



# The experimental study of a hybrid solar photo-Fenton and photovoltaic system for water purification



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## ABSTRACT

A new hybrid system that integrated a photovoltaic (PV) panel with a solar photo-Fenton (SPF) reactor was constructed to treat wastewater and generate electricity for the first time. The decolorization and photovoltaic performances of the hybrid system were tested outdoors by discoloring three dyes: Acid Red 26 (AR26), Malachite Green (MG) and Reactive Blue 4 (RB4). Lab scale experiments also had been done to confirm the impact of temperature on the SPF process. The lab scale results show that SPF process was more efficiency for decoloring the different dyes, compared with dark Fenton. The SPF followed a pseudo-first-order reaction and the reaction rate constant was improved about 3.5, 4.5 and 0.61 times for AR26, RB4 and MG respectively as the wastewater temperature increased from 20 to 50 °C. The decolorization difficulty of the three dyes followed this order: MG > AR26 > RB4. The results of the hybrid systems tested outdoors show that 200 mg/L MG had achieved 98.6% color removal after 3 h of treatment at a low catalyst dose ( $\text{Fe}^{2+} = 5 \text{ mg/L}$ ) under sunlight. For 100 mg/L MG, 99.3% color removal was observed after 70 min. The treatment time required for decolorization of AR26 and RB4 was more shorter. In the present of the water layer, the wastewater temperature was increased and that of the hybrid system was decreased. The average output power of the hybrid system was more than 12 W and sufficient to drive the system during all of the outdoor experiments. Our results suggest that the system could realize decolorization of different dyes and automatic operation.

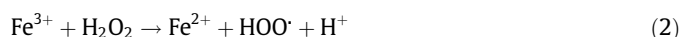
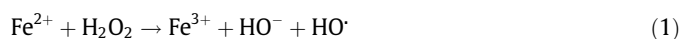
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## 1. Introduction

Water pollution has become a worldwide problem, especially with the industrialization in urban areas. The textile industry is one of the most water consumption sectors [1]. Dyes lost in the effluents after dyeing are highly stable and bio-refractory [2,3]. The colored wastewater hindered the photosynthetic activity of aquatic organisms and seriously threatened the ecosystem by strongly absorbing sunlight [4].

In the previous studies, it was proven that advanced oxidation processes (AOPs) using ozone, ultra violet (UV), titanium dioxide ( $\text{TiO}_2$ ), and Fenton's reagent ( $\text{H}_2\text{O}_2$  and ferrous ion), etc. could effectively degrade less biodegradable wastewater [5–7]. Hydroxyl radical ( $\text{HO}\cdot$ ) that has a high standard potential is the main oxidizing agent for AOPs. A further advantage of  $\text{HO}\cdot$  is that it is not selec-

tive toward organic pollutants. Solar photo-Fenton (SPF) reaction is one of the most cost effective and easiest to operate methods among AOPs. Ferrous sulfate is always employed as iron resource in the SPF process since it is economical and nontoxic, less corrosive and more soluble than other ferric salts. Iron would precipitate if the  $\text{H}^+$  concentration was too low. A high concentration of  $\text{H}^+$  can cause a negative effect during the SPF process, as it would work as a scavenger of the  $\text{HO}\cdot$  [8,9]. The proper pH should be in the range of 3–5 [10]. Another reagent for the SPF process is  $\text{H}_2\text{O}_2$ , it is inexpensive, easy to be handled and consumed in the oxidation process. Compared with Fenton reaction, solar irradiation, mainly the UV and near UV parts, increases the generation of  $\text{HO}\cdot$  during the SPF process. The reactions involved are described as below:



When irradiation is involved, the photolysis of  $\text{Fe}^{3+}$  generated by Eq. (1) facilitates  $\text{Fe}^{2+}$  regeneration:

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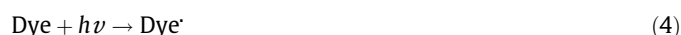
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### Nomenclature

PV	photovoltaic	PVT	photovoltaic-thermal hybrid systems
SPF	solar photo-Fenton	FF	filled factor, %
AR26	Acid Red 26	$V_{oc}$	open-circuit voltage, V
MG	Malachite Green	$P_m$	the maximum output power, W
RB4	Reactive Blue 4	$I_{sc}$	short-circuit current, A
AOPs	advanced oxidation processes		
UV	ultra violet		



Dye molecules also could increase the  $\text{Fe}^{2+}$  regeneration by absorbing light during dye degradation [11].



As the solar spectrum is wide, it will not be fully used for one purpose. Hybrid systems were constructed and studied to improve the utilization efficiency of solar energy. For example, photovoltaic-thermal hybrid systems (PVT) simultaneously produced electricity and hot water [12,13]. Regarding the use of the solar spectrum, a solar water disinfection reactor integrated with a photovoltaic module was constructed since UV spectrum was mainly used for bacterial disinfection and the visible and near infrared parts were preferred by silicon cells [14,15]. The water layer on the PV module absorbed the UV and far infrared light and reduced the solar cell operating temperature. Vivar et al. [16–18] also constructed hybrid devices that integrate photocatalysis reactors and PV modules for wastewater treatment. Although the system could realize automatic operation, the output power was significantly decreased mainly because of the scattering and absorption of the suspended  $\text{TiO}_2$  in the water layer on the PV module.

Different from using Ultraviolet A (UVA) lamp, using solar light in SPF reaction is environmentally friendly and much more economical. The same as  $\text{TiO}_2$  photocatalytic oxidation, SPF process mainly uses the UV and near UV parts of the solar spectrum. Aside from the enhancement of light, the reaction rate would be improved as the temperature increased within a certain temperature range [19]. Wastewater temperature would increase in sunlight as it absorbs the far infrared spectrum. On the other hand, it is different with  $\text{TiO}_2$  photocatalysis, since SPF is a homogeneous reaction and the transmittance of visible and near infrared spectrums that can be used by PV panels is higher. It would be more suitable to integrate a SPF reactor with a PV panel into a single unit. However, this type of hybrid system combining solar photo-Fenton and photovoltaics has not been studied.

The main dyes that correspond to azo compounds account for about 70% of the world dye production [20]. Azo dyes contain one or various azo groups ( $-\text{N}=\text{N}-$ ) attached to aromatic systems with lateral  $-\text{OH}$  and  $-\text{SO}_3\text{H}$  groups [21]. Anthraquinone dyes are also widely used in the textile industry. However, relatively fewer studies dealing with decolorization of wastewater containing Anthraquinone dyes have been conducted [22]. Triphenylmethane dyes are most commonly used for dyeing cotton, silk, paper, bamboo, and leather [23]. Therefore, azo dye Acid Red 26 (AR26), anthraquinone dye Reactive Blue 4 (RB4) and triphenylmethane dye Malachite Green (MG) were chosen to study the performance of the hybrid system during this study.

The main purpose of this work is to construct a hybrid system that integrates a SPF reactor with a PV panel for treating dye

wastewater and generating electricity simultaneously. To our knowledge, it is the first instance of integrating solar photo-Fenton with photovoltaics in this style. The hybrid system could use the entire solar spectrum. Photochemical reactions could be activated by solar UV/near UV photons. The visible and near infrared spectrums was used by the PV panel. Thermal reactions involved in the ferric ion reduction by absorbing the far infrared spectrum [24].

Both light and temperature would influence the photo-Fenton reaction when the wastewater was treated outdoors. The impacts of light and temperature on SPF were investigated with a lab-scale solar simulator under controlled conditions. The iron concentration used was below the discharge limit to reduce the costs of the iron removal process during the experiments. The photovoltaic and decolorization performance of the hybrid system was tested under actual climatic conditions in Tianjin, China.

## 2. Materials and methods

### 2.1. Reagents

In order to simulate organic pollutants, AR26 (CAS: 3761-53-3, chemical formula:  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_7\text{S}_2$ , MW: 480.42,  $\lambda_{\text{max}}$ : 505 nm, supplied by Tokyo chemical industry Co., Ltd.), RB4 (CAS: 13,324-20-4, chemical formula:  $\text{C}_{23}\text{H}_{14}\text{Cl}_2\text{N}_6\text{O}_8\text{S}_2$ , MW: 637.43,  $\lambda_{\text{max}}$ : 598 nm, supplied by Runtai company China) and MG (CAS: 569-64-2, chemical formula:  $\text{C}_{23}\text{H}_{25}\text{N}_2\text{Cl}$ , MW: 364.91,  $\lambda_{\text{max}}$ : 618 nm, supplied by Yuanli company China) were selected.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$  (35% w/w) and reagents ( $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$ ) used for adjusting pH were purchased from Jiangtian company China. All chemicals used during the study were analytical grade.

### 2.2. The lab-scale experimental device

The lab-scale experiments were performed with the device as Fig. 1 shows. Light was provided by a solar simulator equipped with a 6000 W xenon, ozone-free lamp, emitting 5.6% photons in 280–400 nm range. The global irradiance and UV irradiance were 830 and 47  $\text{W}/\text{m}^2$  respectively measured by global radiometer (300–3000 nm) and the UV radiometer (280–400 nm). The reactor was a double-wall cylindrical reactor made of borosilicate glass (height: 15 cm, outer diameter 18 cm, inner diameter 14 cm, effective exposed surface 153.86  $\text{cm}^2$ ). The water temperature was controlled with a thermostat (LS27-1000, accuracy:  $\pm 0.5\%$ , Jiale company, China). 1 L wastewater was agitated with a magnetic stirrer during the indoor experiments.

### 2.3. The hybrid system performed outdoors

The main part of the hybrid system is the absorber which was fabricated by integrating a rectangular channel with a dimension of 515 × 459 × 16 mm on a mono-crystalline silicon solar cell as

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