Photocatalyst for Degradation of Brilliant Bluedye by $CuTa_2O_6$ –A Green Chemistry Approach

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Abstract:
In present article photocatalytic degradation of Breliant blue dye using $CuTa_2O_6$ is scientifically reported. The photocatalyst $CuTa_2O_6$ was synthesized by environmentally friendly solid state synthesis method. The structural and microstructural properties of synthesized photocatalyst was investigated different analytical techniques, like Infra red Fourier Transform Spectroscopy, Diffused Reflectance UV-visible Spectroscopy, X-ray Diffraction, Scanning Electron Microscopy with EDAX and Transmisssion electron microscopy along with Selected Area Electron Diffraction. The study validate that, the synthesized $CuTa_2O_6$ is cubic polycrystalline in nature. Average particle size of the photocatalyst shows particle size of 180 nm with band gap 3.89 eV.

Keywords: Photocatalyst, Green chemistry, Indigo carmine, XRD, SEM

INTRODUCTION:

The earth is facing intricate problems regarding global environment and energy resources. Abundant amount of solar energy irradiating on the earth therefore it is suggested to utilize solar energy to serve human. The important advantage of solar energy is that it is ecological pure, accomplishing energy cycle without heating of the earth and without polluting the environment. The catalysis under light irradiation called photocatalysis is attracting a great deal of attention from view points of fundamental science and application. Today's society is producing waste products. There is practically no human activity that does not produce waste products and in addition there is a direct relationship between the standard of living in a society or country and the amount of waste products produced. Water is basic requirement in all industrial processes, domestic and viable activities, wastewater generated from different activities contains various contaminants which are harmful[1].

A large number of organic substances are now days introduced into the water system from various sources such as industrial effluents, agricultural runoff and chemical spills. Synthetic dyes are toxic chemicals, which generate dark color to water and are hazardous to the environment. The industrial operations mainly pharmaceutical, textile, pesticides, and other chemical manufacturing industries generate waste water containing various contaminants causing pollution. These effluents are intensely murky colored and contaminated with high amount of compounds such as suspended and dissolved salts and many other unmanageable compounds. Even small concentration of these compounds present in the effluent causes toxicity and foul odor to the water. If these effluents are not properly treated, they will impose a serious threat to all aquatic species.

Various methods physical, biological and chemical methods have been suggested to handle the pollutants in water. These methods include the biodegradation[2], coagulation, adsorption, advanced oxidation process

and membrane process. Physical methods include different precipitation methods (coagulation, Flocculation, sedimentation), adsorption[3] (on activated charcoal, biological sludge, silica gel), filtration, reverse osmosis etc... Biological treatments differ according to presence and absence of oxygen. All these processes have some advantages or disadvantages over the other method. A balanced approach is therefore needed to look into worthiness on choosing appropriate method, which can be used to degrade the dye. Among these techniques, advanced oxidation process appears to be promising field of study, which has been reported to be effective for the near ambient degradation of organic contaminants from waste water[4-6]. There is increasing demand of newer material that can be used to minimization of pollution.

In this article, the synthesis and optical properties of polycrystalline $CuTa_2O_6$ powders synthesized by simple mechanochemical method using green chemistry approach and it is utilized for the Brilliant bluedye degradation.

MATERIALS AND METHODS

Synthesis of $CuTa_2O_6$ Photocatalyst

Various methods are available for synthesis of heterogeneous metal oxides such as; Sol-gel[7], Hydrothermal[8], Thin film vapor disposition method[9]. These methods are complicated, cost effective and main disadvantage is that they cause environmental pollution. Solid-state, mechanochemical synthesis is a environmentally friendly method[10-12], easy and which gives less energy to the environment. A green chemistry approach has adopted for the synthesis of heterogeneous metal oxide photocatalyst. A.R. grade equimolar amount of CuO with Ta_2O_5, in $CuCO_3$ (Batch No. : 5400210, Research Lab), and Ta_2O_5 (Batch no. : T3687 Chemsworth) mixed thoroughly and calcinated at 400 ^oC for five hours. The mixture obtained was crushed to obtain powder, heating was continued further at 900 ^oC following grinding after each three-hour time interval with mortar and pestle, calcination was continued for next twenty hours with milling at the end mixture heated up to the terminal temperature. The product $CuTa_2O_6$, thus obtained, was used for characterization and photocatalytic application purpose.

Photocatalytic activity

Photocatalytic activity of synthesized $CuTa_2O_6$ was evaluated by studying degradation of Brilliant blue-G 250 dye as a representative pollutant. Three types of observations were recorded. In one set 100 mL 50 ppm solution of a dye was irradiated using 0.3 g of photocatalyst, $CuTa_2O_6$, in uv-visible photoreactor. A similar second set was kept in dark. The third set containing only dye solution was exposed in uv-visible photoreactor. The decrease in absorbance due to degradation was recorded on double beam UV–visible spectrophotometer (Equiptronics model EQ-825) after every 30 min.

RESULTS AND DISCUSSION

Characterization of $CuTa_2O_6$

The vibrational frequency of the synthesized catalyst was studied by FTIR-8400S (Shimadzu) in the range of .400–4000 cm^{-1}.The infrared absorption spectrum of the synthesized $CuTa_2O_6$ catalyst is shown in Figure 1. Vibrational frequency band around 433 cm^{-1}, 672 cm^{-1} indicates the presence of Cu–O vibrations and frequency around 524 cm^{-1} indicates presence of Ta–O vibrations of $CuTa_2O_6$.

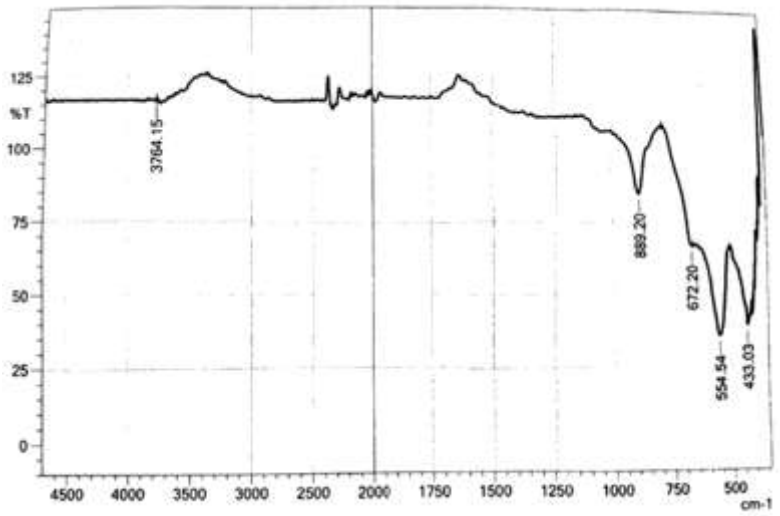

Figure 1: IR Spectra of synthesized $CuTa_2O_6$

The optical property of the synthesized product was studied by using UV–visible Spectrophotometer-λ-950. $CuTa_2O_6$ photocatalyst was scanned over wavelength range of 200-800 nm. Figure 2 represents the UV-visible diffused reflectance spectra of the synthesized $CuTa_2O_6$ photocatalyst. The diffused reflectance spectra shows that absorption goes into UV-visible region absorption edge cut-off at 330 nm with corresponding band in the visible region. The band gap energy (Eg = hc/λ) for the compound was found to be 3.89 eV. The broad absorption edge shoulder in the curve reveals the formation of $CuTa_2O_6$ may possess excellent photocatalytic activity.

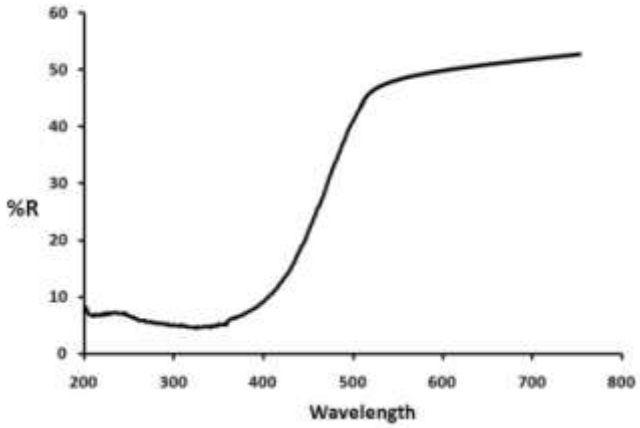

Figure 2: UV-Visible Diffused Reflectance spectra of $CuTa_2O_6$

The structural property of the material were studied using X-ray diffractometer-DMAX-2500 (Rikagu) with Cu-Kα radiation, having λ = 1.5406 A°. Figure 3 shows XRD pattern of $CuTa_2O_6$ powder formed after heating. The structure of the CuTa2O6 was found to be orthorhombic and the d-line pattern matches with JCPDS data card No-70-0611. The d line pattern at an 2θ angle 23.74, 33.83, 41.75, 48.6, 54.78 and 71.18 matches with the planes in JCPDS data card at 200, 220. 222, 400, 420, and 440 confirming cubic phase.

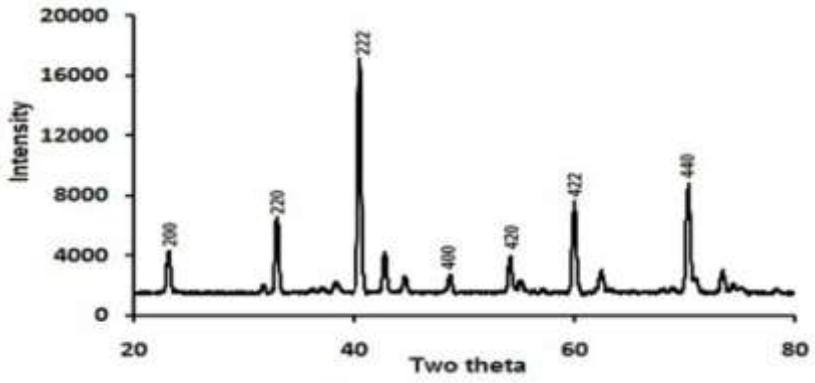

Fig-3: XRD Pattern of Synthesized $CuTa_2O_6$

The surface morphology and chemical compositions synthesized catalyst was analyzed using a Scanning Electron Microscope-JED-2300LA (JEOL) coupled with an Energy Dispersive spectrometer-JED-2300LA (JEOL). The surface morphology and associated chemical composition of synthesized photocatalyst was analyzed using a scanning electron microscope (SEM) coupled with EDAX and is shown in Figure 4. It is very clear from the SEM micrograph that very fine particles of $CuTa_2O_6$ are joined with each other forming the cluster of particles looking cubic shape. It appears from SEM micrograph that the average crystalline size of pure $ZnSnO_3$ is nearly 100-120 nm. The EDAX data furnishes elemental composition in conformity with the respective molar proportions taken.

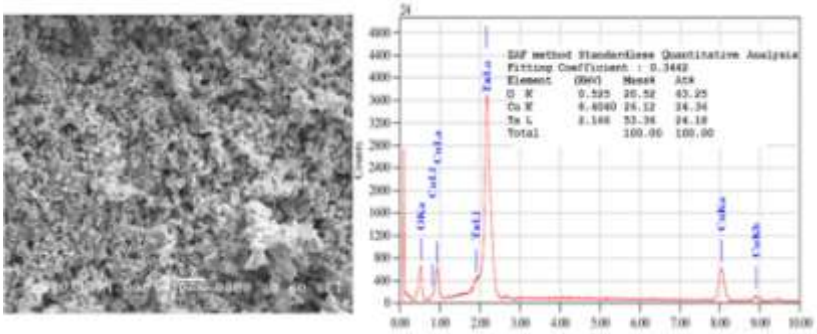

Figure 4- SEM and EDAX of $CuTa_2O_6$

The TEM image along with the selected area of the diffraction pattern (SAED) recorded for the sample corresponding to the $CuTa_2O_6$ is shown in Figure 5. TEM image along with SAED pattern of synthesizes $CuTa_2O_6$ catalyst. It is clear from TEM image that the shape of particles are cubic in nature. The dark spot in the SAED pattern reveals which is in good agreement with XRD pattern.

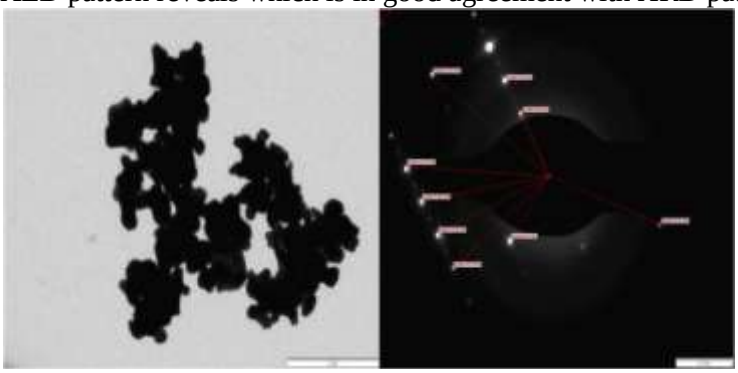

Figure 5- TEM and SAED pattern of $CuTa_2O_6$

Photocatalytic property of $CuTa_2O_6$

Photocatalytic property of $CuTa_2O_6$ was evaluated by photodegradation of Brilliant blue (860-22-0, Batch no 80-46, Sr. No. Al 2546 of Alpha Chemika), as a representative dye.

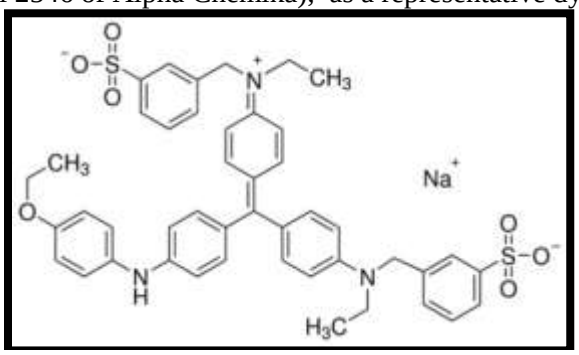

Figure 6: Structure of Breliant blue- G 250 dye

Brilliant blue dye is usually used in the textile and food industries. The consumption of the dye can also prove fatal, as it is carcinogenic to animals. It causes skin burn and eye irritation. The photodegradation of the dyes were studied by measuring the absorbance at 620 nm every after every 30 min on Equiptronics double beam spectrophotometer. Figure 5 indicates graphical representation of percentage degradation of dyes, In the figure curve-Z, in the graph represent the decrease in the absorbance of the Breliant blue dye solution in presence of $CuTa_2O_6$ photocatalyst when kept in dark. The curve-Y in the graph represents degradation Breliant bluedye solution in absence of catalyat when exposed to the UV light. Curve-X in the graph indicate degradation of Breliant bluedye solution in presence of 0.3 g of $CuTa_2O_6$ when exposed to the UV- light. The curve-W in the graph represents degradation Breliant bluedye solution when 0.6 g of photocatalyst exposed to the UV light. From curve-Z indicates that there is no degradation of the dye in presence of catalyst when kept in the dark, whereas very little degradation takes place in absence of the photocatalyst when exposed to the UV light and it is observed that very faster degradation was reported in presence of the photocatalyst when dye solution exposed to the uv light.

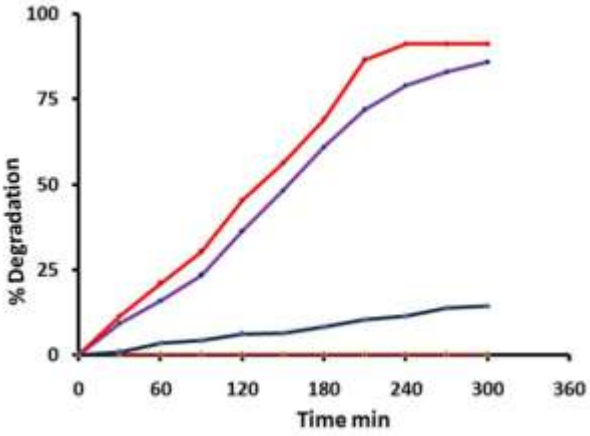

Figure 7: Degradation study of Brilliant blue dye

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 (6) curve a, b, c, and d shows that, there is no significant reduction in photocatalytic performance in photodegrading direct black, thus this indicates the stability of $CuTa_2O_6$ as a photocatalyst.

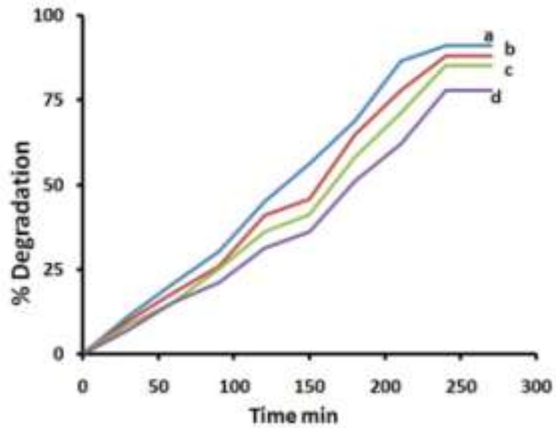

Figure 8: Resubality of photocatalyst on Brilliant blue dye

The probable mechanism involved for the degradation of studied dyes can be explained as follows. Absorption of efficient photon (hν ≥ Eg = 3.37 eV) by $CuTa_2O_6$

$(CuTa_2O_6) + h\nu \rightarrow e^-_{CB} + h^+_{VB}$ ……………………...……(1)

Oxygen ion adsorption

$(O_2)_{ads} + e^-_{CB} \rightarrow O_2^{\cdot -}$ ……………………………(2)

Neutralization of OH^- groups into OH· radical by photoholes

$(H_2O \leftrightarrow H^+ + OH^-)_{ads} + h^+_{VB} \rightarrow H^+ + OH\cdot$ ....(3)

Oxidation of Brilliant bluedye via successive attacks by OH· radicals,

$R + h^+ \rightarrow \cdot R + H_2O$ ………………….….(4)

Or by direct reaction with holes

$R + h^+ \rightarrow R^+ \rightarrow$ degraded product ....(5)

Considering the last process, holes react directly with carboxylic acid, generating CO_2.

$\cdot R + O_2 \rightarrow ROO^{\cdot} + \rightarrow CO_2$ ……………………….…..(6)

On the basis of experiment, a tentative mechanism for photocatalytic degradation of dye may be proposed as and dipcited in Figure 7, the photocatalyst $CuTa_2O_6$, absorbs radiations of suitable wavelength electrons from valence bond are promoted to the conduction band to produce an electron hole pair. These entities migrate to the catalyst surface; the electron vacancy react easily with surface bound H_2O to produce OH·, where as electrons react with O_2 to produce superoxide radical anion of oxygen, $O_2^{\cdot -}$. The OH· and $O_2^{\cdot -}$ produced in above manner then react with Breliant blue dye to form other species leading to nearly colorless product.

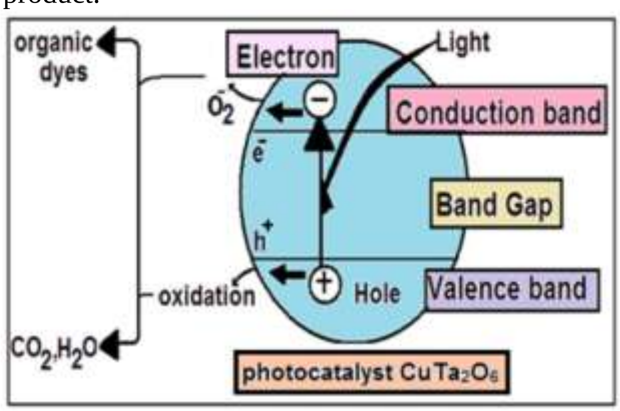

Figure 9: Path way of degradation of Breliant bluedye

CONCLUSION

The polycrystalline photocatalyst, $CuTa_2O_6$ was synthesized by green chemistry approach using solid state, mechanochemical method. Synthesis of $CuTa_2O_6$ and degradation of Breliant blue dye was carried out successfully. The band gap energy of the photocatalyst was 3.89 eV with average particle size 120 nm. In a sense, the effective photodegradation of dye by $CuTa_2O_6$ photocatalyst under stimulated sunlight is a very exciting respect in Photocatalytic area, and this work may provide new insight into the development of novel sunlight photocatalyst.

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