



Hybridization of photocatalytic fuel cell with oxygen nanobubbles: A synergistic approach for energy-efficient degradation of azo dye

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ABSTRACT

Advanced oxidation processes (AOPs) are currently being extensively studied, specifically photocatalytic fuel cells (PFCs) and nanobubble technology. However, the performance of PFC decreases at higher pollutant concentrations. Hence, this study investigated the hybridization of PFC and oxygen nanobubbles (PFC/O₂NBs) for treating azo dye wastewater. Four key parameters: contact time, initial concentration, pH, and light intensity were optimized using methyl orange as synthetic azo dye. Meanwhile, oxygen nanobubbles (O₂NBs) were analyzed using a Zetasizer Nano, and the bubble size was confirmed to be in the range of 49.3 to 387.9 nm, with moderate stability (ζ -potential = -11.4 to -15.0 mV). Results showed that the individual PFC achieved 69.1% removal efficiency under optimized conditions, whereas O₂NBs showed complete degradation (100%) under optimum conditions of 3 h, due to enhanced DO levels (66%). The hybrid PFC/O₂NBs system exhibited much greater performance, achieving complete degradation (100%) within 10 min with 34% increase in DO concentration. In addition, the hybrid PFC/O₂NBs system demonstrated higher electricity generation ($P_{\max} = 139.201 \mu\text{W cm}^{-2}$) and improved energy efficiency, with significantly lower energy consumption ($E_{\text{EO}} = 2.53 \text{ kWh}\cdot\text{m}^{-3}\cdot\text{order}^{-1}$) compared to the individual systems. The synergistic index further confirmed the superior performance, with contact time showing the highest ($f = 24.11$).

1. Introduction

Industries such as textiles and food processing generate large volumes of wastewater containing persistent organic pollutants [1,2]. Among these, azo dyes are of major concern due to their chemical stability and resistant to biodegradation [3]. Their persistent, colour intensity and potential toxicity highlight the need for more robust and energy-efficient treatment technologies beyond conventional methods [4,5].

Conventional methods for the treatment of organic wastewater commonly rely on biological processes such as aerobic and anaerobic digestion. However, various physicochemical and catalytic technologies, including photocatalysis, electrocatalysis, and electrocoagulation, have also been widely explored for the degradation of organic pollutants. Despite their effectiveness, biological treatments are often limited by long retention times with large volumes of recalcitrant organic compounds at low pH [6]. In photocatalytic systems, Zhong et al. [7] reported that a hollow optical fiber TiO₂ photocatalytic system showed good photocatalytic activity for synthetic wastewater degradation.

However, the system was temperature-dependent (20–55 °C), indicating that additional energy input is required to maintain the operating conditions, which may increase operational costs for large-scale applications.

These limitations have driven growing interest in non-conventional treatment systems, particularly advanced oxidation processes (AOPs), which rely on the in-situ formation of highly reactive species capable of degrading organic pollutants [8]. Hydroxyl radicals ($\bullet\text{OH}$) with a redox potential of $\sim 2.8 \text{ V}$, are particularly effective due to their rapid, short-lived, and non-selective reactivity [9–11], making AOPs a promising route for dye degradation.

In recent years, sustainability and energy recovery have become central to wastewater treatment research. Photocatalytic fuel cells (PFCs) provide dual functionality by degrading organic pollutants at the photoanode while simultaneously generating electricity. During operation, dissolved oxygen (DO) participated in the oxygen reduction reaction (ORR) at the cathode to facilitate electron transfer. However, traditional undoped PFC systems often suffer from oxygen and photon limitations, insufficient oxygen availability, slow ORR kinetics, and

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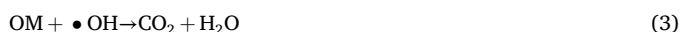
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reduced light penetration at higher pollutant concentrations, which limits the $\bullet\text{OH}$ generation, lower removal efficiencies and power output [12,13].

To overcome oxygen limitations, previous studies have incorporated macrobubbles aeration, which improved DO levels and overall PFC performance [14,15]. Nevertheless, macrobubbles quickly rise and burst at the water surface [16–18], resulting in low gas-liquid contact time and inefficient oxygen transfer. Nanobubbles (NBs), with diameter $< 1 \mu\text{m}$, provide a distinct advantage. Due to their negative surface charge and interfacial stability, they remain suspended for extended periods [19–21]. As a result, oxygen nanobubbles (O_2NBs) can maintain elevated DO levels with significantly higher oxygen transfer efficiency than conventional aeration.

Moreover, nanobubbles have emerged as physical AOP, where reactive oxygen species (ROS) are generated through interfacial processes and bubble collapse [22,23], without requiring external chemical reagents. As a result, O_2NBs alone have been demonstrated to degrade organic pollutants [24–26].

When introduced into photocatalytic systems, nanobubbles indirectly enhance reactive oxygen species (ROS) formation by sustaining oxygen availability during electron transfer reactions. At the PFC cathode, dissolved O_2 derived from O_2NBs participates in the two-electron ORR pathway to form hydrogen peroxide (Eq. (1)) which may subsequently decompose into $\bullet\text{OH}$ radicals and oxidize organic matter (Eqs. (2) and (3)).



This mechanism suggests that nanobubble aeration may enhance pollutant degradation and electricity generation when integrated with PFCs. While nanobubbles have been coupled with photocatalysis, ozonation and microbial fuel cell [23,26,27], to best of our knowledge, no prior studies have reported the integration of nanobubbles with PFCs. Establishing this synergy is scientifically relevant because it may simultaneously address oxygen transfer limitation and photon-limiting effects at higher pollutant concentrations.

In addition, energy consumption metrics such as electric energy per order (E_{EO}) has remained largely unreported for both standalone PFCs and nanobubbles systems. E_{EO} is a critical figure of merit for assessing the viability and scalability of emerging AOPs, where a lower E_{EO} corresponds to higher removal efficiency [28,29]. This absence of such energetic evaluation represents a significant research gap.

In this work, oxygen nanobubbles (O_2NBs) were integrated into a ZnO/Zn PFC system. It is hypothesized that nanobubbles will overcome oxygen and photon limitation at higher pollutant concentrations by improving oxygen mass transfer, sustaining ORR pathways and enhancing radical generation, thereby synergistically increasing both removal efficiency and power output.

Therefore, this study aimed to:

1. Optimize the performance of standalone PFC, standalone O_2NBs and hybrid PFC/ O_2NBs systems based on their methyl orange removal efficiencies; and
2. Evaluate the energy performance (E_{EO} and power output) of all systems.

2. Materials and methods

2.1. Chemicals

Commercial zinc oxide (ZnO, 99.92% purity) powder and methyl orange (MO, $\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$, M.W. = 327.33 g/mol) were obtained from Bendosen. Ethanol (99% purity), sulfuric acid (98% purity), and

sodium hydroxide (1 mol L^{-1} aqueous solution) were also supplied by Bendosen. Zinc foil (99.999%) and platinum (Pt) wire (99.99%) were purchased from BDH Limited (England). All chemicals were analytical grade and used without further purification, and all solutions were freshly prepared using distilled water.

2.2. Fabrication of ZnO/Zn photoanode

The ZnO/Zn photoanode was prepared using a heat-attachment method [31] with a slight modification. A zinc plate ($5.0 \text{ cm} \times 2.0 \text{ cm}$, 0.38 mm thickness, 99.999% purity) was ultrasonically cleaned in 100 mL ethanol solution and rinsed with distilled water. A ZnO suspension was prepared by adding 1.0 g of commercial ZnO powder in 100 mL of distilled water, in which the cleaned Zn plate was immersed and ultrasonicated (Daihan Scientific, WUC-D03H) for 2 h. The coated plate was then oven-dried (Protech Lab Dryer, Model BS-100) for 24 h at 90°C , rinsed with distilled water to remove any loose particles, and annealed in a furnace (Elite Thermal Systems Ltd., Model: Economy chamber furnace; Temp. controller: Eurotherm 2216e) at 300°C for 1 h. The prepared ZnO/Zn photoanode was stored at room temperature prior to use. Fig. 1 shows the overall preparation process of the fabrication of ZnO/Zn photoanode.

2.3. Experimental setups

2.3.1. Photocatalytic fuel cell (PFC) system

The PFC system (Fig. 2a) was adapted from [13] with slight modifications. The set up consists of a fabricated ZnO/Zn photoanode and a platinum (Pt) wire cathode ($5.0 \text{ cm} \times 2.0 \text{ cm}$) positioned 5 cm apart in 500 mL of MO solution (10 mg L^{-1}), with 1.0 g NaCl added as supporting electrolyte. The initial pH was adjusted to 2. The cathode was aerated using an air pump (SOBO, China; Model: SB222; 5 W) under ambient lighting (98 lx) and voltage was recorded using a voltmeter (XEOLE, China; Model: XL830L) across a $10,000 \Omega$ resistance. Polarization curves and maximum power density were obtained by varying the resistance between 1 and $90,000 \Omega$ (Shanghai Domo, Model: ZX21D).

2.3.2. Oxygen nanobubbles (O_2NBs) system

Oxygen nanobubbles were generated in 500 mL MO solution using an O_2 Grow emitter (O_2 Grow U.S., 2010) (7 W titanium-mesh electrolytic device) (Fig. 2b). Similar to the PFC system, 1.0 g NaCl was added as supporting electrolyte.

2.3.3. Hybrid PFC/ O_2NBs setup

In the hybrid system (PFC/ O_2NBs), the aerator (air pump) in the PFC setup was replaced by the nanobubble generator (O_2 Grow emitter) as shown in Fig. 2c, allowing simultaneous photocatalysis and nanobubble generation. All initial conditions followed those described in Section 2.3.

2.4. Characterizations of ZnO/Zn photoanode

Surface morphology before and after fabrication was characterized using field emission scanning electron microscopy (FE-SEM) (JEOL, Japan, Model: JSM-IT500HR) at $1000\times$ and $10,000\times$ magnification and 10 kV accelerating voltage. Elemental composition of the formed ZnO layer was confirmed by energy-dispersive X-ray spectroscopy (EDX).

2.5. Characterization of oxygen nanobubbles

Nanobubble size distribution was analyzed by dynamic light scattering (DLS) technique using a Zetasizer Nano ZS (ZEN3600, Malvern instrument) after generating bubbles in 500 mL distilled water containing 1 mM NaCl to enhance conductivity [32]. Samples were collected after 10 min and 60 min of bubbling. Measurements were conducted at 25°C with a backscatter angle of 173° . Zeta potential was determined using the same instrument with a U-shaped capillary