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Nitrate remediation in a novel upflow bio-electrochemical reactor (UBER) using palm shell activated carbon as cathode material

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ABSTRACT

This study investigated the biological denitrification method which is a treatment method able to reduce inorganic nitrate compounds to harmless nitrogen gas. Autohydrogenotrophic denitrifying bacteria were used in this study to prevent any problematic outcomes associated with heterotrophic microorganisms. An upflow bio-electrochemical reactor (UBER) was used to accommodate hydrogenotrophic denitrifying bacteria employing palm shell granular activated carbon (GAC) as the biocarrier and cathode material. Bicarbonate as the external inorganic carbon source was fed to the reactor and hydrogen as the electron donor was generated in situ through electrolysis of water. Central composite design (CCD) and response surface methodology (RSM) were applied to investigate the effects of two operating parameters, namely electric current (I) and hydraulic retention time (HRT), on performance of the UBER. Electric current range of 0–20 mA and HRT range of 6–36 h were examined and results showed that nitrate can be entirely reduced within application of a wide operational range of electric current (10–16 mA) as well as HRT (13.5–30 h). However, increase of pH at cathode zone up to 10.5 inhibited nitrite reduction, and it was not reduced to the satisfactory level.

1. Introduction

Nitrate in drinking water threatens human and animal health. It is known to cause gastric cancer and also methaemoglobinemia syndrome [1,2]. Researchers from different parts of the world reported high concentration of nitrate in ground and surface waters [3]. Several reasons have been reported for this globally increasing problem such as high-solubility and high-mobility nature of nitrate in water and soil, anthropogenic sources of the nitrate (i.e. agriculture, stockbreeding, industries), and difficulties in treatment of nitrate through conventional treatment techniques [3–5]. Various physical–chemical methods have been reported to be applied in water treatment which fail to treat nitrate and are only able to separate nitrate from water stream and form a brine waste solution, for which either disposal or a cumbersome treatment is inevitable. On the other hand, biological treatment of nitrate (hereafter is referred as to denitrification) become a solution to treat nitrate and reduce it to harmless nitrogen gas. In this regard, addition of external carbon substrate to water is unavoidable. Ghafari et al. [6] discussed about disadvantages associated with heterotrophic denitrification pathways and highlighted that one of the most promising autotrophic techniques can be autohydrogenotrophic denitrification through in situ electrochemical generation of hydrogen. Advantages of this technique in brief are:

(i) Unlike heterotrophic pathways, this method stays away from toxic residuals or byproducts of organics; inorganic substrates (bicarbonate/CO_2) and in situ production of H_2 are stoichiometrically cheaper than organic substrates; no post treatment method is required to remove nontoxic residuals of inorganic carbons; and also inorganics result in less biomass production meaning less possibility for clogging in reactors.
(ii) Unlike the other autotrophic methods, residual H_2 in water is insignificant due to low solubility of H_2; hydrogen is also harmless and no obligation for removal of residuals, if any; electrolysis of water produces in situ H_2 that eliminates risk of explosion in transfer and storage of H_2 tanks; electricity is inherently dirt-free and easy to control, and facilitates handling of the process; gently continuous supply of H_2 through hydrolysis of water implying that there will be no H_2 shortage due to its low solubility in water.

The term “bio-electrochemical method” generally refers to the process where electric current passes through a proper electrode system and it enhances the biological degradation of the contaminants in this system. This method operates at low electric currents, in fact much lower than what pure electrochemical methods work on. In spite of the fact that bio-electrochemical denitrification is a

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fairly new technique, use of this method in water treatment is under extensive research, and researchers found that denitrification was stimulated by passing electric current in the reactor [7–13]. In these processes, electrolysis of water results in production of oxygen at anode and hydrogen gas at the cathode [6]:

$$5H_2O \rightarrow 2.5O_2 + 10H^+ + 10e^- \quad (1)$$

$$10H_2O + 10e^- \rightarrow 5H_2 + 10OH^- \quad (2)$$

The hydrogen gas generated at cathode serves as the electron donor for denitrification to proceed:

$$2NO_3{}^- + 5H_2 \rightarrow N_2 + 4H_2O + 2OH^- \quad (3)$$

Besides, diverse techniques and bioreactors have been employed to prepare a proper connection amongst microbes, substrates and pollutants. The use of immobilized (or supported) cells, namely biofilm, has found applications in a wide range of biological processes from the production of ethanol to the degradation of pollutants [12], and denitrification is not an exception. Moreover, because the filling ratio of fixed bed reactors is usually greater than that of fluidized bed reactors, denitrification rate of fixed bed reactors seems to be greater than that of fluidized-bed reactors [14]. Accordingly, biofilm reactors with various solid supports have been used. Amongst the solid supports, activated carbons offer the advantages of a large adsorptive capacity as well as an irregular shape, which makes it function well as a shelter for bacteria against high fluid shear forces [15,16].

The authors previously reviewed different bio-electrochemical reactor designs and their effects on the denitrification [6]. That survey pointed out some effective designs such as concentrically arrangement of cylindrical cathodes [8] and successive parallel installment of plane cathodes [17]; however, to the best of our knowledge, there was no an upflow design using granular activated carbon (GAC) with dual role as cathode material and support for autohydrogenotrophic biofilm thus far. Therefore, in this study, a lab scale upflow bio-electrochemical reactor (UBER) was designed and operated for 3 months to test the feasibility of bio-electrochemical nitrate remediation of contaminated water (20 mg $NO_3{}^-$-N/L). At the cathode zone of UBER, electrochemical method creates a favorable anoxic environment for autohydrogenotrophs, and generates H_2 (electron donor) in situ. The purpose of this research is to investigate the effect of electric current intensity (I) and hydraulic retention time (HRT) on the electrochemical stimulation of nitrate remediation in water using the aforementioned UBER. In this regard, central composite design (CCD) and the statistical method of response surface methodology (RSM) were used to design the experiments and study the influences of these individual factors (I and HRT). This methodology considers the interactive influences of I and HRT through less experiments rather than conventional methods used in previous studies, where effects of factors were investigated in succession. Those methods consider effect of one factor at a time, and neglects interactive effects of factors. Furthermore, polynomial models were developed, and analysis of variance (ANOVA) provided the statistical results and diagnostic checking tests to evaluate adequacy of the models.

2. Experimental

2.1. Experimental apparatus

Two sets of enclosed 2.1 L Plexiglas cylindrical UBER as illustrated in Fig. 1 were used in this study to provide a desirable anoxic environment at the cathode zone by means of electric current. These reactors were fabricated of 30 cm long Plexiglas cylinders with 9.5 cm inside diameter. An aluminum plate was installed at the bottom of the reactor (touching GACs) and 13 stainless steel rods in height of 5 cm screwed the plate to the base for fixing plate and also providing a better distribution of electricity among GAC grains. The anode was a stainless steel mesh (wire mesh, hole size 2 mm × 2 mm) placed 1 cm below the outlet level and was attached to the cap using four stainless steel rods. From beneath the reactor and top surface of the cap, stainless steel rods were connected to a programmable DC power supply (IPS-3202, RS Components, England). Four inlet ports were installed on the wall of the cylindrical column at 1 cm above the bottom and one outlet port located at 25 cm from the bottom to make a 5 cm head space. One sampling port (SP) was installed at height of 20 cm in order to withdraw samples from outside of the cathode zone. Palm shell granular activated carbon (supplied by Bravo Green Sdn. Bhd., Sarawak, Malaysia) in size range of 1–2 mm was used as the solid support and cathode materials in the UBER. Before inserting in the UBER, GACs were washed with deionized water for several times and were dried in the oven. To provide a sticky surface on GAC surface, it was saturated in 2% agar solution at about boiling temperature and was left to cool down to about 50 °C and inserted into the UBER. The column of GAC, 17 cm from the bottom of UBER, was working as the cathode zone. Therefore, total volume of cathode zone was 1.2 L, and considering 66.5% GAC bed porosity, the working volume (void volume) was 800 mL.

2.2. Microorganisms and synthetic contaminated water

A mixed culture containing denitrifying bacteria was originally provided by an activated sludge collected from an upflow anaerobic sludge blanket (UASB) reactor of treatment plant in a brewery factory located in Selangor, Malaysia. The acclimatized autohydrogenotrophic denitrifying bacteria obtained from the former study [18] were used as the inoculums. Hydrogen gas and sodium bicarbonate were used as electron donor and inorganic carbon source, respectively, for growth and adaptation of bacteria enabling them of treating 20 mg $NO_3{}^-$-N/L/d. Acclimated mixed culture was kept in a solution consisting of $NaNO_3$ (0.3 g/L), K_2HPO_4 (1.6 g/L), KH_2PO_4 (0.4 g/L), $MgSO_4$ (0.1 g/L), $CaCl_2$ (0.03 g/L) and preserved in refrigerator (4 °C) prior to being inoculated into the UBER. The acclimated mixed culture liquor was pumped into the UBER through four inlets of the reactor and was circulated until all the bacteria were trapped in the porous GAC cathode zone and a transparent supernatant was left. Biofilm formed gradually throughout the experiments and a dark grey color covered the activated carbon granules within 1 month.

The synthetic contaminated water was prepared fresh by dissolving 0.122 g $NaNO_3$/L, 1.250 g $NaHCO_3$/L, 0.650 g K_2HPO_4/L, 0.170 g KH_2PO_4/L, 0.1 g $MgSO_4$/L, 0.027 g $CaCl_2$/L in deionized water. The original pH of this solution was about 8 and it was adjusted to 7 using CO_2 (gas was bubbled through a commercial gas diffuser) before being injected to the UBER.

2.3. Sample preparation and analytical method

Water taken from SP was used for determination of pH and nitrate/nitrite contest after treatment. The withdrawn water (3 mL) was filtered using 0.2 μm syringe filters to be analyzed for the nitrate and nitrite contents by a high performance liquid chromatography (HPLC). Operational conditions (I and HRT) for each run were maintained until steady state in the nitrate and nitrite removal. Then, samples were taken after fulfilling the hydraulic retention times for at least three successive HRTs. A Shimadzu HPLC comprising of a GP50 gradient pump, LC25 chromatography oven and an AD20 absorbance detector was used. All the experiments were carried out in triplicate to satisfy reproducibility and three samples were withdrawn for each run. Experiments were repeated if there was an error higher than 5% in analysis of sam-