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Evaluation of an electro-flotation-oxidation process for harvesting bio-flocculated algal biomass and simultaneous treatment of residual pollutants in coke wastewater following an algal-bacterial process

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ABSTRACT

This study investigated the feasibility of employing an electro-flotation-oxidation process that employs a pair of boron-doped diamond (BDD) and aluminum (Al) electrodes for electrochemical harvesting of green microalgae (*Scenedesmus quadricauda*) and treatment of residual pollutants in coke effluent, following an algal-bacterial process. Electro-coagulation-flotation with polarity exchange and with direct electro-flotation at 15 mA cm^{-2} or more for 40 min allowed almost complete harvesting of microalgae. Similar harvesting efficiencies were achieved using direct electro-flotation, without electro-coagulation, under different electrical densities because algal biomass formed flocs with the other microorganisms in the activated sludge (AS). These results also indicate that the proposed approach of inducing bioaggregation *via* floc-forming microorganisms with microalgae is an efficient alternative to chemical flocculation, because it can minimize the release of toxic metal coagulants during electrochemical harvesting. During sequential electro-oxidation, anodic oxidation using the BDD electrode simultaneously mineralized residual soluble chemical oxygen demand (SCOD) and thiocyanate (SCN^-), which are not degraded by algal-bacterial mixed cultures. Although the degradation rate of SCN^- was much higher than that of SCOD under certain current densities, further investigation is needed to clarify the mechanism of SCN^- mineralization during BDD-anodic oxidation. To satisfy the standard level of electrical power consumption for wastewater treatment, an electric current density below 15 mA cm^{-2} must be supplied. The proposed electrochemical approach involving bioflocculation could be used as an efficient post treatment of microalgae-mediated process for treating coke wastewater.

1. Introduction

Remediation of nitrogen pollutants, especially ammonium-nitrogen (NH_4^+-N), from wastewater effluents, has become a major issue, particularly for the iron- and steel-producing industries that produce large amounts of coke effluent (> 13,000 ton d^{-1} in Republic of Korea). Such effluent contains toxic chemicals mainly phenolic compounds, polynuclear aromatic hydrocarbon (PAHs), and cyanide-compounds, which are harmful to many microorganisms [1,2]. Over the past few decades, activated sludge (AS)-based biological processes, consisting of aerobic nitrification and anaerobic denitrification steps, have been developed to treat nitrogen compounds in these wastewaters [1,2]. However, these systems are prone to sudden failures of the AS-based nitrogen removal process, because the bacteria used in the nitrification step of these processes, particularly ammonium-oxidizing bacteria (AOB) and nitrate-oxidizing bacteria (NOB), are susceptible to the toxic chemicals in the coke effluent [2]. Furthermore, sulfur-oxidizing bacteria, such as *Thiobacillus* sp., in the AS can hydrolyze thiocyanate

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(SCN^-) to NH_4^+-N, resulting in accumulation of nitrogen pollutants after removal of biological nitrogen from the coke wastewater [3,4].

Photosynthetic microalgae, which efficiently utilize a wide variety of nitrogen compounds, such as NH_4^+, nitrate (NO_3^-), and urea, could be efficiently used for nitrogen removal from toxic wastewater, especially when coupled with phosphate uptake for growth [5]. Some species of green algae can even tolerate some of the toxic chemicals present in coke effluent, such as cyanide, phenolic compounds, and PAHs [6–10]. A recently proposed algal-bacterial process reported the consumption of almost 30-fold less electricity than a typical AS process [11]. Thus, a microalga-mediated process is a promising alternative for treatment of various nitrogen pollutants from toxic industrial wastewater [12].

However, there are two major constraints to the direct application of a microalgal process to wastewater treatment, particularly toxic industrial wastewater. First, it is difficult to separate out microalgal cells, most of which are < 10 μm in diameter, have densities similar to water, and have negative surface charges, and this can lead to electrostatic repulsion and the formation of stable suspensions [13]. Second, complete degradation of residual pollutants, especially organic matter, using microalgae or microbial symbiosis with other microbes, is difficult.

A flocculation technique using cationic metal ions, which is most studied methods for separation, has been widely employed to separate fine solid particles or microbes from wastewaters and/or culture medium [14]. However, the flocculation efficiency of microalgae may be reduced by the negative effects of chemical properties of the liquid medium or wastewater, such as high salinity and changes in pH, resulting in poor separation and an increase of flocculating agent [15]. Although numerous approaches have used novel materials as alternatives, such as magnetic nanoparticles modified by cationic polymers, a natural low molecular weight cationic polymer, and crystalline nanocellulose, these techniques are difficult to scale-up due to the high cost of raw materials [13,14,16–23].

In recent years, many studies have examined electrochemical techniques for the harvesting of algal biomass, due to their higher harvest efficiency, rapid reactions, and process simplicity [24–26]. During electrolysis, polyvalent cations (*e.g.* Al^{3+} or Fe^{2+}/Fe^{3+}) dissolve at the anode, and their positively charged metal hydroxides, strongly bind to the surface of microalgal cells (which are negatively charged), leading to charge neutralization, a process called electrocoagulation [26]. The bubbles (O_2 and H_2), simultaneously produced by the electrolysis of water, tend to capture these algal flocs and lift them hydrodynamically to the surface of the solution. This allows easy separation of these floating cells from freshwater and seawater medium [13]. Furthermore, this electrical approach is cost-effective for the harvest of algal biomasses, with an energy expenditure of 1.08 kWh kg^{-1} algal biomass [13,24]. A drawback of this electrochemical separation technique, however, is that it also requires a coagulation step to improve harvest efficiency.

In addition, electrolysis reactions can also be used to treat organic and/or nitrogen pollutants in wastewaters [27]. These reactions are mediated by direct or indirect anodic oxidation, which can generate strong oxidants such as hydroxyl radicals (OH•) [28]. Because the removal efficiencies of contaminants and the corresponding energy consumption during anodic oxidation strongly depend on the type of anodic electrode, researchers have examined various anode materials for wastewater treatment, including graphite, platinum (Pt), iridium oxide (IrO_2), rubidium oxide (RuO_2), tin oxide (SnO_2), lead oxide (PbO_2), and boron-doped diamond (BDD) [27]. Some of these electrodes had poor organic degradation (*e.g.* IrO_2 and RuO_2) or very high energy consumption (*e.g.* graphite and Pt), due mainly to their lower oxygen (O_2) evolution potential [29]. Compared with other electrodes, BDD electrodes have a relatively high O_2 evolution potential, as well as good resistance to corrosion, non-reactive surface, resistance to deactivation, and good oxidation capacity [29]. These advantages have led to the widespread use of BDD electrodes for electrochemical anodic oxidation for the mineralization of various of non-degradable organic carbons and remediation of biologically treated wastewater effluent [30].

Consideration of these electrochemical reactions lead to the hypothesis that proper combinations of electrodes with polarity exchange can provide a system that allows harvesting of microalgal cells and simultaneous degradation of residual pollutants in a single chamber following a microalgal-mediated wastewater treatment. However, no previous work has applied this merged system to such work.

The first specific aim of this study was to examine the feasibility of using a mixed algal-bacterial culture as an efficient alternative to the typical activated sludge process, involving nitrification/denitrification, to treat organic- and nitrogen-pollutants from toxic coke effluent in a photofermentor with a 4-L working volume. The second aim was to develop a system that provides direct electrochemical harvesting of microalgae and simultaneous anodic oxidation for degradation of residual pollutants, including organic compounds and thiocyanate (SCN^-), from treated coke effluent using a BDD electrode with polarity exchange. Additionally, the effects of an aluminum (Al) release step on the performance of electrochemical harvesting and oxidation were assessed.

2. Materials and methods

2.1. Preparation of coke wastewater and microbial seeds

Coke wastewater was obtained from a full-scale wastewater treatment facility in the coke plant of a steel manufacturing company in the Republic of Korea. The sample was filtered through a 0.22-μm membrane (Sartorius Stedim Biotech, Göttingen, Germany) and stored in sterilized bottles at 4 °C. Table 1 shows the physicochemical parameters of the coke wastewater. The major pollutants were phenol, soluble COD, NH_4^+-N, and SCN^-.

An activated sludge as a bacterial seed was collected from an aerobic reactor installed in a local municipal wastewater treatment plant in Daejeon, Republic of Korea.

A microalgal strain, *Scenedesmus quadricauda* (AG10003), was provided by the culture collection center of the Korean Research Institute of Bioscience and Biotechnology (KRIBB, Daejeon, Republic of Korea) because the genus of *Scenedesmus* is known to be tolerant of phenol and cyanide which are main pollutants of coke wastewater and simultaneously accumulate the NH_4^+-N under illuminated condition [8,10]. A seed culture was cultivated at 120 rpm and 25 °C in Tris-acetate phosphate (TAP) medium (pH 7.0), consisting of: Beijerinck's solution

Table 1
Characteristics of the coke wastewater used in this study.

Parameter	Unit	Initial wastewater[a]	After treatment[b]
SCODcr	mg O_2 L^{-1}	645.0 ± 11.3	275.5 ± 8.5
Phenol	mg L^{-1}	97.3 ± 3.6	ND
NH_4^+-N	mg L^{-1}	20.2 ± 0.2	ND
NO_2^--N	mg L^{-1}	1.4 ± 0.2	ND
NO_3^--N	mg L^{-1}	ND	ND
SCN^-	mg L^{-1}	53.3 ± 0.2	53.7 ± 0.4
Chlorophyll-*a*	mg L^{-1}	ND	10.3 ± 0.2
Chlorophyll-*b*	mg L^{-1}	ND	3.1 ± 0.1
Total carotenoid	mg L^{-1}	ND	2.6 ± 0.1
VSS	mg L^{-1}	10.0 ± 0.0	1180 ± 56.6
EC[c]	mS cm^{-1}	1.7 ± 0.0	1.6 ± 0.0

ND: Not detected.
All data are means from duplicate experiments with standard deviations.
[a] Initial coke wastewater after a 5-fold dilution.
[b] Treatment was with an algal-bacterial culture in a 4-L photofermentor under illumination with 2% CO_2 supplementation.
[c] Electrical conductivity.