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## Review

## Current advances of VOCs degradation by bioelectrochemical systems: A review

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## ABSTRACT

The volatile organic compounds (VOCs) impose severe environmental issues such as haze, photochemical smog, ozone depletion, and global warming. The degradation of VOCs in the gas phase is determined by the gas-liquid mass transfer and/or the microbial activity depending on the properties of the VOCs such as solubility, bioavailability, and toxicity. Bioelectrochemical systems (BESs), integrating microbial-electro-chemical removal mechanisms, have been intensively investigated for the organic compound removal in wastewater. In BESs, the interaction between the microbes and electrodes facilitates the electron transfer rate during the organic compound degradation and hence have a great potential to enhance the microbial activity. Currently, BESs are also under development for the refractory VOCs removal both in the liquid phase and gas phase. This review summarizes the current advances of the VOCs removal by BESs in terms of the mechanisms, pathway, removal efficiency, and coulombic efficiency. Furthermore, the challenges and future perspectives on the development of the efficient BESs for VOCs removal with a high coulombic efficiency are briefly discussed. It is believed that this review provides a new insight into the biological removal of VOCs.

## 1. Introduction

Volatile organic compounds (VOCs) with a boiling point ranging from 50 to 250 °C have been regarded as a contributor of haze, photochemical smog, ozone depletion, and global warming [1–6]. In 2015, China emits 31.12 million tons of VOCs. The typical industrial sources, such as chemical plant, pharmaceutical plant, waste water treatment plant, adhesives production, petrochemical plant, and miscellaneous storage tanks, account for approximately 50% of the total emissions in China [7,8]. It features multiple compositions, wide concentration ranges, and significant fluctuation in the gas flow rate [9,10].

To control VOCs emissions, Chinese government listed the VOCs as one of the four main air pollutants in 2010 [11]. In 2015, the government charged the emission fees from petrochemical and printing industries. In addition, the government aims at reducing VOCs emissions from the typical regions and industries by 10% compared to those in 2015 during the Chinese 13th Five-Year Plan (2016–2020).

Driven by the stringent emission standards, various technologies, including condensation, membrane, absorption, adsorption, thermal

combustion, catalytic combustion, non-thermal plasma, and biotechnology have been proposed for VOCs removal [1]. Biotechnology is regarded as a cost-efficient and green process [12–14]. Generally, the gaseous VOCs are removed by the biotechnologies as follows: 1) gas-liquid mass transfer of VOCs into liquid phase; 2) diffusion of VOCs into the biofilm, and 3) degradation of VOCs by the microorganisms in the biofilm. Therefore, the performance of the gaseous VOCs removal by the biotechnologies is limited by gas-liquid mass transfer of VOCs, its microbial degradation, or both of them depending on the properties of the treated VOCs. For the hydrophobic VOCs (Henry's low constant:  $H_c = C_g/C_l$  ranging from 1 to 70), their removal efficiency is mainly controlled by the mass transfer limitation, whereas, for the hydrophilic VOCs ( $H_c$  ranging from 0.0001 to 0.099) [15], the microbial activity plays a more important role. For moderately hydrophilic VOCs ( $H_c$  ranging from 0.1 to 0.99), both mass transfer limitation and microbial activity determine their removal efficiency [16,17].

To address the mass transfer issue, various bioreactors have been developed for the VOCs removal [18–21]. The advances of the mechanism and kinetics of the conventional bioreactors, such as biofilters,

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biotrickling filters, and bioscrubbers, for VOCs removal have been well documented in the literatures [22,23]. The packing materials with a specific high surface area can facilitate the gas-liquid mass transfer and provide a high biomass loading, facilitating the VOCs removal. In general, the biofilter and biotrickling filter are promising for the removal of hydrophilic VOCs as the bioreactors with biofilm possess a high biodegradation rate. However, for the hydrophobic VOCs, the mass transfer of VOCs from the gas phase to liquid phase is slow due to their high Henry's law constant, resulting in a low bioavailability of VOCs to biofilm [24]. In addition, the biodegradability of the hydrophobic VOCs is slower compared with the hydrophilic counterparts. Therefore, the conventional bioreactors exhibit a low removal efficiency for the hydrophobic VOCs [25].

Subsequently, two-phase partitioning bioreactors (TPPBs) are under development to enhance the mass transfer of the hydrophobic VOCs [26]. TPPBs employ a non-aqueous phase (NAP) to facilitate the mass transfer of the hydrophobic VOCs. Typically, the NAPs comprise of the liquid solvent such as n-hexadecane, perfluorocarbons, silicone oils or ionic liquid and solid adsorbent such as polyurethane, vinyl acetate and ethylene copolymers, styrene/butadiene triblock copolymer, or dimethylsiloxane polymer [15]. The selection of the NAPs depends upon the properties of the VOCs. Compared with the solid NAPs, the specific drawbacks of TPPBs with liquid NAP in VOCs removal were foaming, NAPs adhesion to reactor internals, and emulsification [15]. However, the employment of the solid NAPs not only increase the energy consumption because of stirring. Moreover, the NAPs toxicity to the microorganisms may also retard its practical application [27]. The mass transfer and degradation mechanisms of VOCs in TPPBs have been summarized in the literatures [15,28]. Overall, based on the literature data, the TPPBs outperform the conventional bioreactors for the hydrophobic VOCs removal [29,30].

The bioelectrochemical systems (BESs) are currently regarded as a novel and promising platform for the environmental remediation. As shown in Fig. 1, BESs provide both oxidation and reduction reactions pertained to the anode and cathode chamber which integrate the biological-electrochemical removal mechanisms, resulting in its ability to remove various types of substrates [31]. The electrons transfer between the microorganism and the electrode occurs via the extracellular

electron transfer (EET). In general, the EET is categorized into two main mechanisms: direct electron transfer (DET) and mediated electron transfer (MET). DET requires physical connections between bacteria and the redox active surface, and the diffusion of a mobile electron shuttle to and from the cell is not necessary. The electron shuttle is required to transport the electrons by the MET. Overall, DET-based systems overperform the MET counterparts in term of the electron transfer because the electron transfer path of DET-based system is shorter than the MET, resulting in a lower electron transfer loss, which has been demonstrated in the literature [32–35]. However, the integration of both the inherent DET of exoelectrogens and the MET to enhance the bio-electrocatalysis at electrodes can be one of important strategies to enhance the electron transfer rates [36,37].

Microbial fuel cell (MFC) and Microbial electrolysis cells (MEC) are two typical BESs. MFC, bio-catalyzed electrochemical hybrid systems, converts chemical energy to electricity via a series of redox reactions with the microorganisms [38,39]. Various types of the organic compounds can be used as the fuels for the electricity generation with their simultaneous removal in the MFC, making the MFC eco-friendly [40]. MEC employs the microbes attached at the anode to degrade the organic compound and release electrons which are transferred to the cathode for  $H_2$  production or other reduction reactions [41]. It should be noted that the microbial electrolysis is endothermic and cannot spontaneously occur. Therefore, the external electricity needs to be imposed to initiate the microbial electrolysis reaction [42]. MEC could greatly lower the over potential of electrochemical reactions and thus lead to higher removal efficiencies and rates. As a result, the pollutants removal in MEC consumes less energy compared to the conventional electrochemical process [43].

Currently, MFC and MEC have been also used to facilitate the VOCs degradation. Although the removal of organic compound in the wastewater has been comprehensively documented [31,44,45], none of published review pays special attention to the VOCs degradation by BESs. This review will focus on the current advances and challenges of the VOCs degradation by the BESs. The future perspectives on the development of the efficient BESs for VOCs degradation are briefly discussed.

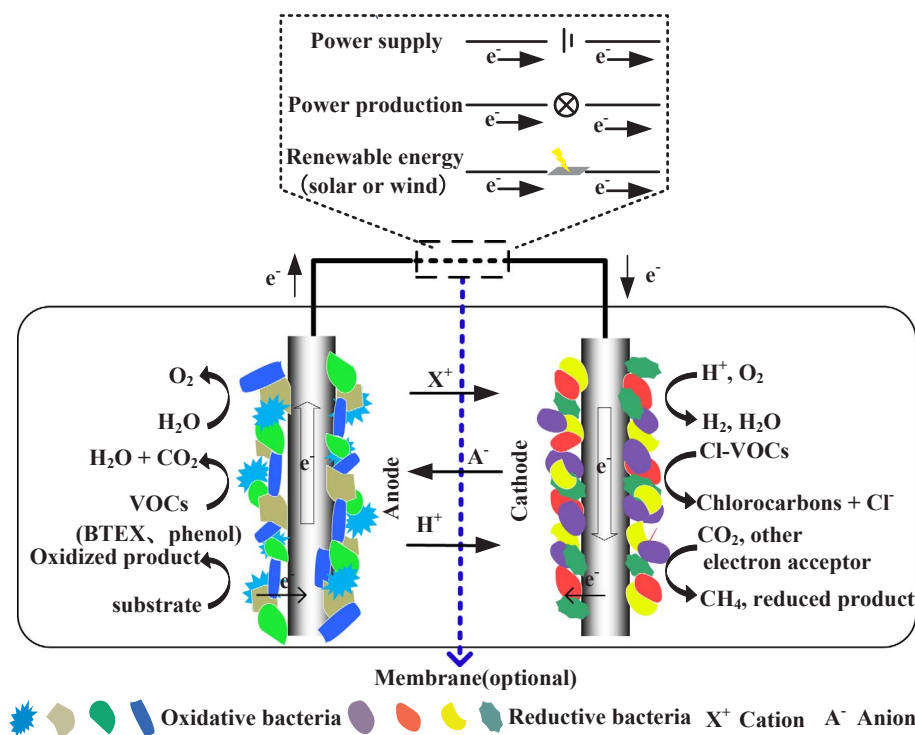


Fig. 1. Microbe–electrode interaction-based microbial bioelectrochemical systems.

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