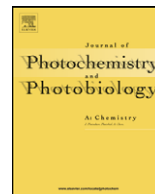




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Photocatalytic activity on TiO₂-coated side-glowing optical fiber reactor under solar light

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ABSTRACT

A novel optical fiber reactor (OFR) that employs side-glowing optical fibers (SOFs) as a means of light transmission medium and TiO₂ supporter has been developed, characterized, and investigated. Different from existing ones, the SOF here is made up of quartz core with a silicon cladding, which can emit light from side surface more uniformly and can transmit light for longer distance since attenuation of light through SOF is slow; furthermore, SOF is flexible enough to be entwined into U-shapes. The crystal phase and microstructure of TiO₂ coating are investigated by XRD and SEM. Solar light collected and transmitted to SOF by automatic sun-tracing equipment (ASE) was utilized to excite the titania coating for photocatalytic degradation of 4-chlorophenol (4-CP). Compared to traditional solar collectors, the present one can collect solar light efficiently while occupying smaller area, moreover, ASE allows a long distance light transmission to somewhere such as indoor or sub-surface for photocatalytic applications. Results show that 79% of 4-CP had been decomposed under sunlight irradiation for 8 h.

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1. Introduction

TiO₂-based heterogeneous photocatalysis is considered to be an effective means of removing organic and inorganic contaminations from water and air streams [1–5]. Due to the difficulty of nano-sized photocatalysts separating from aqueous or gaseous pollutants after reactions in suspended reactor, fixed-bed system appeared, in which the photocatalysts were immobilized on the walls of the reactor, on the supported substrates, or around the light source [6–9], however, with a cost of diminishing the effective reactive area between photocatalysts and contaminants. Recently, many groups found [10–13] that employing substrates with large surface area, i.e. active carbon, hollow microbeads, zeolite, could solve the problems mentioned above. But the shadowing effect appeared, as the particles suspended in the medium which increased the turbidity of the medium, and would actually decrease the depth of light penetration, and drastically lower the rate of photocatalytic reaction [14].

The idea of using optical fiber as both a means of light transmission and support for photocatalysts was originally proposed and theoretically evaluated by Ollis and Marinangeli in the late 1970s and early 1980s [15–17]. Subsequently in 1994, Bauer and co-workers [18] first proved the idea with experiments that designing a TiO₂-coated quartz optical fiber (QOF) and employing it to photocatalytic degrade 4-CP in solution. Due to the ultrafine diameter of the QOF, this reactor configuration supplied large active surface area, and furthermore, the light traveling in the optical fiber could directly excite TiO₂ particles, avoiding the absorption and scattering by the reaction medium. Therefore, it is feasible to provide higher light utilization efficiency. Compared with Degussa P25-slurry system, Bauer found that both degradation rates of 4-CP and the destruction of total organic carbon (TOC) were improved in the QOF reactor under UV irradiation. Because light is lose-free, it can adopt lower intensity light when optical fibers were used. For instance, it is possible to use solar light substituting for artificial UV light to excite photocatalytic reactions in the optical fiber reactor, which is an energy-saving application.

However, due to the large extinction coefficient of side surface, nude QOF can emit light less than 1 m, so, it is not suitable to be used in long length and to construct large reactors. For the sake of substituting nude quartz fiber, we produced a new side-glowing

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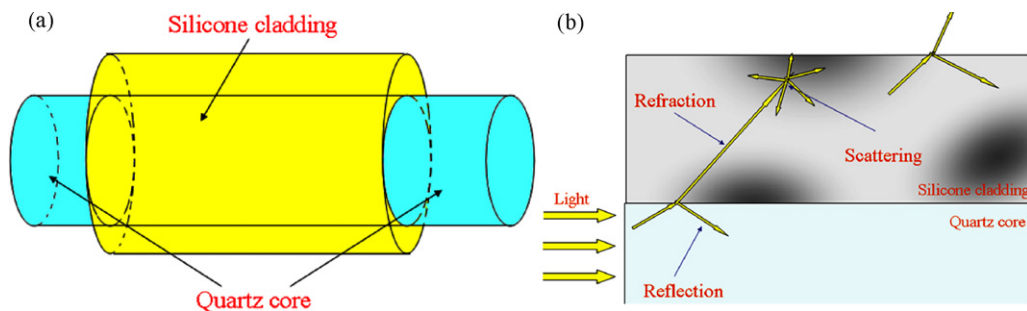


Fig. 1. Schematic diagram of single SOF (a) and its segment under irradiation (b) higher density regions in cladding layer were indicated as blacker fields in the figure.

optical fiber (SOF) with nude quartz glass fiber as the core, and silicone buffer as cladding. The density of silicon cladding was controlled by partial crystallization method, so that part of the light can be scattered in the buffer layer and emanate out of SOF surface (Fig. 1.) [19,20]. It is found that the new SOF can emit light from its side uniformly for more than 10 m, and due to better flexibility, it can be twisted into various shapes which are suitable for constructing a reactor in pilot-plant scale.

In this article, a 40 L of TiO₂-coated SOF reactor was designed. In addition to the physical characterization of the reactor, it was used to investigate the photocatalytic degradation of 4-CP under solar light irradiation. And it was found that 4-CP can be decomposed efficiently in such reactor.

2. Experimental

2.1. Preparation of TiO₂ coating on SOF

The aqueous TiO₂ sol was prepared through a sol-gel method, using Ti(OBu)₄ as molecular precursor. Through adding the mixture of Ti(OBu)₄ and *i*-PrOH gradually into abundant water with pH value of 2.5, and refluxing, the stable and semitransparent TiO₂ sol was obtained. Infusing SOFs in the TiO₂ sol for some times, and drawing out at a speed of 2 cm min⁻¹, TiO₂ sol could be deposited onto the surface of the SOFs layer by layer to obtain different films thicknesses. And then those SOFs were dried at 373 K for 2 h.

2.2. Characterization of SOF and TiO₂ coating

The schematic diagram of light transmission through SOF was shown in Fig. 2. After traveling in the SOF for Δx m, the import light with intensity of I_0 , exported from the other end with the intensity of I_{TX} . It is hypothesized that except the light glowing from side of SOF with intensity of I_S , all the other light is absorbed by SOF when traveling in it. Therefore, the intensity of export light I_{TX} could be expressed as follows:

$$I_{TX} = I_0 \cdot e^{-k\Delta x} \quad (1)$$

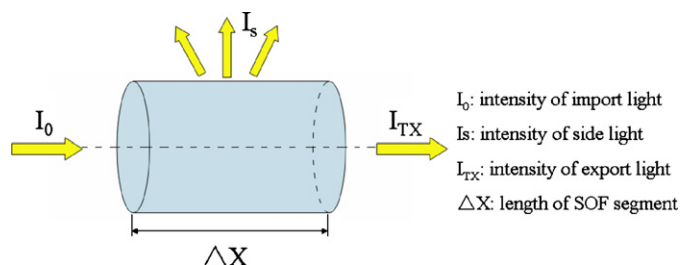


Fig. 2. Schematic diagram of light import and export through optical fiber.

So, the intensity of side-glowing light I_S can be expressed as:

$$I_S = I_0 - I_{TX} = (4\pi)^{-1} \cdot I_0 \cdot (1 - e^{-k\Delta x}) \quad (2)$$

where k is the side-glowing coefficient. It is easy to realize that the larger k value, the higher I_S value.

When the light imported from two ends of SOF, I_S was expressed as:

$$I_S = (4\pi)^{-1} \cdot I_0 \cdot [2 - e^{-k\Delta x} - e^{-k(L-\Delta x)}] \quad (3)$$

The crystal phase of TiO₂ samples were identified by X-ray diffractometer (XD-3A, Shimadzu Corporation, Japan) using graphite monochromatic copper radiation (Cu K α) at 40 kV, 30 mA over the 2θ range of 20–80°.

The morphology of TiO₂ films loaded on the SOFs was analyzed by field-emission scanning electron microscope (Sirion, FEI, Netherlands). The change in concentration of 4-chlorophenol (4-CP) solution was measured through UV-vis spectrophotometer (8500, Shanghai).

2.3. Bundled-SOFs reactor utilizing solar light

Up to now, applications of solar light for photocatalysis have been studied intensively. Among those researches, wastewater treatment seems to be one of the most promising fields of application of solar detoxification. In this research, each bundled-SOFs consisting of 1500 SOF with a length of 1 m, and entwining in U-shape, were coated with TiO₂ films. Two bundled-SOFs dispersing by distribution disk were settled in a cylinder reactor with a volume of 90 L. Automatic sun-tracing equipment (ASE) was used to collect and transmit solar light to SOFs. During the reaction, 0.4 g 4-CP was dissolved into 40 L distilled water, the concentration was adjusted to be 10 mg L⁻¹. Then the solution was mixed and aerated by air pump in a pre-treatment vessel. A water pump with the flow rate of 2.0 L/min was used to ensure the cycle of water solution between pre-treatment vessel and reactor (as shown in Fig. 3). The solar light intensity from ASE was 185.7 mW cm⁻² at maximum and 42.9 mW cm⁻² at minimum measured by solar radiometer (FZ-A, 400–1000 nm). (Sunny day in the October of Nanjing, China)

3. Results and discussion

3.1. Capability of SOF

The schematic diagram of light transmitted through nude QOF and SOF both with TiO₂ coating was shown in Fig. 4. In the nude QOF, the TiO₂ coating with a refractive index n_a of 2.5 in anatase phase, was deposited directly on the quartz core whose refractive index n_q is 1.458, and in the SOF, there was a silicone buffer cladding with lower refractive index n_s of 1.41. The Snell's refraction law: $n_1 \sin \theta_1 = n_2 \sin \theta_2$ states whether the light is reflected or refracted. Where n is the refractive index, θ_1 the angle of incidence, and θ_2

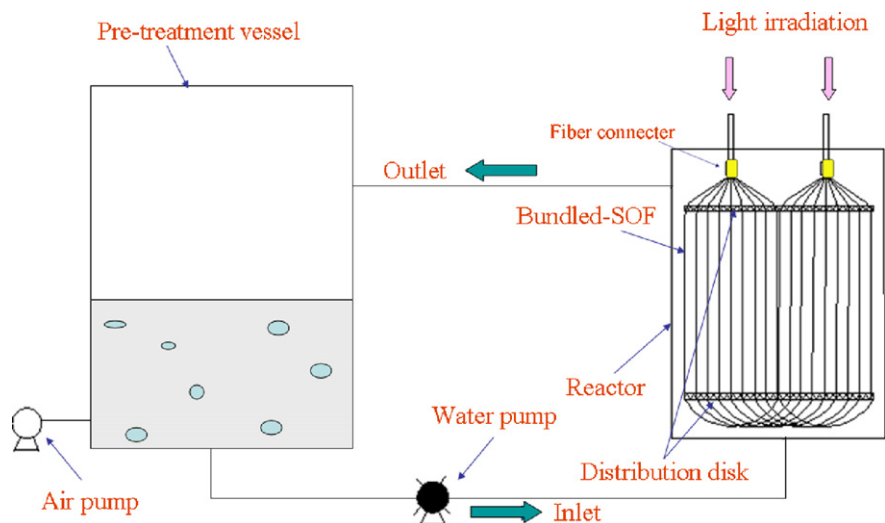


Fig. 3. Schematic of bundled-SOFs reactor.

the angle of refraction. The critical incidence angle (θ_c) which is a border line whether the light is refracted totally, is defined when $\theta_2 = 90^\circ$ since $\sin \theta_c = n_2/n_1$. In nude QOF, as shown in Fig. 4(a), with $n_q < n_a$, the reflected and refracted occurred for all the θ_1 value, while in the SOF, $n_q > n_s$, some light with $\theta_1 < \theta_c$ could be reflected and refracted, some light with $\theta_1 \geq \theta_c$, could only be reflected. Due to the occurrence of total reflection, the light could transmit in SOF for a longer distance.

The function of I_s/I_0 of SOF with its length was shown in Fig. 5. It was found that as irradiation light importing from one end, the I_s value was reduced exponentially with the increasing length of SOF. While irradiation light was imported from both ends, the I_s value was larger than one end importing and became much uniform along the SOF. The measured mean side-glowing coefficient k (m^{-1}) was $0.31 \pm 0.03 m^{-1}$. The light intensity I_s would be $65 \mu W cm^{-2}$ at middle point of the fiber, with the input light intensity of $1.0 m W cm^{-2}$, which is the UV ($\lambda = 365 nm$) intensity under the natural solar light in sunny day of Nanjing. According to Ohko et al. [21] who investigated the kinetics of photocatalytic reactions under extremely low-intensity UV illumination on titania thin films, this I_s from SOF in our work was high enough to induce photocatalytic reactions.

3.2. Characterization of TiO₂ photocatalyst

Regarding the titania phase character, amorphous TiO₂ seldom displayed photocatalytic activity due to some non-bridging oxygen

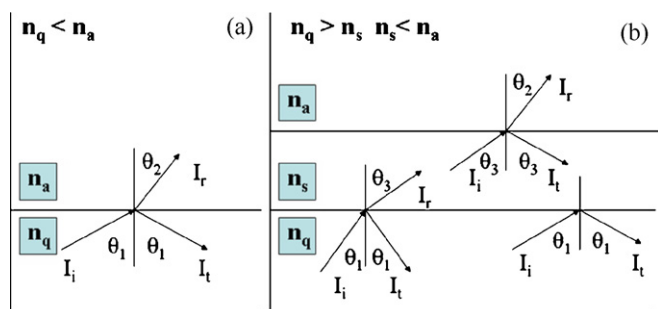


Fig. 4. Schematic diagram of light transmission in the TiO₂-coated on nude optical fiber (a) and on SOF (b).

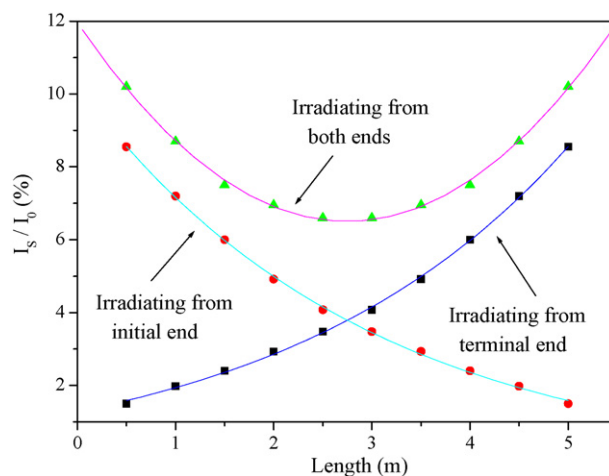


Fig. 5. The function of I_s/I_0 of SOF with its length.

(NBO) in bulk TiO₂ as defects. The XRD patterns of TiO₂ particles were shown in Fig. 6. The presence of peaks ($2\theta = 25.4^\circ, 37.8^\circ, 47.9^\circ, 54.6^\circ, 62.8^\circ, 69.8^\circ, 75.2^\circ$) was regarded as an attributive indicator of anatase which was thought to be the most active phase for photo-

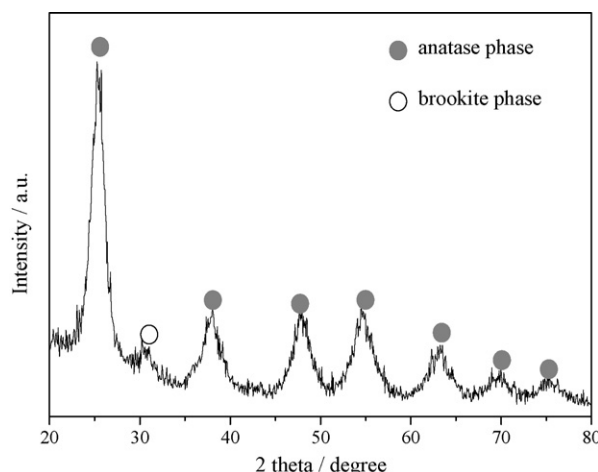


Fig. 6. XRD patterns of as-prepared TiO₂ particles.

catalysis [22], and a weak broaden signal at 31.0° was attributed to the brookite phase. It means that phase transformation from amorphous to anatase structure, which commonly requires 673 K at least, could be achieved by digesting and peptizing treatment of TiO_2 sol under mild condition in this research. Broad diffraction peak at 1 0 1 plane ($2\theta = 25.4^\circ$) was due to its small crystallite size of TiO_2 sol particles. The mean size of the single crystallite can be determined from full-width at half-maxima of corresponding X-ray diffraction peaks by using Scherrer's formula: $D = (K\lambda)/(\beta \cos \theta)$, where λ is the wavelength of the X-ray radiation ($\lambda = 0.15418$), K the Scherrer constant ($K = 0.9$), θ the characteristic X-ray radiation ($\theta = 12.7^\circ$) and β is the full-width at half-maximum of the (1 0 1) plane (in radians) [23]. The estimated nanocrystallite size of TiO_2 sol sample was 5.54 nm.

The microstructure of TiO_2 films on SOF observed by SEM was shown in Fig. 7. It showed that, the TiO_2 coating had been homogeneously dispersed on SOF surface without large crack, and its thickness was about 600 nm.

3.3. Feasibility of using solar energy as light source in SOF-based reactor

The solar heterogeneous photocatalytic detoxification process may be defined as that collecting solar photons with appropriate energy (wavelength) efficiently and transmitting them into reactor to promote specific catalytic reactions, which may be the most attractive application from the economical and environment friendly viewpoint. [24] In solar photocatalysis, technique of designing an apparatus to collect and transmit solar light to photocatalysts and constructing appropriate reactor are very indispensable. An effective and popular used solar collector is the compound parabolic concentrator (CPC), the shape of CPC usually consists of two half cylinders of parabolic profiles set side by side. The center line is located closely above the connection of the two parabolic profiles. So, different from conventional flat plates which could only illuminate the front of collector, CPC construction was able to concentrate the receiver radiation from almost any direction that arrives within the collector [25]. Limited by the collector, current solar photocatalytic reactors only used in outdoor place and need large area of land to fix collectors [25–27].

Although optical fiber reactor (OFR) is suitable for using solar energy, few articles were related to sunlight utilization in OFR. In this research, OFR reactor was employed to treat model wastewater under solar irradiation, and ASE was used to collect solar light. It can automatically trace the direction of the sun and focus the sunlight by sensor and Fresnel lens, and send the collected light to SOFs.

Table 1

Corresponding degradation ratio of 4-CP to films with different thickness

Titania layer thickness (nm)	300	600	800	1 100
Degradation ratio (%)	67.16	79.24	70.35	62.58

This SOFs-based reactor supplied large active surface area, which is benefit to photocatalytic degradation, due to ultrafine diameter of the fibers. While the space occupied by SOFs was only 0.09% of reactor volume, the ratio of A_c to V has been reached 94 m^{-1} , where A_c was the surface area of irradiated catalysts, and V was the total volume of contaminated water. Compared to the reported A_c/V value of 16.3 m^{-1} for TiO_2 fixed-bed system in cote-mesh reactor (CMR) [28], the value of SOF-based reactor improved sharply, and near to that of 81 m^{-1} in TiO_2 -coated nude optical fiber reactor [29].

To concentrate enough energy onto reactor surface, most solar collectors have large collecting area. In our study, we use four Fresnel lens which have total surface area only 0.07 m^2 to focus the sunlight onto the import end of bundled-SOFs, while 40 L of 4-CP was dealt with.

Compared to “front-irradiation” in annular and other reactors, optical fiber reactor is a representative “backside irradiation” system. Thus, the thickness of the titania coatings play an important role on photocatalytic activity. Therefore, in this article, the effect of different thickness of photocatalyst layer on photocatalytic activity was investigated.

The photolytic rate was quite negligible as we had investigated the photodecomposition of 4-CP by SOF reactor in the absence of photocatalyst, about 1% of the total 4-CP was decomposed, therefore, the decomposition of 4-CP was attributed to photocatalysis by TiO_2 . As for titania coating of 600 nm, the 4-CP concentration decreased from 9.261 mg L^{-1} to 7.614 mg L^{-1} due to the absorption of TiO_2 , and then reduced continuously to 1.581 mg L^{-1} under the solar light irradiation for 8 h. The decomposition percent was 79.24%. While the degradation ratio was 67.16%, 70.35%, and 62.58% for titania coating thickness of 300 nm, 800 nm and 1100 nm, respectively (as shown in Fig. 8 and in Table 1). The kinetic linear curve, $\ln(C_0/C)$ as a function of irradiation time was as follows:

$$\ln\left(\frac{7.614}{C}\right) = -0.092 + 0.185 \times t$$

The correlative coefficient $R = 0.980$, apparent rate constant $k = 0.185 \text{ h}^{-1}$.

IUPAC has recommended the use of standard figures-of-merit. The parameter provides a direct link to the solar-energy efficiency of advanced oxidation technology (AOT), independent of the nature

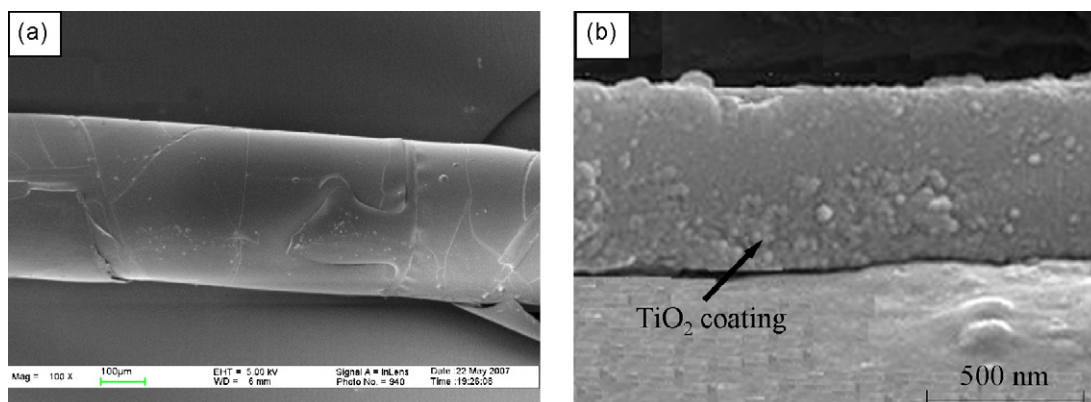


Fig. 7. SEM images of TiO_2 films coated on SOF.

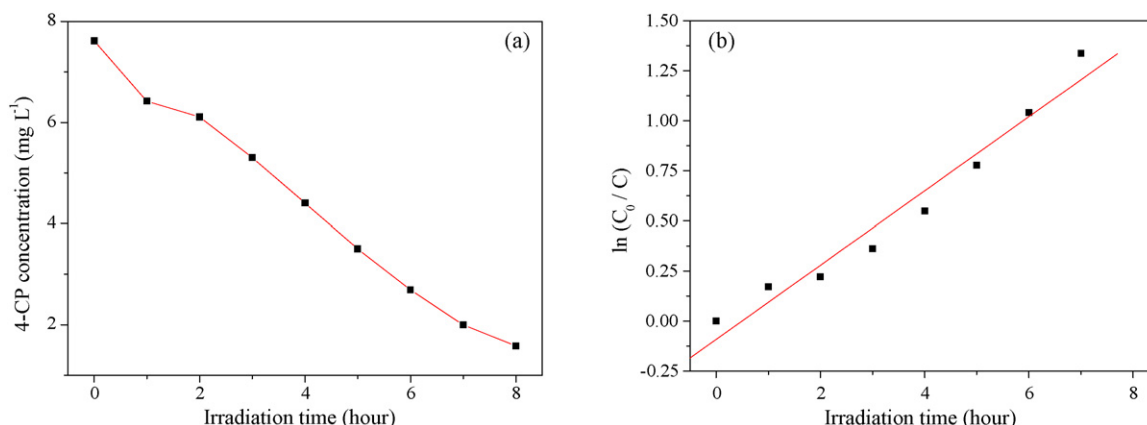


Fig. 8. Variations in 4-CP concentration (a), and $\ln(C_0/C)$ (b) as a function of irradiation time in SOFs reactor under solar light.

of the system, and therefore allow for direct comparison of widely different AOTs. In the case of solar-energy driven system, the electric energy (kWh) used in the conventional treatments is replaced by the solar energy (kWh) collected by collector [30]. As there is no cost for solar energy, the cost of collector is a substantial capital. And usually, the capital cost for solar collector is proportional to its area and hence figures of merit based on the solar collector area are appropriate [31].

The solar irradiance E_S varied with the time in one day. And the average solar irradiance \bar{E}_S over the time of a given experiment is obtained by

$$\bar{E}_S = \frac{\int_{t_i}^{t_f} E_S(t) dt}{t_f - t_i}$$

Where $E_S(t)$ is the function of irradiation time, t_i and t_f are the initial and final times, respectively.

The collector area per order (A_{CO}), which is the collector area required to reduce the concentration of pollutant in water or air in a unit volume (m^3) by one order of magnitude in a time t_0 (h) when the incident solar irradiance is 1000 W cm^{-2} .

The A_{CO} [$m^2/(m^3\text{-order})$] can be calculated by [31]

$$A_{CO} = \frac{A \cdot \bar{E}_S \cdot t}{V \cdot \lg(c_i/c_f)}$$

Where A (m^2) is the collector area, t (h) is the irradiation time, V (L) is the treated volume, and c_i and c_f are the initial and final pollutant concentrations (M).

It is worth noting that the higher A_{CO} , the lower photoreactor efficiency [32]. The coated catalyst in our reactor is equivalent to 0.00096 g/L in suspended system. The A_{CO} values obtained in our experiment of degrading 4-CP is just $2.54 \text{ m}^2/\text{m}^3$.

4. Conclusion

SOF can emanate light from its side uniformly for more than 10 m, a longer distance than ordinary QOF. And it can be entwined into any shapes due to its flexibility. These characters made SOF much suitable for building large OFR.

This work demonstrated that combined TiO_2 -coated SOF with solar energy for photocatalysis was feasible. The SOFs based reactor shown low value of A_{CO} and high photocatalytic efficiency. In addition, the SOF-ASE system allows for the long distance delivery of solar light up to several kilometers. So it can be used for the treatment of contaminated sites in the subsurface environment or other places without sun-light.

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