Bioelectrochemical System Application for Pesticides Removal: A mini-review

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Abstract. The widespread use of pesticides for agricultural purposes results in their presence in the environment. Pesticide occurrence is causing potential negative impacts on human health and environmental deterioration in general. One of the interdisciplinary field to implement a technology for converting and conserving resources is bioelectrochemistry. An integrated system based on bioelectrochemical processes, namely Bioelectrochemical System (BES), has been well developed to date. The application of BES to remove various materials in the bioremediation process has been well established in the combination with diverse technologies. The set up of integrated BES with Granular Activated Carbon (GAC) is one of the promising solutions to enhance the removal of the pesticide in water. The BES in situ has been implemented to remove contaminants in groundwater. This mini-review discusses the recent development of pesticide removal and environmental remediation using bioelectrochemical approaches, offering new insight into the big scope of green technology application.

Keywords: Environmentally friendly, natural attenuation, renewable energy, water remediation

1 Introduction

The necessity of sustainable energy and environmental awareness propels the exploration and development of sustainable bioenergy resources [1]. One of the biotechnological approaches to implementing novel means of converting and conserving resources is the use of Bioelectrochemical Systems (BES) [2, 3]. BES can thereby be utilized to generate bioelectricity from renewable (often waste) carbon sources or to sustainably produce platform chemicals through the interaction of microorganisms with a polarized electrode [4]. Therefore, BES is also a device that can be applied in the bioprocess of platform chemicals conversion [5].

As a bioprocessing system, BES involves microbial whole-cell biocatalysts to drive oxidation and reduction (redox) reactions at solid electrodes [6]. One example of a BES technology is the Microbial Fuel Cell (MFC). In this system, the microorganism catabolizes

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the organic matter and the electron produced from this catabolism reaction will be accepted by the BES anode [7]. To generate electricity, this electron moves through an external circuit to a cathode, where it combines with oxygen and protons to form water [8]. A potentiostatically controlled BES is usually used to simplify the BES study in the laboratory. In general, a potentiostatically controlled BES consists of the working electrode (anode), at which the microbial oxidation processes take place, a counter electrode (cathode), and a reference electrode, which has a stable and well–known electrode potential [9].

The extracellular electron transfer mechanism between microorganisms and electrodes can be differentiated into Direct Electron Transfer (DET) and indirect (mediated) electron transfer [10]. DET involves physical contact of the bacterial redox-active membrane with the anode of the BES, *e.g.* through nanowires and c–type cytochromes. On the other hand, MET involves a redox shuttling compound as the primary electron transfer pathway, which can either be exogenous (artificially added to the system) or endogenous (naturally synthesized by the microorganism) [11, 12].

The use of BES, specifically MFC has shown promising potential in degrading organic matter and generating electricity for wastewater with high loading of organic content or organic substrate with a concentration in a range of hundredth up to thousands mg L^{-1} [13]. However, there were limited studies focused on trace organic compounds, such as pesticides in water with a concentration of one to hundredth µg L^{-1}, to date [14]. In this mini-review, a literature study on BES application to remove pesticides from the water was conducted. Moreover, the use of Granular Activated Carbon (GAC), the common adsorbent media to remove pesticides, as bioanode is discussed.

2 Occurrence of pesticides in water

Pesticides are used in agriculture to control insects, weeds, slugs, and snails. Several countries, either upper-middle– and lower-middle– countries have experienced growth in the intensity of pesticide use, resulting in an increase in pesticide pollution to water [15]. Sometimes, in its application, unwanted residues of pesticides can be washed into water bodies, either to surface water and groundwater, from the soil by rainfall or surface runoff [16]. The widespread use of pesticides results in their presence in raw water in drinking water treatment and in sewage water treatment.

Several pesticides are non-biodegradable compounds, that persist in soil, sediment, and water. Improper selection, use, and management of pesticides may lead to water pollution which ultimately causes carcinogens and other toxic effects on humans and other aquatic biotas [15]. Additionally, pesticides also have the ability to affect biodiversity, by killing weeds, pests, and/or herbs, thereby causing negative impacts on the food chain.

3 Current methods for pesticides removal in water

The treatability of pesticides depends on their physical and chemical properties, such as whether the pesticides are polar or non–polar, are hydrophobic or hydrophilic, and/or are aromatic or aliphatic [17]. Several methods have been developed to remove pesticides in water, including physical, chemical, and biological methods. The most common method to remove pesticides in water is through physical adsorption using Activated Carbon (AC). AC is an organic material with a highly porous structure that is produced through the activation process, making it efficient in adsorbing small–organic compounds in water, such as pesticides [18]. However, some polar pesticides such as metaldehyde are weakly adsorbed to AC, making them poorly removed using conventional adsorption using AC [19].

Advanced Oxidation Processes (AOPs) are considered to be efficient in treating water and wastewater containing pesticides. AOPs involve the generation of highly oxidizing species, such as OH–radicals, which are able to degrade organic substances which may also involve ozonation and UV irradiation [20]. However, incomplete degradation and formation of toxic by-products are some of the limitations of using AOPs [21], making a high dosage of chemicals is sometimes required to remove pesticides and their by-products completely from the water.

The biological method usually performs a complete conversion of pesticides into less harmful end products, making this method is considered to be environmentally friendly [22]. However, this method itself is highly affected by operational conditions, such as the level of the organic loading, pH, temperature, and oxygen level in the system. A combination of chemical oxidation with the biological process to remove pesticides was also being explored as it demonstrated a high removal of 90 % to 100 % for pesticide dethamerthin in 210 min [23].

4 Application of BES for pesticide removal

4.1 The BES application for in situ water remediation

BES can be used as an efficient and cost-effective monitoring device that allows information on microbial respiratory activity and the concentration of substrate or contaminants in contaminated aquifers to be obtained. This process is the concept of applying bioremediation or natural attenuation. The method has been applied in the utilization of organic carbon to stimulate the biodegradative activity of reducing metals bacteria, such as Geobacter. Basically, the system can be used to track the activity of either reducing or oxidizing contaminants by microorganisms that depend on electrodes serving as electron donors or acceptors [24]. A critical review published in 2014 suggested that BES was able to remove recalcitrant pollutants from water, including chlorophenols which is a particular group of chlorinated pollutants that are toxic and difficult to be degraded naturally [25].

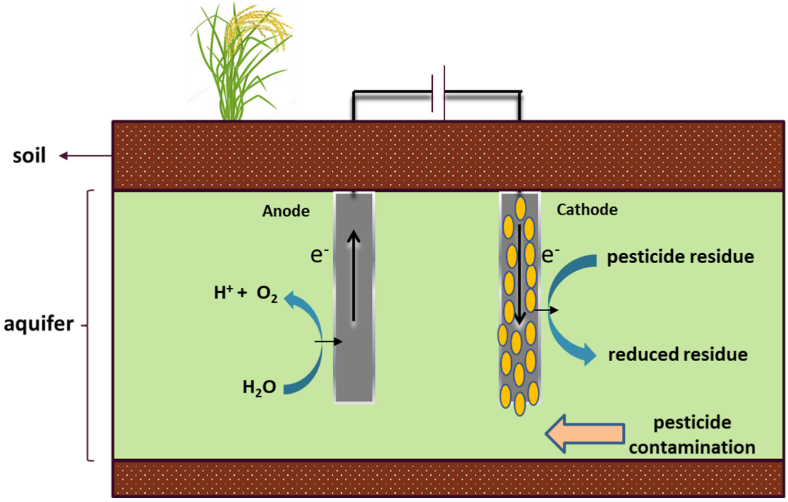

Fig. 1. Schematic image of a BES for in situ groundwater contaminated with pesticide (adopted from [24])

Currently, bioelectrochemical methods have mostly been tested using electrodes that function as electron donors to reduce oxidized organic and inorganic contaminants (including chlorinated hydrocarbons, nitrates, perchlorates, and metals). In bioremediation, microorganisms need a suitable electron donor. Therefore, this contaminant bioremediation method is usually based on a continuous supply of chemicals, as electron donors, to maintain microbial degradation activity. In this process, various substances such as hydrogen gas, acetate, lactate, alcohol, and organic substrates which are durable and not easily degraded, are able to be decomposed slowly (release of H2 and acetate) [26].

The BES set up for in situ groundwater contaminated with pesticide remediation can be seen in Figure 1. Electrodes made of conductive and non–corrosive materials are placed in the aquifer to form a permeable and reactive barrier that resists contamination. Bacteria that interact with the electrode surface will use contaminants as electron donors. Biologically, the contaminants are converted into products that are not toxic or precipitate. Anodic reactions are indicated by the conversion of water oxygen to molecular oxygen. In this case, the oxygen generated at the anode can play a role in further biodegradation processes along the aquifer pathway [24].

4.2 Granular activated carbon (GAC) as electrode

In the past decade, research on MFCs has expanded from electricity production and wastewater treatment to remediation technologies, chemicals production, and low power applications. Recently, capacitors have been implemented to improve the power output of these systems when applied in wastewater treatment processes. Specifically, the use of granular capacitive materials (*e.g.* granular activated carbon, GAC) as bioanodes has offered new opportunities for reactor designs and upscaling of the technology [27]. One of the main features of these systems is that charge and discharge processes can be separated, which offers multiple advantages over more conventional reactor types.

The phenomena that occurred in GAC as bioanode are: (i) the GAC will have electroactive biofilm growth on its surface area and (ii) current will be produced by the biofilm through the substrate or contaminant oxidation which later is stored in the carbon pores forming electrical double layer [27]. The performance of GAC as a bioanode is highly dependent on its physicochemical properties, specifically its surface area [27]. The surface area represents active sites where contaminants can be adsorbed and, in some cases, react chemically. As bioanode, GAC with a large external surface area to volume ratio was preferable [27]. In general cases of organic compound adsorption on carbon, the higher the surface area, the higher its adsorption ability towards the compound [28]. Biofilm formation on GAC is also an important aspect to be considered [27]. GAC was shown to be a suitable media for the attachment of microorganism biofilm, making it has the ability to biosorb heavy metals and organic contaminants in water [29]. However, the suitability of GAC to be used as bioanode is not solely based on its surface area or its ability to support biofilm formation, the source material of GAC, its chemical properties, such as pH, pH at zero point charge, and surface functional groups of the GAC are also important to be considered.

As the GAC has the charge storage capacity and is possibly applicable for intermittent operation, GAC bioanode can be designed into different types of reactor, namely: (i) fixed or packed bed reactor, where the contact with the current collector is constant and the operation can be continuous or intermittent; (ii) a cell where GAC is mobilized; and (iii) a fluidized and recirculated bed reactor to a smaller cell where the GAC will be in contact with the anode electrode [27]. Opting for the type of reactor depends on the density of the GAC, clogging risk, and the energy required for the reactor operation.

4.3 Application of BES with GAC electrode for removing pesticides

MFCs have been used as biosensors for water quality monitoring, where electrochemically active microorganisms convert certain organic compounds into energy. A recent study on a mini membrane-less single-chamber MFC biosensor showed a promising ability of MFC in detecting atrazine at a low concentration of 0.05 mg L^{-1} to 10 mg L^{-1} [14], suggesting that MFC has the potential to be used to degrade other pesticides in water through an electrochemical and biological process.

A study [30] on pesticides removal by microbial cells adsorbed to magnetite may indicate that other adsorbent media, such as GAC potentially aid the degradation of pesticides by MFC. A similar process to antibiotic removal using MFCs [31], a pesticide may act as an electron acceptor or carbon source in the bioanode, which is GAC in this case.

As GAC is a versatile adsorbent media, GAC may have a high affinity and attract pesticides, making it a suitable bioanode. Pesticides then are degraded by microorganisms in the cathode or by an electrochemical reaction.

5 Conclusions

In recent years, BES has shown its potential to treat contaminants in water and is seen as an environmentally–friendly approach to treat water containing recalcitrant pollutants, such as pesticides. Recent studies showed the BES potential to be applied for in situ groundwater contaminated with pesticide remediation. Moreover, this review has shown the opportunity the use GAC as a bioanode for BES application to remove pesticides from water. However, further research on the role of GAC whether as an adsorbent and/or bioanode in BES system is still required prior to its application.

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