1} indicates the presence of the Cu–O and frequency band at around 721, 773, and 858 cm^{-1} indicates presence of the Ge–O vibration of $CuGeO_3$.

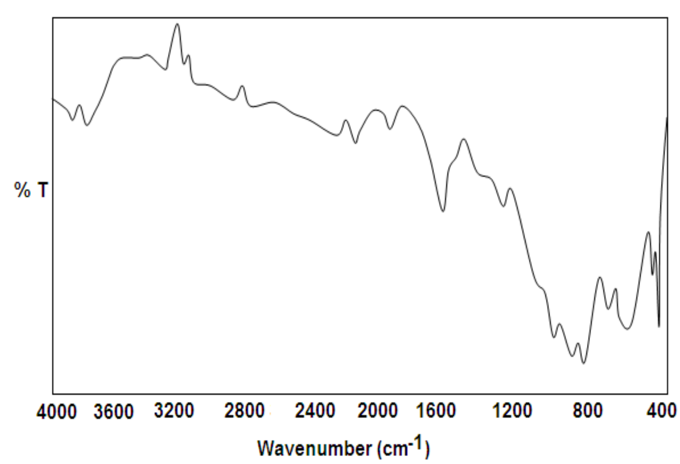

Figure (1) : IR spectra of $CuGeO_3$

Figure (2) represents the UV-Visible diffused reflectance spectrum of the synthesized $CuGeO_3$ photocatalyst. The diffused reflectance spectrum depict that the absorption goes into UV-Visible region. The DRS of the $CuGeO_3$ has absorption edge cut-off at 335 nm with corresponding band in the visible region. The band gap energy ($Eg = hc/\lambda$) for the compound was found to be 3.7 eV. The result implies that the $CuGeO_3$ catalyst may possess excellent photocatalytic activity.

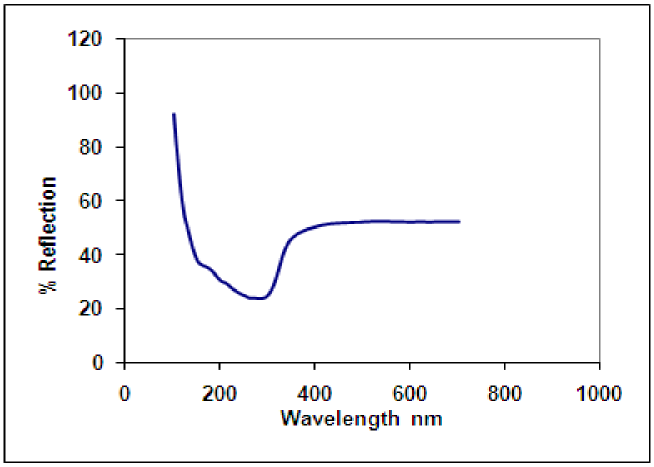

Figure (2) : UV-visible spectra of $CuGeO_3$

Figure (3) shows X-ray powder diffractogram of the synthesized $CuGeO_3$ powder. The d-line patterns of the X-ray diffractogram matches with the standard JCPDS data card No-74-0302. These peaks at scattering angles (2 theta in degrees) of 20.90, 27.83, 35.54, 37.116, 38.8, 42.34, 49.79, 53.45, 56.59, 57.77, 59.21, 63, 70.23, 75.32 and 78.95 corresponds to the reflection from 020, 120, 101, 021, 210, 040, 230, 041, 141, 150, 231, 002, 122, 331, and 260 crystal planes (hkl) respectively and confirming the orthorhombic structure of the $CuGeO_3$.

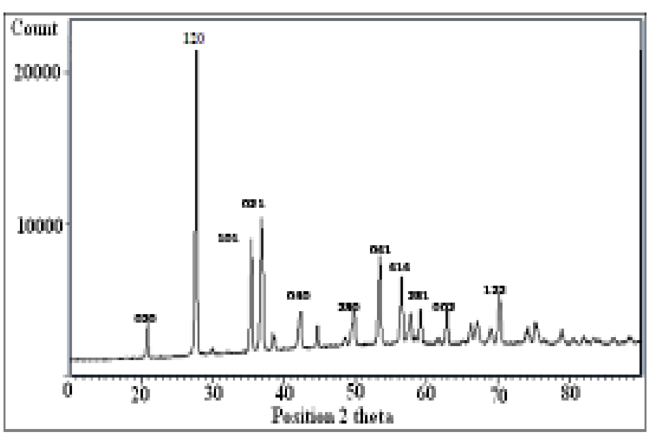

Figure (3) : X-ray diffraction pattern of $CuGeO_3$

The surface morphology and associated chemical composition of synthesized photocatalyst was analyzed by using a scanning electron microscope (SEM) coupled with EDAX. It is clear from Figure (4) that, fine particles of $CuGeO_3$ are joined with each other forming the cluster of particles. The SEM micrograph reveals the polycrystalline nature of $CuGeO_3$. The EDAX data furnishes elemental composition in conformity with the respective molar proportions taken. The observed mass percentage of Cu in $CuGeO_3$ is 38.64 %, Ge in $CuGeO_3$ is 35.38 % and that of oxygen is 25.98 %, which confirm the $CuGeO_3$.

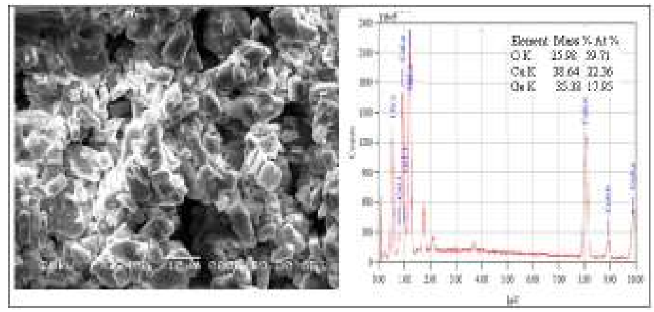

Figure (4) : SEM and EDAX of $CuGeO_3$.

The Nitrogen adsorption-desorption isotherm and the pore size distribution plots calculated from the desorption branch of N_2 isotherm by the Barret, Joyner and Halenda (BJS) method of the synthesized $CuGeO_3$. The pore size distribution showed a narrow range for synthesized photocatalyst, $CuGeO_3$, implying good homogeneity of the pore. The surface area (SBET); is 16.03 m^2/g, pore volume (Vp); is 0.04376 cc/g, and pore diameter (Dp); is 24.80 A° for the synthesized compound depicted in Figure (5).

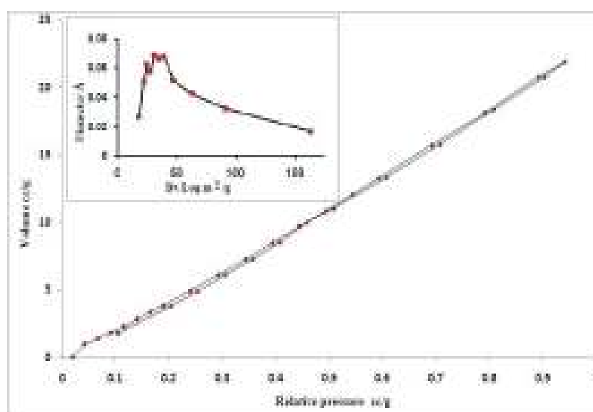

Figure (5) : BET surface area and pore volume of $CuGeO_3$

3.2 Photocatalytic property of $CuGeO_3$: Figure (6) indicates phtodegradation study of the direct black dye when exposed to the sunlight in presence of photocatalyst $CuGeO_3$. Figure (7) represent the percentage degradation of acid black dye. When the dye solution containing photocatalyst $CuGeO_3$ was exposed to the sunlight, rapid degradation (color removal) was observed with respect to time. When dye solution containing photocatalyst was kept in dark no change in color was observed and very negligible degradation was observed when only dye solution was exposed to the light. This study reveals that, degradation take place only in presence photocatalyst, $CuGeO_3$ and light.

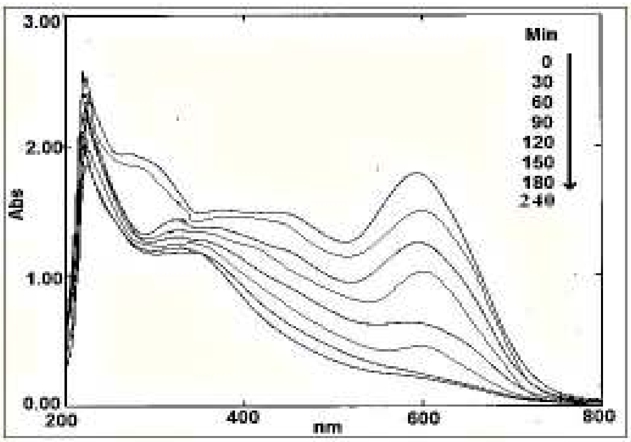

Figure (6) : UV-visible spectra of degraded dye

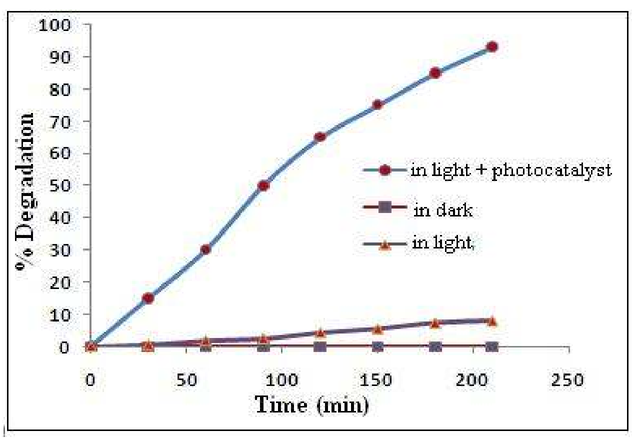

Figure (7) : Percentage degradation of dye

3.3 Reuse of Photocatalyst : The reusability of photocatalyst was investigated in order to study the stability and degree of photodegradation of the dye solution of the photocatalyst. The recovered photocatalyst was then reused four times as in the previous degradation process. The result depicted in Figure (8) shows that, there is no significant reduction in photocatalytic performance in photodegrading direct black, thus this indicates the stability of $CuGeO_3$ as a photocatalyst.

3.4 Kinetic study of degradation : The rate of degradation follows pseudo first order kinetics shown in Figure (9). The photocatalytic degradation of the herbicide is believed to take place according to the following mechanism. When a catalyst is exposed to UV radiation; electrons are promoted from the valence band to the conduction band. As a result of this, an electron–hole pair is produced.

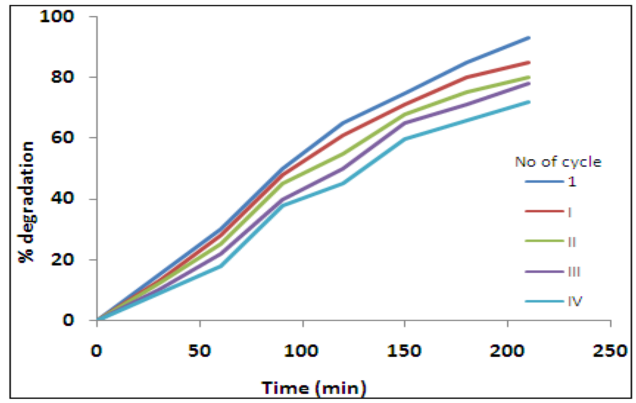

Figure (8) : Reusability of photocatalyst

$CuGeO_3 + h\nu \rightarrow e^-$ (conduction band) + h^+ (Valence band) (1)

where, e− (conduction band) and h+ (valance band) are the electrons in the conduction band and the electron vacancy in the valence band, respectively. Both of these entities migrate to the catalyst surface, where they can enter in a redox reaction with other species present on the surface. In the most the cases h^+ (valance band) react easily with surface bound H_2O to produce •OH radicals, whereas e−(conduction band) react with O_2 to produce superoxide radical anion of the oxygen.

$H_2O + h^+$ (valance band) $\rightarrow$ •OH + H^+ (2)

$O_2 + e^-$ (conduction band) $\rightarrow O_2^{-\bullet}$ (3)

This reaction prevents the combination of the electron and the hole, which are produced in the first step. The •OH and O^{2-}• produced in the above manner can then react with the dye solution to form other species and is thus responsible for the degradation.

$O_2^{-\bullet} + H_2O \rightarrow H_2O_2$ (4)

$H_2O_2 \rightarrow 2$•OH (5)

•OH + dye $\rightarrow$ dye$_{ox}$ (6)

$$\text{dye} + e^{-}(\text{conduction band}) \rightarrow \text{dye}_{red} \quad (7)$$

It may be noted that, all these reaction in the photocatalysis are possible due to the presence of both dissolved oxygen and water molecules. The rate constant for the degradation was found to be 0.5 x 10-3 min^{-1}.

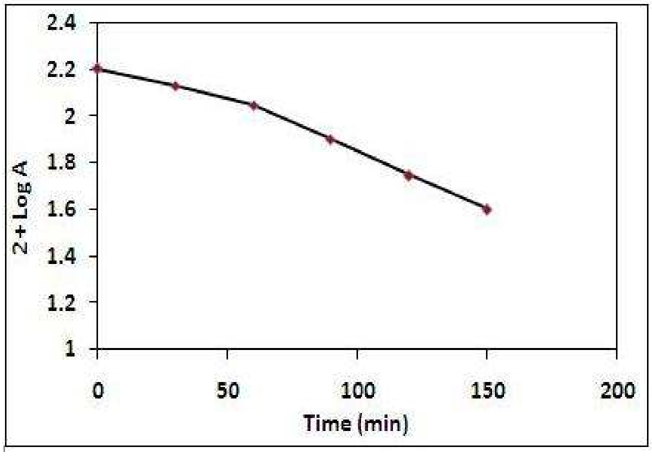

Figure (8) : Kinetics of degradation

Conclusion : $CuGeO_3$ photocatalyst was successfully synthesized by green chemistry approach with mechanochemical solid state synthesis method. The photodegradation study reveals that, the photodegradation take place only in presence of the photocatalyst and sunlight. The study reveals that photocatalyst can be reused without considerably change in its photocatalytic activity. The rate of the degradation follows pseudo first order kinetic.

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