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CONCISE OVERVIEW OF PHOTOCATALYTIC FUEL CELL TECHNOLOGY FOR THE GENERATION OF ELECTRICITY AND DEGRADATION OF ORGANIC WASTEWATER

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Abstract – *With the increase in population the need of present generation increases which eventually results in increase in wastewater generation. Water pollution has adverse effects on all life forms so there are many treatment processes that are being employed to treat these pollutants. Wastewater contains various organic compounds (such as fatty acids, amino acids, and carbohydrates, etc.) that have a significant amount of chemical energy. Considering this fact, the Photocatalytic Fuel Cell (PFC) can provide a new approach in developing technology for simultaneous organic pollutants removal from wastewaters and power generation, but it also has disadvantages, such as requires more cost and complexity. To present a concise overview of the current state of the development and progress in this treatment process this study is done. This review discussed the study covering PFC aspects, with a focus on the working mechanism of photocatalytic fuel cell, pollutant degradation, power generation, different photoanode and photocathode materials as well as the application of the Fenton process in PFCs and further scope of this technology.*

Key Words: **Photocatalysis, Photocatalytic fuel cells, Pollutant degradation, Electricity generation, Fenton PFC**

1. INTRODUCTION

Conventional water and wastewater treatment processes are not effective in removing and/or degrading a number of pollutants. An efficient solution to overcome this challenge is to add an additional unit of advanced oxidation processes (AOPs) to conventional water treatment equipment (Liu et al., 2019[7]). Advanced Oxidation Processes (AOPs) including three photochemical technologies namely, UV-Ozonation, UV-Peroxidation with hydrogen peroxide and Photocatalysis are very effective. However, the high cost of generation of ozone and hydrogen peroxides promotes the use of Photocatalysis. On the other hand, the organic compounds in sewerage can be used as sources of carbon and energy that can be applied. The Photocatalytic Fuel Cell (PFC) is a successful scheme for wastewater treatment and synchronous recovery of chemical energy from the wastewater (Lee et al., 2018[5]). The non-selective properties of the photocatalyst lead to the degradation of an extensive range of pollutants such as dyes, antibiotics, heavy metal ions, alcoholic compounds and removal of toxicity.

1.1 Photocatalysis

Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In catalyzed photolysis, light is absorbed by an adsorbed substrate. In photo-generated catalysis, the photocatalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (e.g. hydroxyl radicals: OḢ) able to undergo secondary reactions. Change in the rate of a chemical reaction or its *initiation* under the action of ultraviolet, visible or infrared radiation in the presence of a substance – *the photocatalyst* –that absorbs light & is involved in the chemical transformation of the reaction partners. Chlorophyll of plants is a typical natural photocatalyst.

1.1.1 Mechanism of photocatalysis

On the absorption of UV radiation from sunlight the electron of VB becomes excited. Excess energy of this electron promotes the electron to CB which leads to creation of negative-electron (e^-) & positive-hole (h^+) pair. These electron and hole reach the surface of photocatalyst and oxidizes the substances.

2. OBJECTIVES OF OVERVIEW

- To study basic process of Photocatalysis and its amalgamation to fuel cell.
- To study mechanism of degradation of wastewater pollutants by photocatalysis and generation of electricity by PFC.
- To study the performance of PFC in dye degradation and simultaneous electricity generation.
- To study the Fenton-PFC hybrid model for improvement of PFC.

3. PHOTOCATALYTIC FUEL CELL

The PFC needs a photoanode carrying photocatalyst and light radiation (LR) to generate electrons (e^-) to decompose organic pollutants and generate power. The radiation energy should be higher or equal to the photocatalyst energy band. The UV irradiation of the anode detaches the photo generated e^- and h^+ as on receiving energy more than band gap the

electrons of valence band excites and jump to conduction band and leaves a hole in valence band.

The hole generates oxidizes the organic compounds to simpler form by formation of hydroxyl ions. For power generation, due to the organic compounds' decomposition in the anode, e^- are provided and transmitted to the cathode by means of an external circuit. The hydrogen ions generated by the photo-oxidation process are transferred to the cathode by diffusion using a proton exchange membrane (PEM). Oxygen is provided at the cathode and the transferred e^- react with O_2, thus resulting in water or superoxide radicals.

In dual photoelectrode PFC unit both electrodes are of photocatalytic material such as $BiVO_4$ photoanode and Cu_2O/Cu photocathode (He et al., 2020[14])

The various reactions at the cathodes and anodes which take place in fig. 1 are as follows(Lee et al., 2018[6]):

- **Photo excitation of photocatalyst:**

$$Photocatalyst + h_v \rightarrow h^+ VB + e^- CB \quad (1)$$

- **Generation of OḢ**

$$h^+ VB + OH^- \rightarrow O\dot{H} \quad (2)$$

$$h^+ VB + H_2O \rightarrow O\dot{H} + H^+ \quad (3)$$

- **Redox reactions**

$$h^+VB + Organics \rightarrow Organics^{\cdot +} \quad \text{(oxidation of organics)} \quad (4)$$

$$O\dot{H} + Organics \rightarrow Organics^{\cdot} \quad \text{(degradation of organics)} \quad (5)$$

$$Organics^{\cdot} + O_2 \rightarrow Organics - OO^{\cdot} \quad \text{(degradation of organics)} \quad (6)$$

$$O_2^- + Organics^{\cdot} \rightarrow Organics - OO^{\cdot} \quad \text{(degradation of organics)} \quad (7)$$

$$e^- + Organics \rightarrow Organics^{\cdot} \quad \text{(reduction of organics)} \quad (8)$$

$$Organics^{+\cdot} \rightarrow Organics^{++} + e^- CB \quad \text{(injection of electron in the CB)} \quad (9)$$

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O \quad (10)$$

$$2H_2O + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (11)$$

- **Generation of Superoxides:**

$$e^- CB + O_2 \rightarrow \dot{O}_2^- \quad (12)$$

$$e^- + O_2 \rightarrow \dot{O}_2^- \quad \text{(reaction at the cathode)} \quad (13)$$

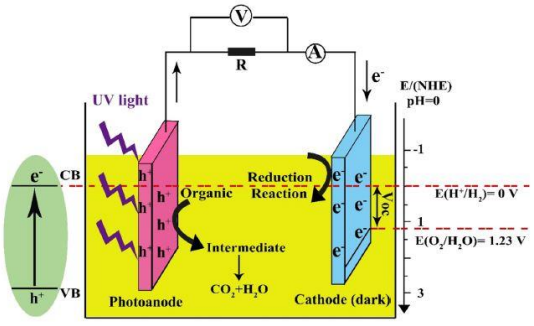

Fig. 1: Schematic illustration of the working principle of a PFC system based on photoanode and cathode.
Source: *Lee et al.(2018)*

4. POLLUTANT DEGRADATION

Water pollution has adverse effects on all life forms so there are many treatment processes that are being employed to treat these pollutants. Wastewater generally consists of water that has been utilized in some capacity that negatively impacts the quality of water. Common constituents of wastewater are nutrients (P, N_2 & C), organic and inorganic compounds, refractory organics, and heavy metals, dissolved inorganic. Among the various technologies the PFC system has been approached to treat a wide range of colored wastewater containing organic matter.

Based on PFC mechanism (Eqs. (1)-(13))when a photoanode is irradiated by light energy, the photogenerated electrons of the photocatalyst will be excited from valence band (VB) to the conduction band (CB)(Eq. (1)) and then flow to cathode through external circuit and hence electricity generated. At the same time, the photogenerated holes at photoanode will be reacted with water molecules or hydroxide ions (OH^-) to form hydroxyl radicals (OḢ) (Eq. (2) and (3)). Hence, the produced OḢ radicals can oxidize the organic pollutants to the mineral end-products (Eq. (4)-(11)). Thus when a wastewater is subjected as a fuel in PFC the simultaneous oxidation of the various organic or inorganic pollutants occur at the photoanode by the hydroxyl ions and superoxide anions, as shown in fig. 2.

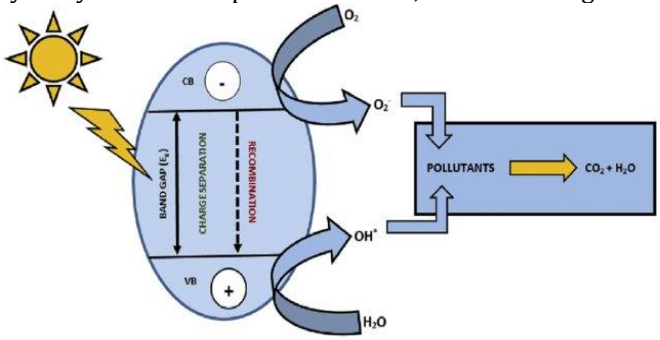

Fig. 2 : Mechanism of pollutant degradation by photocatalyst. *Source: Srikanth et al. (2017)*

5. ELECTRICITY GENERATION

Under Light radiation, the e^- and h^+ of a photocatalytic semiconductor are separated and a photo-voltage is created. The photo-generated h^+ and e^- are the major cause of oxidation and reduction in the n-type and p-type semiconductors.

In order to ensure that the photo-generated e^- would be excited from the photocatalyst VB to the CB, light energy incident on photocatalyst should be more than or equal to the band gap energy of semiconductor. The potential discrepancy between the Fermi levels of two electrodes creates the driving force that causes e^- transfer from photoanode to the cathode.

The h^+, which have strong oxidability to decompose different organics, react with the organic pollutants to oxidize and degrade them to CO_2, e^- and protons ($C_xH_yO_z + O\dot{H} \rightarrow CO_2 + H^+ + e^-$) (Lee et al., 2018). At the same

time, the e^- generated from photocatalysis and oxidations of organics at the photoanode side are transferred to the cathode side, generating electricity in PFC unit.

6. PFC AND FENTON PROCESS

The most important constraints of PFCs are the radical reactions taking place on the photoanode and photocathode surfaces. However, the surface area cannot be significantly enlarged, which is a serious constraint on PFCs in the degradation of organic pollutants (Zhao et al., 2017[17]). The combination of hydrogen peroxide and UV radiation with a Fe^{2+} or Fe^{3+}ion produces more hydroxyl radicals and in turn, it increases the rate of degradation of organic pollutants. Such a process is known as the photo-Fenton processes.

The PFC system can generate its external voltage through the self-bias between photoanode and cathode. If ferrous ions are added, a self-bias Fenton-PFC system will be created to decompose organic pollutants and simultaneously produce power. The mechanism of pollutant removal in the hybrid Fenton-PFC system is as follows (Nordin et al., 2017[11]):

At PFC anode

$Photocatalyst + h_v \rightarrow anode\ (h^+ + e^-)$ (14)

$h^+ + Reactant \rightarrow Oxidized\ product$ (15)

At Fenton cathode

$2H^+ + O_2 + 2e^- \rightarrow H_2O_2$ (16)

At Fenton anode

$Fe \rightarrow Fe^{2+} + 2e^-$ (17)

At PFC cathode

$4H^+ + O_2 + 4e^- \rightarrow 2\,H_2O_2$ (18)

Overall Fenton process

$Fe^{2+} + H_2O_2 \rightarrow O\dot{H} + OH^- + Fe^{3+}$ (19)

It can be concluded that the hybrid Fenton-PFC system is a promising technology for organic pollutants removal and generating electricity simultaneously. In this hybrid system, PFC is employed to produce e_ to produce H_2O_2 electrons as Fenton's reagent. Generally, the unique features of the hybrid Fenton-PFC system result in a fast and stable catalytic system with excellent efficiency (Nordin et al., 2017[11]).

7. RESULTS FROM THE CASE STUDIES

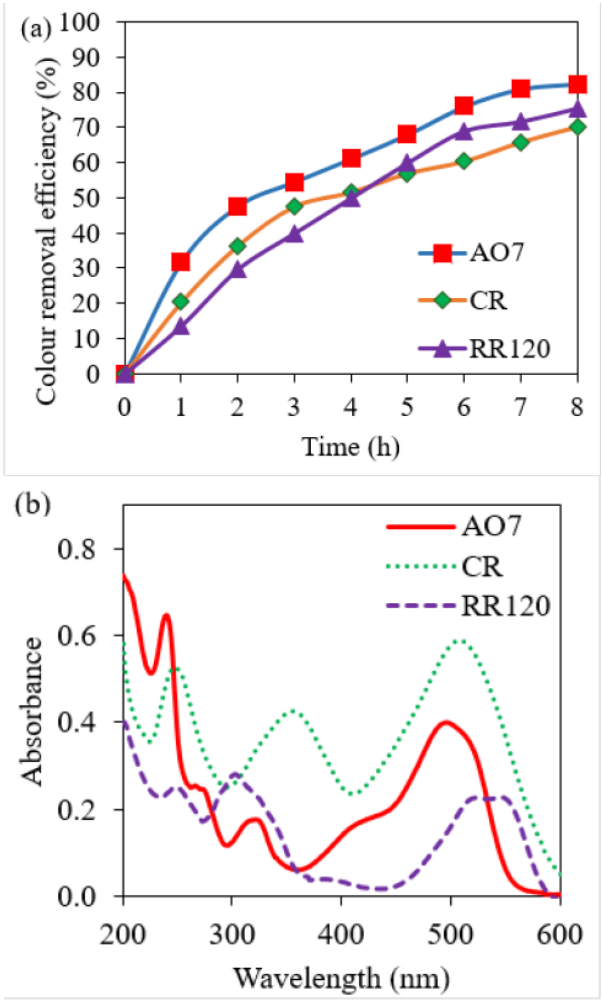

Fig. 3: (a) Color removal efficiency and (b) UV-Vis spectra of different dyes

Source: Ong et al. (2020)

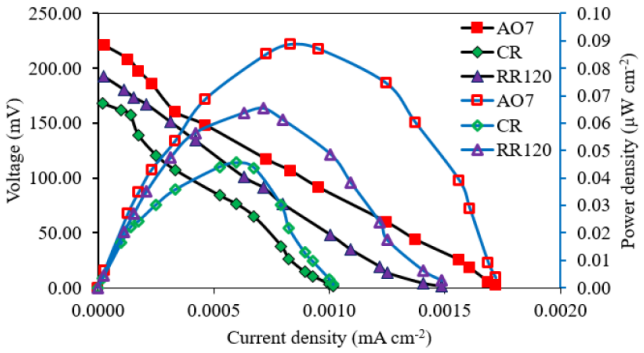

Fig. 4 : Polarization curve for different dyes in PFC.

Source: Ong et al. (2020)

From the experimental results obtained from the study done by Ong et al. [15] for degradation of azo dyes with zinc oxide loaded carbon plate (ZnO/C) photoanode and carbon plate cathode under irradiation of UVA light, it can be observed that

- the color removal efficiency of the acid orange (AO7), congo red (CR) and reactive red 120(RR120) is 82.43%, 75.42% and 70.10%, respectively (Fig. 3(a)). The lower decolorization of CR might be due to the high adsorption of light by CR itself compared to RR120 (Fig. 3(b)).
- the open circuit voltage, VOC for AO7, RR120 and CR was 220.50, 192.70 and 167.80 mV, respectively and AO7 exhibited the highest electricity performance among all the dyes.
- The photocatalytic fuel cell with AO7 as sacrificial agent was able to perform 82.43% of decolorization efficiency, a maximum short circuit current (JSC) of 0.0017 mA cm^{-2} and maximum power density (Pmax) of 0.0886 µW cm^{-2}

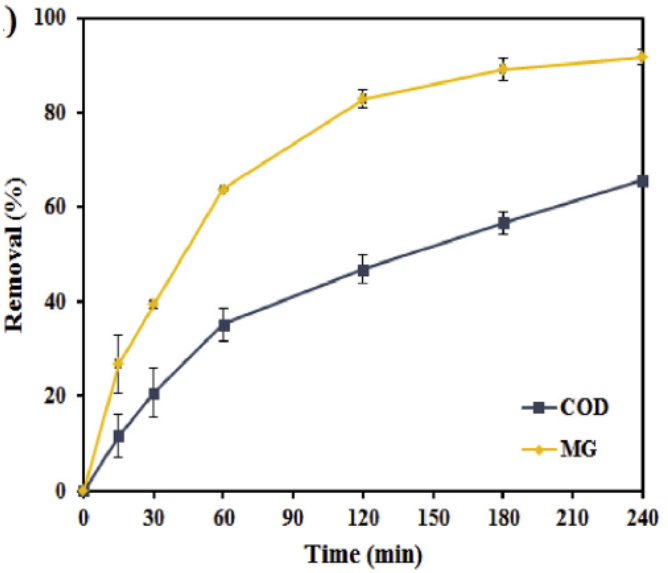

Fig. 5 : MG degradation and COD removal over irradiation period in the real greywater PFC.
Source: Kee et al. (2018)

From the experimental results obtained from the study done by Kee et al.[10] for degradation of methyl green in synthetic and real grey water effluents with ZnO/Zn photoanode and CuO/Cu photocathode, it can be observed that

- COD, BOD_5 removal efficiency are 55% while that of turbidity and nitrogen are 88% and 75% respectively.
- MG degradation and COD removal over irradiation period also increases in the real greywater.
- the low initial BOD_5/COD ratio of 0.10 was improved to 0.98
- experiments using Vigna radiate seeds indicated the reduction of phytotoxicity from 16.2% to 4.4% after the PFC treatment.

Parameter	Unit	As-collected greywater	After 4h of UV irradiation	Removal efficiency (%)
COD	mg L^{-1}	1325	598	55
BOD_5	mg L^{-1}	133	58	55
Turbidity	NTU	242	28.2	88
NH_3-N	mg L^{-1}	4.9	1.25	75
pH		9.76	6.05	

Table 1: Measured real water parameter before and after treatment with PFC

Source: Kee et al. (2018)

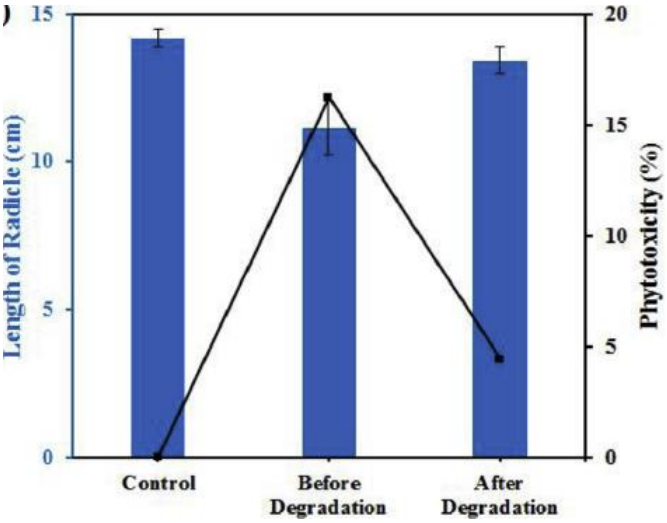

Fig. 6: Phytotoxicity before and after PFC treatment.
Source: Kee et al. (2018)

8. CONCLUSIONS

The following conclusions were drawn:

- The photocatalysis mechanism when combined with fuel cell unit results in a revolutionary technology of Photocatalytic Fuel Cell.
- The performance of PFC is usually specified by the electrodes for different type of organic wastewater. Electrodes based on nanomaterials can lead to enhance efficiency of the degradation of organic contaminants and energy performance.
- The photocatalytic fuel cell with AO7 as sacrificial agent was able to perform 82.43% of decolorization efficiency, a maximum short circuit current (JSC) of 0.0017 mA cm^{-2} and maximum power density (Pmax) of 0.0886 µW cm^{-2} and with the PFC the BOD_5/COD ratio improve to 0.98.
- In the hybrid PFC-Fenton system, as a result of the introduction of ferrous ions into the PFC to strengthen the radicals reaction and promote $O\dot{H}$ production, the

performance of the system is improved for both degradations of pollutant and power production.

This PFC technology is still in embryonic stage and still requires great research in this field to make its application in advanced treatment of wastewater with sustainable energy generation.

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