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Research article

Simultaneous boron (B) removal and electricity generation from domestic wastewater using duckweed-based wastewater treatment reactors coupled with microbial fuel cell

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ABSTRACT

Boron removal from water environment is a critical issue for scientific spotlight because its removal from wastewater is difficult and costly with conventional treatment method. Herein, an innovative, cost effective and attractive method which depends on duckweed-based wastewater treatment systems coupled with microbial fuel cell reactor (DWWT-MFC) was investigated for B-polluted domestic wastewater treatment and simultaneous electricity generation for the first time in an eco-technological study. *Lemna gibba* L. was selected as a model duckweed species, and different reactors were also designed to identify which mechanisms are dominant for B removal in a DWWT-MFC reactor matrix. DWWT-MFC reactor achieved 71% B removal in experiment period, and the plant effect on B removal mechanisms in the reactor matrix was recorded as 37.7 ± 4.92% ($F = 2.543$, $p < 0.05$). However, supplementary aeration and microbial effects on B removal were determined as negligible. Average maximum voltage output was found as 1.47 V, and maximum power density was 34.8 mW/m^2 at a current density of 43.9 mA/m^2 with supplementary aeration. Moreover, DWWT-MFC reactor achieved 84%, 81% and 76% of COD, NH_4^+ and PO_4^{3-} removal efficiencies, respectively. Moreover, *L. gibba* grew well in the anode chamber of DWWT-MFC with an average biomass yield of 218 ± 43 g/m^2 and a total chlorophyll ($a+b$) concentration of 30.2 mg g^{-1}, which indicates that anolyte environment was not toxic for *L. gibba* growth. Consequently, it can be suggested that environmental experts may use DWWT-MFC as an efficient removal method to treat B from domestic wastewater and to produce bioelectricity.

1. Introduction

Boron (B) and its compounds cannot be degraded due to their specific chemistry in abiotic and biotic components of ecosystems, thus they are released to water environments as a result of natural processes such as leaching of salt deposits and weathering of minerals from rocks, as well as anthropogenic origins in wastewater from glass industry, mining activities and runoff effluents from areas where B-containing agrochemicals are used (Hasenmueller and Criss, 2013; Türker et al., 2017b). However, the most significant anthropogenic B pollution route in the aquatic ecosystems depends on a water pathway in domestic wastewater which includes borax in detergents (Hasenmueller and Criss, 2013). In the case of using borax-enriched detergents and cleaning products, the water-soluble B forms such as boric acid are easily discharged with a domestic effluent into sewage treatment systems (Hasenmueller and Criss, 2013; Wolska and Bryjak, 2013). Unfortunately, boron from domestic effluents cannot be substantially removed with conventional methods (reverse osmosis, ion exchange techniques, activated sludge, etc.) in sewage treatment systems due to their high costs of maintenance. Thus boron passes through the sewage treatment processes virtually unchanged, unabsorbed, and undegraded (Hasenmueller and Criss, 2013; Türker et al., 2017a). In this regard, extensive monitoring data associated with concentration of B found in effluents have been collected from sewage treatment plants in United Kingdom (Neal et al., 2010), Turkey (Böcük et al., 2013), USA and Netherlands (Fox et al., 2002).

Duckweed-based wastewater treatment (DWWT) system is a cost-effective and eco-friendly engineered system, which has a high capacity of removing organic matter and various metals and metalloids (B, As, Cd, Cr, Cu, Ni, Pb, and Zn) from wastewater using a series of biological (Böcük et al., 2013; Sasmaz and Obek, 2009; Verma and Suthar, 2014), chemical (Priya et al., 2012), and physical mechanisms (Krishna and Polprasert, 2008; Sims et al., 2013). In a DWWT system, the wastewater is purified through a collaboration between plant uptake and bacterial activity (Priya et al., 2012; Shi et al., 2010). Accordingly, organic materials are oxidized by aerobic bacteria using atmospheric oxygen

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released by duckweed roots, and they are also decomposed by bacteria into ammonium and ortho-phosphate which are products used as nutrients by duckweed (Priya et al., 2012; Shi et al., 2010; Verma and Suthar, 2014). Although various literature reports have shown the great potential of some duckweed species which can be used in DWWT systems to accumulate nutrients or B from wastewater (Sasmaz and Obek, 2009; Sims et al., 2013; Türker et al., 2017b), no direct study has so far investigated the feasibility and efficacy of DWWT combined with bioelectrochemical wastewater treatment methods such as microbial fuel cell (MFC) in order to treat domestic wastewater and generate bioelectricity simultaneously. Specifically, the high amount of biodegradable organic matter and elevated B in the domestic wastewater require a strategic approach which both treats organic based substrates along with B and produces electricity in the same combined system. The present study suggests crucial perspective that could pose one step forward to understand the importance of using eco-technological systems such as DWWT-MFC in practical applications while treating domestic wastewater and bioelectricity production.

In the present experiment, DWWT-MFC reactors were constructed to treat B-polluted domestic wastewater and to generate electricity for the first time in an eco-technological study by evaluating removal efficiencies (B, COD, NH_4^+, and PO_4^{3-}) and bioelectricity production (voltage output, power density, current density and polarization curves). Moreover, B removal pathways in DWWT reactors were employed to investigate B removal mechanisms in the reactor matrix. The performances of DWWT-MFC reactors in terms of B removal and bioelectricity generation under different optional supplementary aeration conditions were investigated. Finally, biomass production, chlorophyll content and antioxidant enzymes activities of catalase (CAT), ascorbate peroxidase (APX), guaiacol peroxidase (GPX) and glutathione reductase (GR) were determined to find out if anolyte solution in anode chamber had any impact on physiological response of duckweed (*Lemna gibba*) while treating wastewater and generating bioelectricity.

2. Material and methods

2.1. Plant material and reactors configuration

Lemna gibba, one of the most common duckweed species in most parts of Turkey, was selected and used as a model plant for the present experiment. *L. gibba* fronds were cultured according to OECD test protocol (Guidelines for the Testing of Chemicals, Revised Proposal for a New Guideline 221, *Lemna* sp. Growth Inhibition Test) during the experiment period. Following the culture period, bright green and healthy *L. gibba* were collected and carefully transferred to the treatment reactors at 600 g fresh *L. gibba* per m^2.

Eight reactors were designed using polyester chambers with 0.35 m length, 0.23 m width and 0.08 m^2 total surface area for each. They were placed in a growth chamber (photosynthetic photon flux density 85 μmol m^{-2} s^{-1} with a photoperiod of continuous light and experimental temperature of 24 ± 2 °C) and divided into two groups (X and Y) based on supplementary air conditions. Accordingly, X refers to the group under supplementary air conditions, and Y corresponds to the group with no supplementary air (Fig. 1). Moreover, each group contains one reactor with *L. gibba* plant and a microbial fuel cell device (DWWT-MFC) and another reactor with *L. gibba* but no MFC device (DWWT). Moreover, two control reactors were also designed for each group in order to evaluate plant and microorganism effect on B removal in the duckweed-based wastewater treatment systems. One of the two control reactors contains a MFC device but no *L. gibba* (unplanted-MFC; control 1), and the other control reactor contains no plants and no MFC device (unplanted-no MFC; control 2). Consequently, eight reactors were named as follows: DWWT-MFC-X (R_1), DWWT-X (R_2), unplanted-MFC-X (R_3), unplanted-no MFC-X (R_4), DWWT-MFC-Y (R_5), DWWT-Y (R_6), unplanted-MFC-Y (R_7), unplanted-no MFC (R_8). All the reactors consisted two compartments as cathode chamber and anode chamber, and the anode chamber and the cathode chamber had 0.05 m^2 and 0.02 m^2 surface area, respectively. Moreover, the cathode chamber and anode chamber were separated with a glass wool layer (0.01 m thickness). Specifically, a piece of graphite (0.02 m × 0.08 m, 0.05 m thickness, 0.0016 m^2 total surface area) as anode and a horizontal rectangular (0.02 cm × 0.08 cm and 0.01 m thickness) piece of magnesium as cathode were used and placed only in DWWT-MFC-X, unplanted-MFC-X, DWWT-MFC-Y and unplanted-MFC-Y. The cathode and anode were connected with insulated copper wires across 1000 Ω. An air diffuser (aquarium air pump, Champion) was placed on the upper section of the aerated reactors in order to inject air (Fig. 1). The graphite anodes for DWWT-MFC-X, unplanted-MFC-X, DWWT-MFC-Y and unplanted-MFC-Y reactors were placed in a sludge for one month prior to the experimental start up under laboratory conditions in order to provide inoculation of electrogenic active bacteria on graphite anodes. The sludge was obtained from an industrial wastewater treatment plant, and no boron was determined in the sludge because the industrial zone does not have any factories which used boron or its compounds in their processes (data not shown). Specifically, electrogenic active bacteria is defined as a biocatalyst which generates electricity by exchanging electrons while oxidizing inorganic or organic matter (Chabert et al., 2015). Furthermore, magnesium electrode was selected due to its high electrical conductivity and its feature of being a nontoxic material for microorganisms and plants. However, it is important to estimate how long the wetland systems may last, and it may be calculated by predicting the lifetime of the components. The lifetime of MFC devices depends on the effectiveness and suitability of the materials used as electrodes, and electrodes are not supposed to be a limiting factor as long as they provide a growth environment for microbial growth. In this respect, the ampere-hour rating of the magnesium electrode depends on the environmental conditions, and a magnesium electrode with 0.45 kg (0.0265-cm^2 initial surface) can be rated at about 500 ampere-hour (Farwest Corrosion Control Company, Gardena, CA 90248). Correspondingly, a magnesium electrode of 0.1 kg (0.016 m^2 initial surface) was used for DWWT-MFC-X, unplanted-MFC-X, DWWT-MFC-Y and unplanted-MFC-Y systems, thus the magnesium electrode can be rated at 111 ampere-hour. Accordingly, the lifetime of magnesium is predicted as: Lifetime (h) with 0.1 kg of electrode = 111 Ah/(0.015A) = 7400 h = 308 days (Shantaram et al., 2005).

2.2. Wastewater dosage and reactor operation

A synthetic wastewater solution was used to simulate organic matter-rich and boron-polluted domestic wastewater. The main composition of this synthetic domestic wastewater was glucose (0.20 g L^{-1}), NH_4Cl (0.15 g L^{-1}), KCl (0.13 g L^{-1}) $NaHCO_3$ (3.13 g L^{-1}), and it also included 1 mL micro elements solution (contained per liter: 5.6 g $(NH_4)_2SO_4$, 2 g $MgSO_4{\cdot}7H_2O$, 200 mg $MnSO_4{\cdot}H_2O$, 3 mg H_3BO_3, 2.4 mg $CoCl_2{\cdot}6H_2O$, 1 mg $CuCl_2{\cdot}2H_2O$, 2 mg $NiCl_2{\cdot}6H_2O$, 5 mg $ZnCl_2$, 10 mg $FeCl_3{\cdot}6H2O$ and 0.4 mg $Na_2MoO_4{\cdot}2H_2O$). Moreover, concentrations of boron (B), chemical oxygen demand (COD), ammonium (NH_4^+) and ortho-phosphate (PO_4^{3-}) in the synthetic domestic wastewater were adjusted to resemble pollutant levels in some local sewage from Turkey (Türker et al., 2013). In this respect, the initial concentrations of boron (B), COD, NH_4^+ and PO_4^{3-} ranged between 4.831 and 5.77 mg L^{-1}, 314–651 mg L^{-1}, 44.1–51.2 mg L^{-1} and 2.85–5.77 mg L^{-1}, respectively during the experiment.

All the reactors were divided into the four phases, each lasting about 7 days, and the reactors were operated for a period of 28 days. During the experiment period, synthetic wastewater (total working volume is 480 mL) was supplied into each reactor by using a peristaltic pump. Moreover, the reactors were operated under the same loading rate of 20 mL/h, and the synthetic B-polluted domestic wastewater was dosed three times every 8 h over the periods of 24 h. Correspondingly, the synthetic B-polluted domestic wastewater was first injected into the