



Sunlight Assiated Degradation of Bentazon Herbicide in an Aqueous Suspension Using ZnGeO₃

KEYWORDS

Photocatalyst, Green chemistry, Herbicide, Bentazon, XRD, TEM

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ABSTRACT This study focuses on photocatalytic degradation of bentazon herbicide in an aqueous suspension of ZnGeO₃ under sunlight. The photocatalyst, ZnGeO₃, was successfully synthesized by a green chemistry approach with mechanochemical method. The synthesized photocatalyst was characterized by using various analytical techniques like UV-DRS, FTIR, XRD, TEM, SEM, BET surface area and TG. The XRD confirm phase purity of photocatalyst and TEM shows average crystal size of 25 nm. The UV diffused reflectance spectrum shows monodispersity and lower particle size with band gap energy 3.44 eV. The BET surface area and BJS pore volume was evaluated to be 32.06 m²/g and 0.02308 cc/g respectively. The photocatalyst was observed thermally stable over a wide range of temperature. The aim of this work is to address the photocatalytic degradation of bentazon, herbicide, in an aqueous suspension using ZnGeO₃ under stimulated sunlight. The intensity of sunlight during the course of experiment was 0.01096 W/cm² to 0.0137 W/cm²

INTRODUCTION

In last few decades, considerable attention has given to the toxic and persistent pollutants coming from agricultural and industrial human activities. Kabra, Gaya and Ester have demonstrated toxic effect of pollutants on human activity [Kabra, 2004, Gaya, 2008, Ester., 2004]. The herbicides are used to get rid of unwanted plant life, which include weeds, brush, unproductive bushes or trees, and other growth that takes nutrients away from crops and other useful plants. Many herbicides are synthetic and can be toxic to "good" plants, as well as to the animals and humans. Most of these compounds are non-biodegradable and live long period in the environment. Most of the pollutants are toxic and potentially carcinogenic in nature. After application of the herbicides on plants, some of herbicide goes into the surface water and some herbicide remains on the plants. Scott reported in his article that the animals were infected by consuming these contaminated plant and water [Scott et.al,2011]. Jianhua and other found herbicides in the surface water, ground water, as well as industrial waste-water [Jianhua et al., 2007]. Bentazon-Molecular formula C₁₀H₁₂N₂O₃S, Chemical name-3-isopropyl-1H-2, 1, 3-benzothiadiazin-4(3H)-one 2, 2-dioxide.

It is a contact herbicide registered in 1975, used for selective control of broadleaf weeds and sedges in beans, rice, corn, and peanuts. Leaching of bentazon through the soil appears to be major route of dispersion in the environment. The bentazon has a low binding affinity to the soil, therefore leach into the ground, and undergo runoff to the surface water. The structure of bentazon is shown in Fig 1.

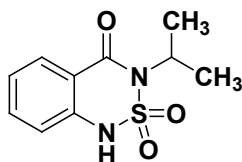


Figure 1: Structure of Bentazone herbicide

Research Literature survey shows that different methods of purifications to eliminate pollutants from water have been executed, which includes, surface adsorption [Jain, 2003], bio-degradation [Francisco 2009, Kapdan, 2007] and ozonation [Ternes, 2003]. All these process have some advantages and disadvantages over one another. Therefore, this environmental cleaning process requires a balance approach to look into worthiness by choosing an appropriate method, which may be used to degrade the pollutants. Various routine methods are available for the synthesis of metal oxide photocatalyst such as; hydrothermal sol-gel synthesis [Aramendia, 2005, Yongfa, 2000], thin films by magnetic sputtering [Baoshun et al., 2005] and thin film vapor deposition method [Sun et al., 2008]. These methods are complicated, cost effective and main disadvantage is that they cause environmental pollution. For the environmental remediation and treatment, application of the photocatalyst has been emerged as active area of the research. The photocatalytic path has some advantages over other water purification processes. The photocatalytic process takes place at ambient temperature. The oxidation of the substrate into CO₂ and other inorganic species is complete. The oxygen required for the reaction directly acquired from the atmosphere. The energy required for the reaction directly obtained from the sun. The catalyst is cheap, innocuous, and can be reused. The photocatalysis process based on the generation of reactive species electron/hole pairs on absorption of light by photocatalyst. In presence of the oxygen, the electron may induce reduction and leads to the formation of superoxide anion. The positive hole oxidizes adsorbed organic substrate or reacts with water leading to the formation of hydroxyl radicals. These radicals are known as strong oxidant and react efficiently with most of the organic substrate leading to complete degradation.

In Past two decades have witnessed intensive studies on photocatalyst and their application such as, antibacterial materials [Diana, 2007], degradation of pesticides [Ioannis, 2003], degradation of insecticides [Kitsiou et al., 2009], anticancer [Blake, 1999], antivirus [Liga, 2011] degradation of

dyes [Borhade, 2012] and degradation medicine like ibuprofen [Fabiola, 2010]. Among various photocatalysts, TiO_2 is widely studied photocatalyst for degradation of dyes and herbicide [Shijun, 2007; Vulliet, 2003]. ZnO is another material studied as photocatalyst for waste-water treatment [Navarro, 2009]. Few reports are available on the studies related to the photocatalytic activity of coupled semiconductor photocatalyst, such as $\text{TiO}_2\text{-SnO}_2$ [Tada et al., 2000] and ZnO-SnO_2 [Wang, 2004]. Very less attention is given to the ABO_3 type of photocatalyst to study photocatalytic activity. Considering water pollution and the importance of photocatalysis for its control, there is a need to synthesize some innovative materials that is useful for environmental cleaning purpose. In the present study, photocatalyst ZnGeO_3 presented to investigate degradation of aqueous bentazon herbicide a model molecule to test the photocatalytic activity under stimulated sunlight.

EXPERIMENTAL

SYNTHESIS OF ZnGeO_3 PHOTOCATALYST

In the present synthesis, a green chemistry, solid-state method with mechanochemical approach has adopted for ZnGeO_3 metal oxide photocatalyst. There are certain advantages of the solid-state, mechanochemical synthesis method like; it is an environmentally friendly, easy, and low cost method. Also, no 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. The mineralization of many organic pollutants in presence of the photocatalyst was successfully achieved. For synthesis of the ZnGeO_3 , A.R. grade equimolar amount of GeO_2 (CAS-3010-53-8, Lot no 10148683, Lancaster U.K.) and ZnO (Merck batch no MD6M561095, India) was mixed thoroughly and calcinated at 500°C for 3 h. The obtained mixture was grinded by mortar and pestle to acquire fine powder. Again the powder was further calcinated at 800°C following milling after each 3 h time interval with mortar and pestle, calcination was continued for next 20 h with milling, at the end mixture heated up to the terminal temperature. The furnace temperature was programmed as 10°C per min from one temperature to subsequent higher temperature. The product ZnGeO_3 , thus obtained, was used for characterization and photocatalysis purpose.

CHARACTERIZATION OF ZnGeO_3

The vibrational frequency of the synthesized catalyst was studied by FTIR-8400S (Shimadzu) in the range of $400\text{--}4000\text{ cm}^{-1}$. The optical property of the synthesized product was studied by using UV-visible spectrophotometer-k-950 (Perkin-Elmer). The ZnGeO_3 photocatalyst was scanned over wavelength range of $200\text{--}800\text{ nm}$. The structural properties of the material were studied using X-ray diffractometer- DMAX-2500 (Rigaku) with Cu-K α radiation, with $\lambda = 1.5406\text{ \AA}$. The surface morphology and chemical compositions of synthesized catalyst was analyzed using a Scanning Electron Microscope-JSM-6300 (JEOL) coupled with an Energy Dispersive Spectrometer-JED-2300LA (JEOL). TEM images were recorded on CM-200 (Philips). The Surface area (SBET), Pore volume(Vp) and Pore diameter (Dp) was evaluated by Quantachrome Autosorb automated Gas sorption System, Autosorb-1 NOVA-1200 and Mercury Porositymeter Autosorb-1C. The effect of temperature on stability of the catalyst was evaluated by thermogravimetric analysis on thermogravimetric analyzer (Perkin Elmer-TG) using Xenon arc lamp. The variation in the sunlight intensity during the experiment was measured by Lux-meter (Kusam-meko, KMLUX).

PHOTODEGRADATION OF BENTAZON HERBICIDE

The photocatalytic property of ZnGeO_3 photocatalyst was evaluated by photodegradation of the bentazon, herbicide. The experiment performed in two set. In the set one, 200 mL bentazon, 40 mg/L solution containing 0.3 g of ZnGeO_3 photocatalyst and only bentazon solution was exposed directly to the sunlight. On the other side bentazon solution containing same amount of photocatalyst was kept in dark to assess effect of photocatalyst in absence of light. The second similar set of the experiment was conducted with 0.5 g of ZnGeO_3 photocatalyst to study the effect of amount of the photocatalyst on degradation of bentazon, herbicide. The bentazon solution was exposed to the sunlight till there is no change in UV spectrum up to three hours. The effect of light/or photocatalyst on bentazon solution was studied by analyzing aliquots on UV-visible spectrophotometer (950-Perkin-Elmer) at after every 30 min..

RESUABILITY OF ZnGeO_3 PHOTOCATALYST

The unique feature of the semiconductor metal oxide photocatalyst is its reusability. The photocatalyst can be used again and again on prior activation. For the activation of the photocatalyst, after completion of degradation, the photocatalyst, the ZnGeO_3 was recovered by filtration and dried in an oven at 110°C . Then, the dried photocatalyst heated in a furnace at 500°C for two hour and cooled to room temperature. The same activated photocatalyst was suspended in 200 mL of 40 mg/L solution of the bentazon for degradation study.

RESULT AND DISCUSSION

Fig 2 shows Infra-red spectrum of synthesized ZnGeO_3 . The vibrational frequency bands at 420 to 534 cm^{-1} indicate Zn-O vibrational frequency while band at 765 to 995 indicate presence of Ge-O vibrations in the synthesized photocatalyst.

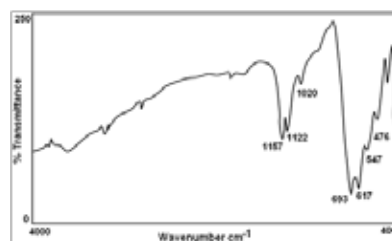


Figure 2: Infra red spectra of ZnGeO_3 .

Fig 3 represents UV-visible diffused reflectance spectrum of the photocatalyst. The spectrum reveals that the absorption goes into UV-visible region. The absorption edge cut-off at 360 nm furnish band gap of ($E_g = h c / \lambda$) 3.44 eV .

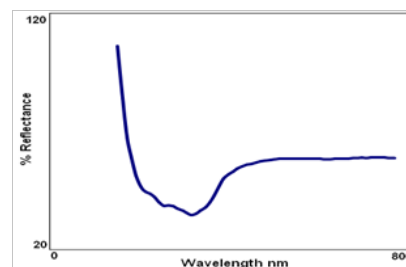


Figure 3: UV-DRS spectra of ZnGeO_3 .

The XRD pattern of ZnGeO₃ powder is revealed in Fig 4. The structure of ZnGeO₃ was found to be hexagonal. D-line pattern of ZnGeO₃ matches with standard JCPDS data card no 70-0205.

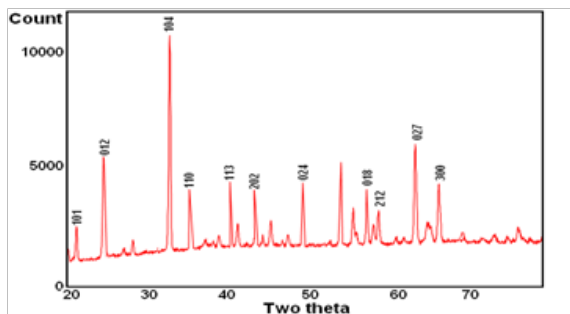


Figure 4: XRD Pattern of ZnGeO₃.

The Fig 5 (a and b) TEM (Transmission electron microscopy) image along with SAED (The selective area of electron diffraction) pattern of synthesized ZnGeO₃. The TEM image reveals that the ZnGeO₃ particles are agglomerated with each other and shows hexagonal structure with average size of 25 nm.

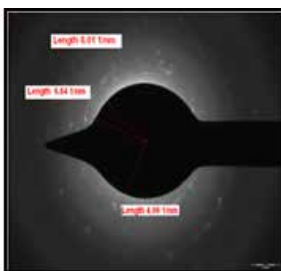
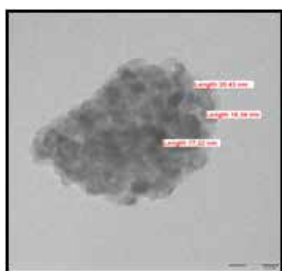


Fig. 5 (a)

Fig. 5 (b)

Figure 5: (a)TEM image of ZnGeO₃. (b) SAED pattern of ZnGeO₃.

The SAED pattern associated with the dark spot reveals occurrence of ZnGeO₃ hexagonal structure, which is in good agreement with the XRD pattern. The dark spot at the distance of 4.06, 6.64, and 8.01 nm indicate 110, 009, and 220 planes respectively, which match exactly with d-line of XRD pattern at 36.2, 60.02, and 76.86 degree respectively. The surface morphology and associated chemical composition of the synthesized ZnGeO₃ photocatalyst evaluated by SEM coupled with EDAX technique depicted in Fig 6.

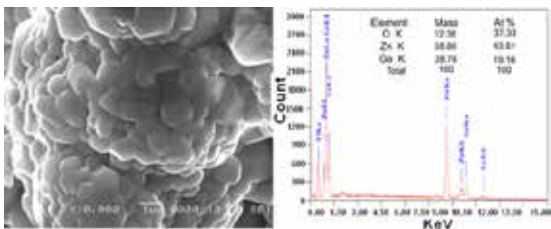


Figure 6: SEM and EDAX of ZnGeO₃.

The SEM image shows that particles are agglomerated with each other and uniformly distributed having high crystalline nature showing hexagonal face. The EDAX data

furnishes information about confirming elemental composition taken for the synthesis of ZnGeO₃. The elemental compositions are 43.51% Zn, 19.61% Ge and 37.33% oxygen. The Nitrogen adsorption-desorption isotherm and the pore size distribution plots calculated from the desorption branch of N₂ isotherm by the Barret, Joyner and Halenda (BJS) method of the ZnGeO₃ material. The pore size distribution showed a narrow range for synthesized photocatalyst, ZnGeO₃, implying good homogeneity of the pore. The surface area (SBET); is 32.06 m²/g, pore volume (V_p); is 0.02308 cc/g, and pore diameter (D_p); is 28.80 Å° for the synthesized compound depicted in Fig 7.

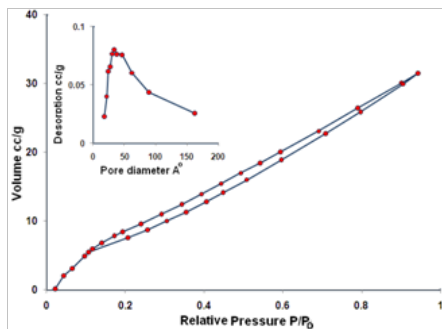


Figure 7: BET surface area and pore volume of ZnGeO₃.

The thermal stability of the ZnGeO₃ was evaluated by thermogravimetric study as shown in Fig 8. The photocatalyst was found to be very stable over wide range of the temperature.

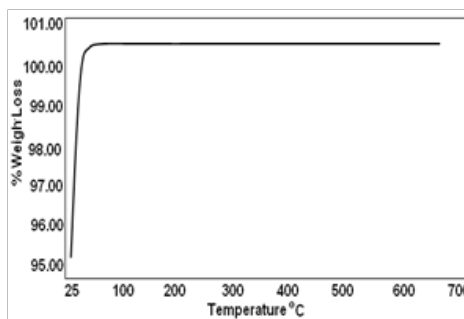


Figure 8: Thermogravimetric plot of ZnGeO₃.

The photocatalytic degradation of the bentazon herbicide with 0.3 g photocatalyst is shown in Fig 9. The effect of amount of photocatalyst on bentazon solution with 0.5 g ZnGeO₃ is shown in the Fig 10. The figures show that the absorption due to the chromophoric peak of bentazon decreased with time in presence of UV-visible light indicating degradation of bentazon.

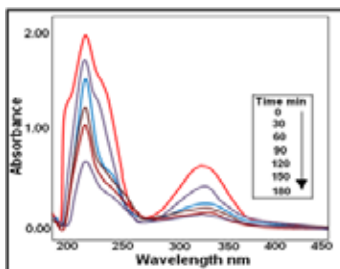


Figure 9: Degradation of bentazon with 0.3g ZnGeO₃

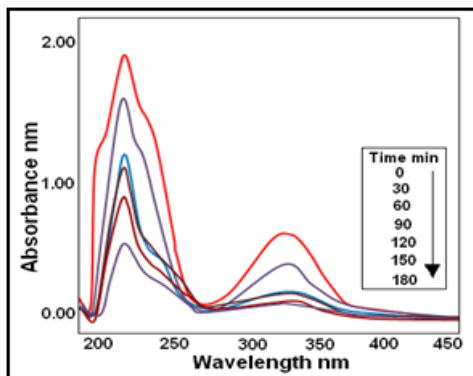


Figure 10: Degradation of bentazon with 0.5g ZnGeO₃

The percentage degradation of the herbicide with different amount of the photocatalyst is shown in the Fig 11. In the figure, curve-a, indicate degradation of bentazon in presence of 0.3g photocatalyst, ZnGeO₃. Curve-b, indicate degradation of bentazon solution in presence of sun light only, curve-c, indicate degradation of bentazon solution in presence of photocatalyst when kept in dark and curve-d, indicate degradation in presence of 0.5 g photocatalyst. In the figure, curve-a and d depicts that, the degradation of bentazon takes place only in presence of UV-visible light and in presence of the photocatalyst. In presence of 0.5 g photocatalyst degradation rate increased, this may be due to increased in number of electron/hole pair than with 0.3 g of photocatalyst.

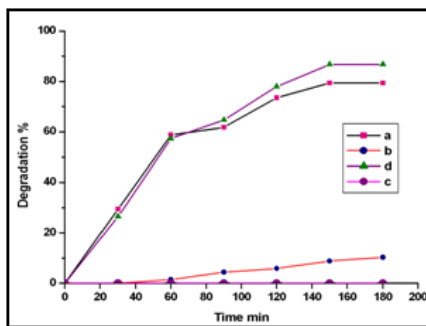


Figure 11: Percentage degradation of bentazon.

The reusability of the ZnGeO₃ was evaluated for the degradation of the bentazon solution. The results are shown in the Fig 12, for 0.3 g of the activated ZnGeO₃ photocatalyst. The photocatalyst was effectively reused by four times. It is observed that the efficiency of the degradation was slightly decreased.

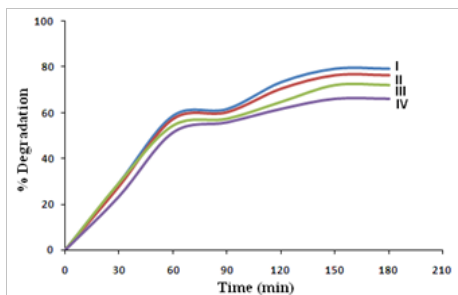
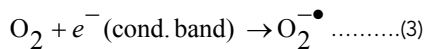
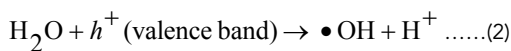
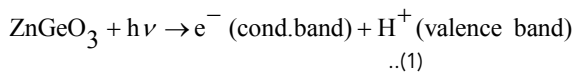


Figure 12: Reusability of photocatalyst.

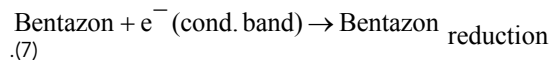
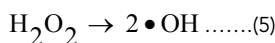
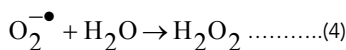
This may be due to adsorption of the some inorganic material on the surface of the photocatalyst. The light intensity varies during hour to hour. The variation in light intensity was found to be 0.01096 W/cm² to 0.0137 W/cm² during course of experiment.

The photocatalytic degradation of the bentazon herbicide is believed to take place according to the following mechanism. When a photocatalyst ZnGeO₃ 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.

Where, e⁻ (cond. band) and h⁺ (valence 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 enter in a redox reaction with other species present on the surface. In this cases h⁺ (valence band) react easily with surface bound H₂O to produce •OH radicals, whereas e⁻ (conduction band) react with O₂ to produce superoxide, O₂^{-•} radical anion of the oxygen



The •OH and O₂^{-•} produced in the above manner can then react with the bentazon herbicide to form other species and thus responsible for the degradation.



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 of degradation of bentazon, herbicide was evaluated and found to follow first order kinetics as shown in Fig 13. The rate constant was observed to be 0.005 min⁻¹.

The reaction rate for photocatalytic process are independent of hydroxyl concentration

$$\frac{-\delta C_{\text{bentazon}}}{\delta t} = K \times C_{\text{bentazon}} \times \text{COH} \bullet \quad \dots(8)$$

Where C bentazon represents the bentazon concentration in ppm. COH. Represents hydroxyl concentration in ppm. The C OH. can be considered as constant. The rate equation (1) can be simplified to

$$\frac{-\delta C_{\text{bentazon}}}{\delta t} = K \times C_{\text{bentazon}} \dots\dots(9)$$

Integrating above equation from C bentazon 0 to C bentazon on the left hand side and 0 to t to the right

$$\int_{C_{\text{bent0}}}^{C_{\text{bemt}}} -\delta C_{\text{bentazon}} = K \times \int_0^t \delta t \dots\dots(10)$$

$$\ln\left(\frac{C_{\text{bentazon0}}}{C_{\text{bentazon}}}\right) = Kt \dots\dots(11)$$

Where C bentazon 0 represents initial bentazon concentration in ppm and K is pseudo first order rate constnsnt, t is time in min, C bentazon represent final bentazon concentration.

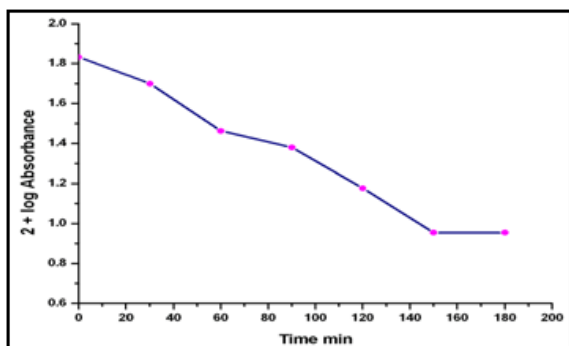


Figure 13: Schematic diagram of photodegradation.

The schematic presentation of the mechanism of generation of oxidative species in a photocatalytic study is shown in Fig 14.

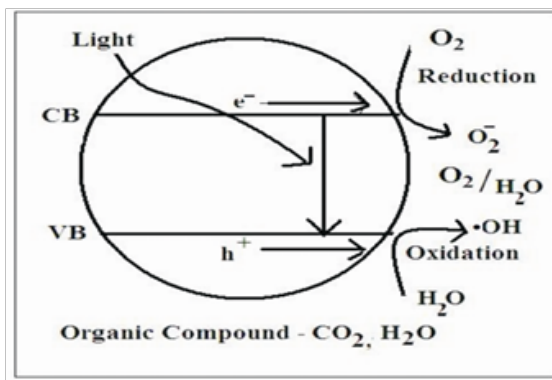


Figure 14: Schematic diagram of photodegradation.

The increase in the catalyst amount actually increases the active sites on the photocatalyst surface thus causing increase in number of holes and electron resulting faster degradation.

CONCLUSIONS

Water pollutant removal appears as the most promising potential application since many toxic pollutants may be organic or inorganic, are totally mineralized. The light-driven photocatalyst ZnGeO₃ was synthesized by eco-friendly mechanochemical method. The photodegradation of Bentazon herbicide was successfully accomplished using ZnGeO₃ under sunlight. The photocatalyst was observed to be hexagonal in nature with band gap 3.44 eV. The surface area, pore volume and pore diameter of the ZnGeO₃ was 32.06 m²/g, 0.02308 cc/g, and 28.80 Å respectively. The study shows that photocatalyst can be reused with very minute change in efficiency. The photocatalytic degradation follows first order kinetics.

ACKNOWLEDGEMENT

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