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Synthesis and Characterization of Zinc Oxide (ZnO) Composite Nanoparticles and its Efficiency in Photo catalytic degradation of Red HRBL dye in Aqueous Solution by Solar Radiation

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Abstract

An investigation of solar light induced photocatalytic decolorization of the Red HRBL reactive dye has been carried out in aqueous heterogeneous medium containing synthesized ZnO composite. ZnO composite was synthesized by chemical combustion method and characterized by X-Ray Diffraction (XRD) and Scanning Electron Micrograph (SEM) studies. The XRD results depicted the crystallite size of the ZnO composite particles were between 8 to 145 nm. The color disappearance of the dye was monitored spectrophotometrically at λ_{max}(512nm). The influence of concentration of ZnO composite, pH of the solution and oxidant addition on rate of decolorization was studied. The synthesized ZnO composite has been experimentally found to be a highly efficient photocatalyst for the decolorization of Red HRBL dye and hence there it has a great potential in the treatment of organic pollutants such as dyes. The optimum decolorization of 98% was recorded at pH 12 within 105 minutes.

Key Words: Photocatalytic decolorization, Red HRBL dye, scanning electron micrographs (SEM), X-ray diffraction (XRD), Zinc Oxide (ZnO) composite.

Introduction

Synthetic dyes are used almost in all branches of the consumer goods industry. About 10000 tons of dyes are produced per year [8] and inevitably, there are dye losses (approximately 12 % of used amount) during manufacturing and processing operations [27]. The effluents from these operations are usually highly colored, toxic, carcinogenic or mutagenic. As the most of the synthetic dyes is resistant to the light or other degradative environmental conditions and demand complete safe removal of these organic industrial dyes before they are released to the environment [3]. Different strategies are being investigated for water remediation, including biological treatment [24, 26], ultra-filtration [22], adsorption methods [30] and others. Such methods are not efficient as they do not achieve complete mineralization of these organic contaminant and they simply transfer the pollutant from one phase to another [34]. Advanced Oxidation Processes (AOP) have been proposed as alternative method for water purification. Among those, oxidation via ozone or hydrogen peroxide has been reported as an effective technique [1, 6, 10, 17]. Unfortunately, such methods may be costly, as ozonation demands artificial UV radiations, and hydrogen peroxide is not available free of charge.

Contaminant complete mineralization with natural solar light seems to be the most practical process for future water purification. A semiconductor photo-catalyst speeds up the action of light by first absorbing photon and producing electrons and holes [13]. With the abundance of costless solar radiations, a low cost catalyst may thus be useful. Different semiconducting materials, in the powder form, have been assessed as photo-catalysts [4, 21]. TiO_2 in its anatase form is the most widely used effective photo-catalyst for its high efficiency, photochemical stability, non-toxic nature and low cost. It has been described for degradation of a wide range of organic contaminants [5, 9, 12, 14, 35-37, 42]. Zinc oxide (ZnO) is a semiconductor with a comparable band gap ~3.2 eV (with wavelength shorter than 400 nm), but has been investigated to a lesser extent in water purification. ZnO is evaluated in many advanced applications such as field-effect transistors, lasers, photodiodes, chemical and biological sensors and solar cells, but to a lesser extent in photo-degradation catalysis [2, 7, 15, 25]. One main advantage for ZnO is that it absorbs a larger fraction of solar spectrum, than TiO_2 does [19]. The performance of ZnO in degrading a number of organic contaminants has been reported [11, 31]. The quantum efficiency of ZnO nano-particles in photodegrading organic contaminants process is higher than that of TiO_2 [18, 20], due to its higher absorptivity in waves shorter than 400 nm, which accounts to about 5 % of the reaching solar light.

A mechanism of the photocatalytic degradation of organic compounds and dyes has been described [38]. In the first step, photons with the energy higher than the band gap energy of ZnO (Eg = 3.2 eV) falls on photocatalysts, electron from valance band jumps to
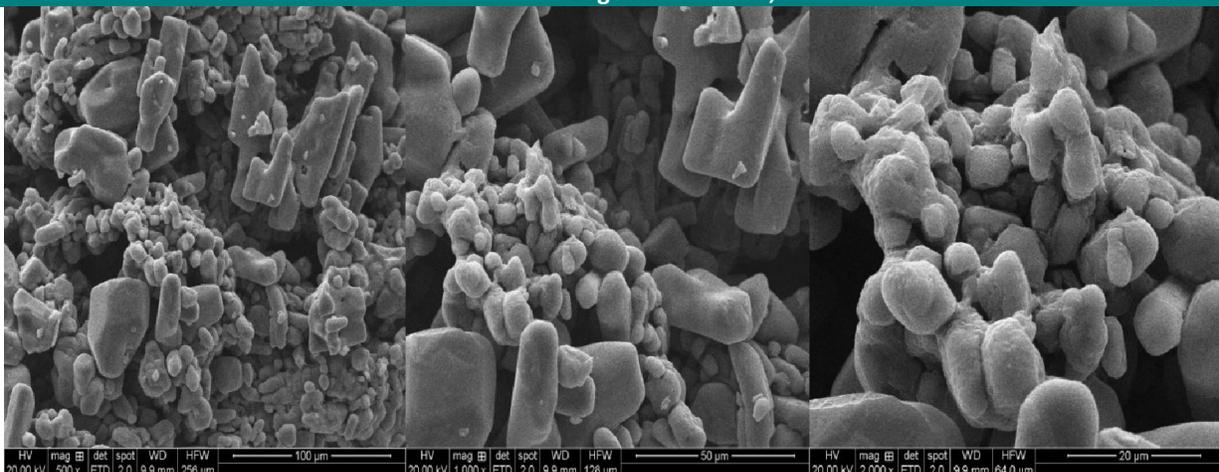
conduction band resulting a positive hole in valance band. The visible light absorbing chromophores of the dye absorb photons creating excited dye molecule. From the excited dye, the electron is injected into the conduction band of ZnO, leaving cationic dye radical [28, 40] or intermediate dye compounds which results in breaking of azo bond and achieves degradation.

In continuation of our study to find out more effective dye degradation method [33, 41] the present study reports the photo-catalytic activity of synthesized ZnO composite in which its feasibility as photo-catalyst to photo-degrade fresh Red HRBL have been investigated. Red HRBL, with molecular structure shown in Fig.1, is an azo dye that is believed to be mutagenic [16] and is also used as a dye in textile industry [32]. It is an example of the widely spread azo dyes [39], which are resistant to complete biodegradation [23].

Materials and Methods
Hydrazine hydrate, 99% LR and Zinc Nitrate ($ZnN_2O_6 \cdot 6H_2O$), AR for the synthesis of ZnO composites were procured from SD Fine chemicals limited, Mumbai and Hi-Media Laboratories Pvt. Limited, Mumbai respectively. Hydrochloric acid (LR, 35.0%) and Sodium hydroxide (LR, $\geq 97\%$), which are used for adjusting the pH of the dye solution were procured from RFCL Limited, New Delhi and MERCK, Mumbai respectively. Model Dye: The dye used for the photocatalytic study that is Red HRBL (reactive dye) was procured from Colour Tex Limited, Surat, Gujrat.

Fig. 1: Structure of Red HRBL dye

The λ_{max} of the dye solution was determined by UV-VIS Spectrophotometer 169 (Systronics, India) and relative absorbance with respect to time was determined by UV-VIS Spectrophotometer 119 (Systronics, India).The water proof pH testr 10 (double junction) were procured from Eutech Instrument, Mumbai was used for determination of the pH of dye solution.

Synthesis of ZnO composite
ZnO composite was prepared by drop wise addition of 5.02 g of hydrazine hydrate (99%) to the beaker containing 11.88 g of zinc nitrate with constant stirring. The obtained white precipitate was diluted to 50 ml by distilled water and stirred for one hour. After centrifugation at 2000 rpm and washing with water several times, the product was dehydrated at 100 - 120° C in hot air oven for 23hours. The final white powder was then crushed manually and stored for further use.

Characterization of ZnO composite

Fig. 2: X-ray diffraction spectra and scanning electron micrographs of ZnO composite.

The X-ray diffraction (Figure 2) of the synthesized ZnO composite confirmed the presence of other contaminants in the prepared composite sample. However, it is very similar to that of ZnO molecular precursors (Joint Committee of Powder Diffraction Standards (JCPDS) card no 80-0075) indicating that the obtained product under the current experimental conditions gives a molecular composite containing ZnO particles. The presence of ZnH_2 (JCPDS card no 47-0982) in traces along with ZnO was also identified. Hence, the new composite product obtained has been named as ZnO composite in this chapter. The scanning electron micrograph images of composite sample have shown the typical texture and morphology of ZnO composite. The x-ray diffraction results showed the crystallite size of the ZnO composite particles were between 8 to 145 nm respectively (Debey Scherrer's formula).

Photocatalytic decolorization experimental procedure
The photo-decolorization of Red HRBL dye solution was studied in the presence of ZnO composite particles and solar radiation in slurry type photo reactor setup. Red HRBL is widely used as a reactive dye in silk yarn dyeing industries and most of the textile industries. Photocatalytic activity of synthetic ZnO composite against Red HRBL dye in presence of solar light reaction experiments were performed in presence of direct sunlight. Standard dye stock solution of 50 ppm was prepared by dissolving 50 mg of Red HRBL in 1000 ml of distilled water and the initial absorbance was recorded (0.579) at 512 nm (λ_{max}). 100 ml of this standard dye stock solution was taken in set (6 numbers including control sample) of Borosil ® glass beakers and prepared ZnO composite at various concentrations (0.1 g, 0.2 g, 0.3 g, 0.4 g, 0.5 g) were directly dispersed to each beakers simultaneously. The absorbance readings at regular time intervals (15 minutes) were compared with initial absorbance for the investigation of photocatalytic activity of prepared ZnO composite at different concentrations and pH (12.9, 7.0 and 3.0).The percentage of decolorization was calculated by using the following formula.

The percentage of decolorization = $[(A_o - A_t) \div A_o] \times 100$
Where, A_o is the initial absorbance of the dye solution; A_t is the absorbance at time interval 't'.

Results and Discussion
Effect of pH
The effects of different pH of Red HRBL reactive dye were studied using UV-VIS spectrophotometer. The effect of pH values on the degradation efficiency of synthesised ZnO nanoparticle was studied in the pH range 3–12 at 50 ppm dye concentration in presence of natural sunlight. Fig. 3 demonstrates the results of decolorization efficiency of ZnO composites after 105 minutes in presence of natural solar radiation at different pH values. A sudden increase in the decolorization of Red HRBL dye solution with increase in the pH value from 3 to 12was observed. The optimum decolorization was achieved at pH 12, i.e., almost 98% in just 45 minutes at all catalyst dosages.

As an amphoteric oxide, ZnO can be dissolved both at acidic and alkaline environment. In this work, for Red HRBL dye at the higher pH value (pH 12) the dissolution of ZnO, the effective catalysts is increased greatly. When pH value is greater than 7 (pH 12), the ZnO surfaces is negatively charged by adsorbing OH$^-$ ions, which favours the formation of hydroxyl radicals. However, in alkaline condition, the ZnO surface is preferentially covered by the dye molecules. Therefore, with the increase of pH value can provide higher OH ions to form more hydroxyl radicals, which consequently enhances the photodegradation efficiency. Due to these factors the highest decolorization efficiency was obtained at pH 12. The degradation efficiency of synthesized ZnO composite was significantly affected by variation in pH of dye solution.
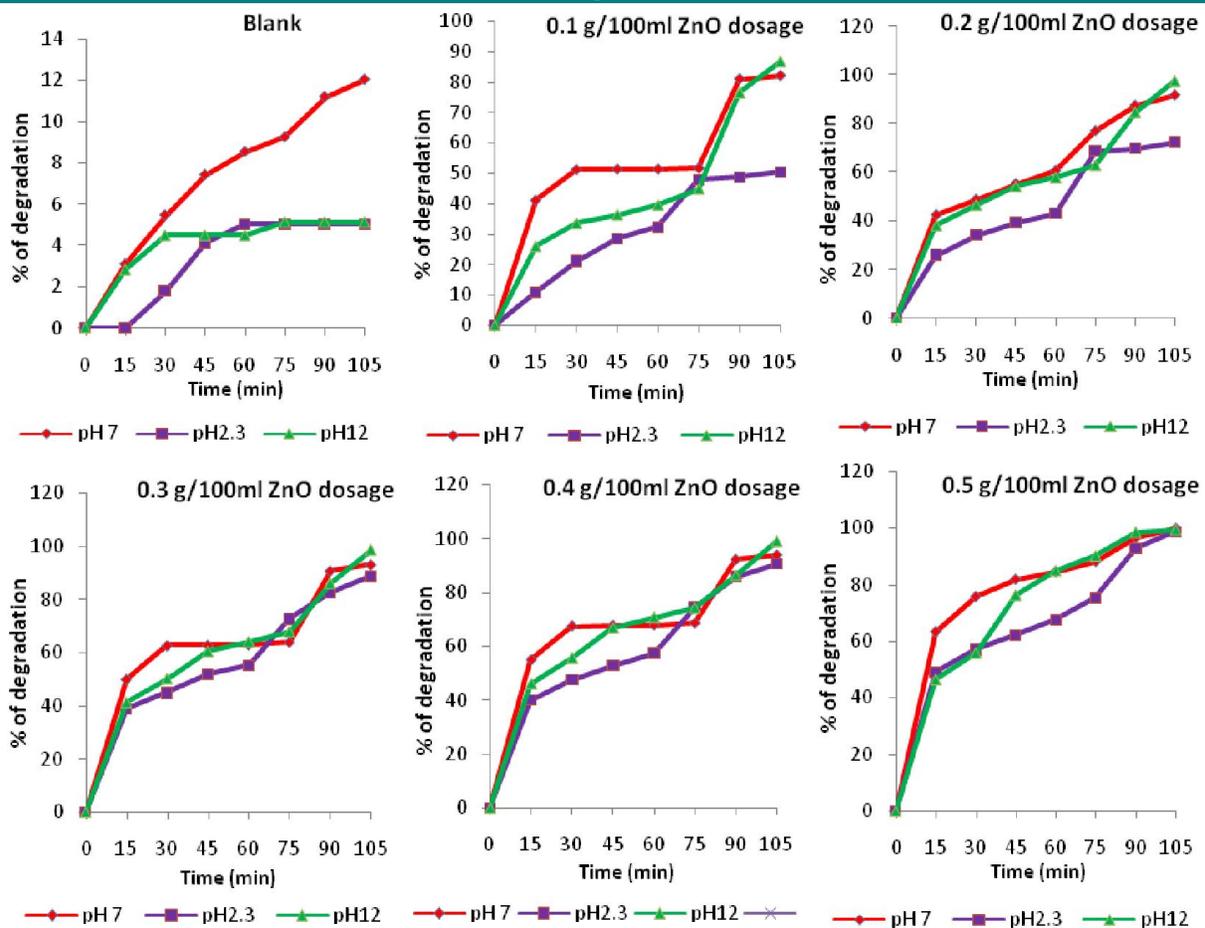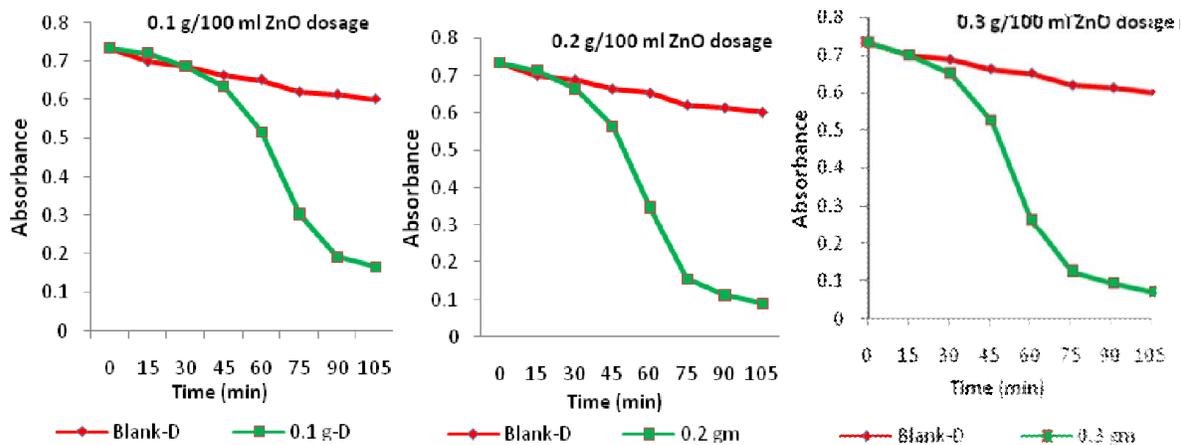
Fig. 3: The photocatalytic degradation of Red HRBL dye solution (50 mg/L) at different pH levels (pH 3, pH 7 and pH 12) in the presence of sunlight.

Effect of ZnO catalyst load
To investigate the effect of catalyst loading on the decolorization efficiency, a series of experiments were carried out by varying the catalyst from 0.1 to 0.5 g/100ml in 50 ppm Red HRBL dye solution. The rate of degradation is illustrated in Fig. 4. It is demonstrated that, the decolorization efficiency is increasing with the catalyst-loading in the presence of natural sunlight. The optimal catalyst dosage for achieving maximum decolorization is found to be 0.5g/10ml of dye solution.
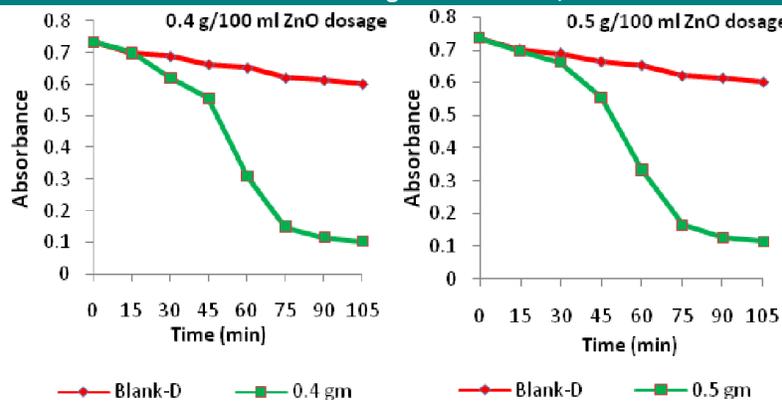
Fig.4: The photocatalytic degradation of Red HRBL dye solution (50 mg/L) at different catalyst dosages (pH 7) in the presence of sunlight.

It is due to the photocatalytic degradation is dependent on the effective surface of catalyst and the adsorption of sunlight, i.e., more catalysts in dye solution increases solar light adsorption which results in activation of photocatalysts. At lower catalyst loading, the adsorption of light controls the photocatalytic process due to the limited catalyst surface.

Effect of addition of oxidant

The degradation efficiency of photocatalysts against organic compounds can significantly be improved either in the presence of oxygen or by the addition of hydrogen peroxide. To verify the influence of H_2O_2 over initial rate of decolorization, we have conducted several experiments taking Red HRBL dye solutions (50 mg/L) in batches at pH 7. We irradiated aqueous dye solutions with blank and catalyst added dye solutions with addition of 1 ml H_2O_2. The result thus obtained is reported in the Fig. 5. The Red HRBL dye decolorization was found to be affected significantly for blank dye solution with H_2O_2, i.e., in the absence of photocatalysts. Further, the decolorization phenomenon was slightly better in the presence of photocatalyst at all loading levels.
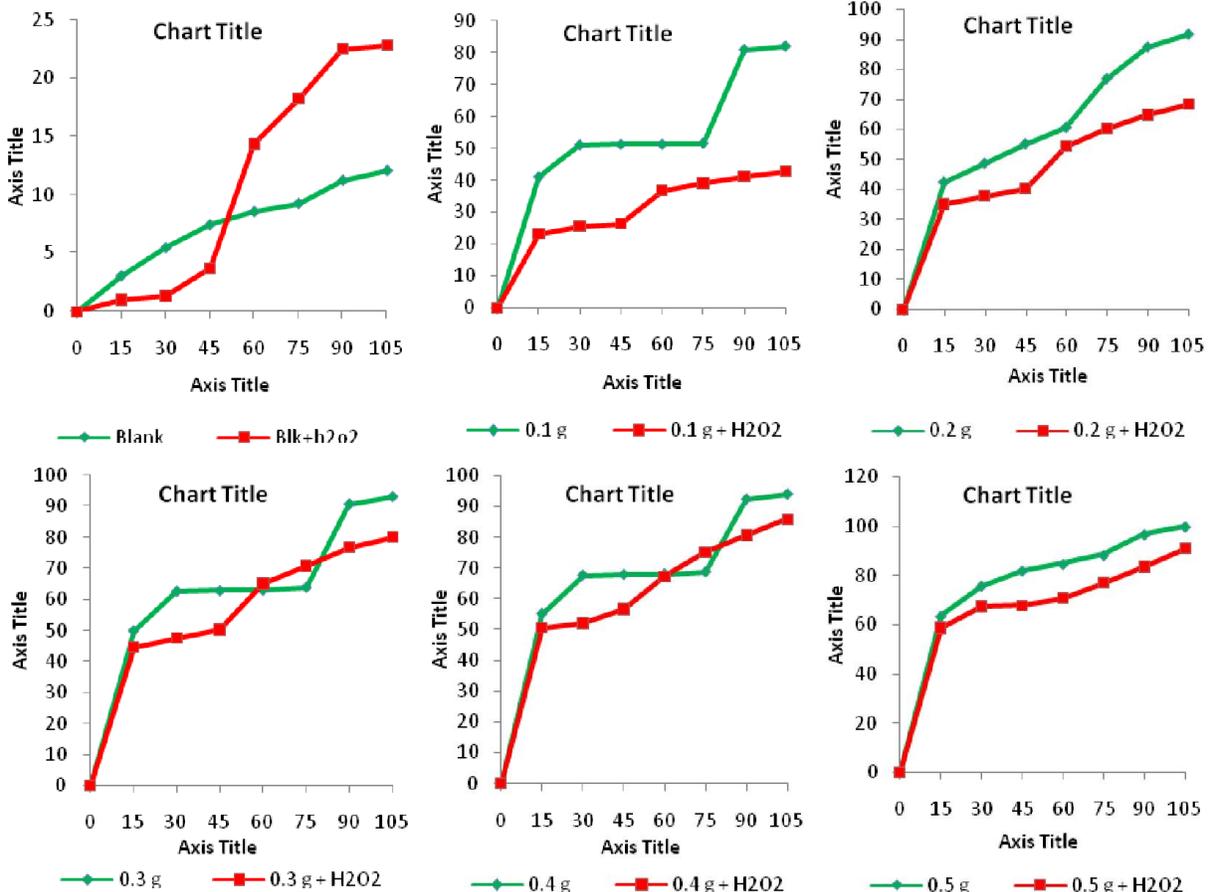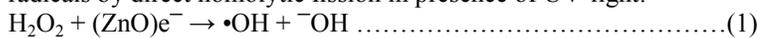

Fig. 5: The photocatalytic degradation of Red HRBL dye solutions (50 mg/L) at different catalyst dosages with H_2O_2 and in absence of H_2O_2 (pH 7) in the presence of sunlight.

This effect of H_2O_2 can be explained by radical reaction mechanism (Eqs. (1)–(3)). The added H_2O_2 can scavange electrons from conduction band of ZnO composite particles to generate excess hydroxyl radicals. The H_2O molecules can also generate hydroxyl radicals by direct homolytic fission in presence of UV-light:

$H_2O_2 + (ZnO)e^- \rightarrow \bullet OH + {}^-OH$ ……………………………………(1)

$H_2O_2 + O_2\bullet^- \rightarrow \bullet OH + -OH + O_2$…………………………………..(2)

$H_2O_2 + h\upsilon \rightarrow 2\bullet OH$ ……………………………..……………………… (3)

As mentioned earlier, •OH radicals are the major oxidant for dye decolorization, therefore, the excess • OH radicals so added to the system, accelerated the decolorization rate.

Conclusion

The XRD results depicted the crystallite size of the ZnO composite particles were between 8 to 145 nm. Nano-scale ZnO composite particles were synthesized by simple solution combustion method and are effectively used as photo-catalysts as an attempt of complete decolorization of Red HRBL dye in presence of Solar radiation. The composite has been effectively used under different working conditions against reactive azo dye in presence of solar radiation and it was found to be affected by pH of the dye solution, catalyst dosage and oxidant concentration. The optimal catalyst dosage was found to be 0.5g/100ml dye solution and optimal pH in achieving 98 % decolorization was pH 12. The experimental results add to credibility of using easily synthesizable ZnO composites in decolorizing azo dye contaminated waters at large scale in presence of abundant natural solar radiation.

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