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Removal of nitrate ion from water by electrochemical approaches

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ABSTRACT

This study is focused on the mechanism of nitrate removal from aqueous solutions by electrochemical denitrification process (EDN) in an undivided electrolytic cell. The sacrificial (Fe and Al) electrodes and Inert (graphite (Gr)) electrode are employed for evaluation of operational parameters, namely current density, electrolysis time and sodium chloride concentration. The experimental results reveal that nitrate-N removal efficiency of 92% for Al–Fe (anode-cathode) and 80% for Fe–Fe are achieved at a current density of 25 mAcm^{-2} and 180 min electrolysis time in 100 ppm of NaCl when the initial nitrate-N concentration is 100 ppm. However, during this process approximately 20 ppm of ammonia-N is also formed. Ammonia-N generated is significantly lower compared to the amount of nitrate-N removal. It can be attributed to the fact that nitrate ion can be removed by both electrocoagulation (EC) and electrochemical reduction (ER) processes simultaneously. Experiments using Al, Fe and Gr as cathodes as well as anodes indicate that the contribution of EC increases when dissolving anodes are used. Further confirmation of nitrate-N removal by EC pathway is obtained by quantitative estimation of nitrate present in the sludge. During EDN, pH of the solution also increases with ammonia generation.

1. Introduction

Groundwater is a major source of drinking water for rural communities in India and other developing countries. Due to extensive use of nitrate fertilizer in agriculture, this valuable groundwater is being contaminated by nitrates. Elevated nitrate contamination in groundwater can cause ‘methemoglobinemia’ in blood leading to blue baby syndrome in children [1,2]. For these reason, a maximum desirable limit for nitrate (NO_3^-) is 50 ppm (10 ppm equivalent nitrate-N) for adults, 15 ppm (3 ppm equivalent nitrate-N) for children and 0.5 ppm of ammonia was permitted by World Health Organization (WHO) [3]. Extensive data collected by Central Ground Water Board of India (CGWB) indicated the presence of 100–800 ppm nitrate levels in many regions of India [4]. Similarly nitrate contamination in groundwater and surface water has increasingly major issues. Thus the removal of nitrate from water gains more and more attention.

Among the various methods available for removal of nitrate, the biological methods [5–7] introduce additional biological impurities and degradation products into the water during treatment. Highly water soluble nitrates require large volumes of adsorbents for their removal [8], leading to the generation of solid waste. Electro-dialysis (ED) [9], nano-filtration (NF) and reverse osmosis (RO) [10] also lead to concentrated nitrate rejects, which require further treatment and disposal. Hence, there is considerable interest in electrochemical denitrification (EDN) processes, which can be operated at a small scale to meet local community demand for drinking water in villages.

The mechanistic studies of EDN exhibit certain unsettled issuses. Electrochemical reduction (ER) and electrocoagulation (EC) processes are the two approaches being investigated for denitrification. Nitrite and ammonia are the main products formed during ER of nitrate ion [11,12]. Direct 5e$^-$ reduction of nitrate to nitrogen gas has been claimed in some reports, supported by the mechanism which deals with the formation of nitrogen gas during chemical reduction of nitrate using Al and Fe powders [13–17]. The suitable

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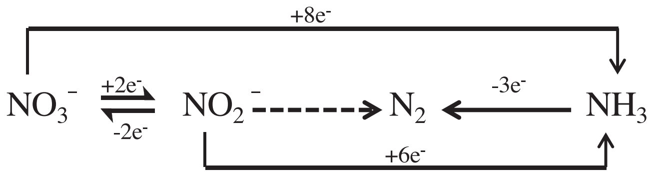

Scheme 1. Electrochemical reduction pathways for nitrate ion.

approach to understand the mechanism can be rendered as the formation of ammonia from nitrate and nitrite at cathode and subsequent re-oxidation of ammonia to nitrogen on the catalytic anode surfaces [18] as shown in Scheme 1. Detailed studies on the mechanism of ammonia oxidation on RuO_2 and IrO_2 coated electrodes [19–21] also support this mechanistic pathway. Residual ammonia-N is found to be less in the ER process when oxide coated Ti was used as the anode [13–15,22]. The complex mechanistic pathways discussed in the literature for the EC mechanism are summarized in Scheme 1.

Energy consumption for EC process is twenty times more than ER process in the faradaic EDN [23]. Hence, more attention has been given for EC pathways in EDN. Both Al and Fe anodes play a substantial role in nitrate removal by EC process. The EC process [23–26] was indeed shown to be more efficient than chemical coagulation using Al^{3+} or Fe^{3+} salts [26]. However, there are contradicting reports on the cathodic process during EC. It has been reported that ammonia is generated only on Al electrodes during initial stages of EC. Direct cathodic reduction of nitrate to nitrogen gas [25] and formation of hydrogen gas [24] has also been suggested as the predominant cathodic process. EC and ER pathways have been proposed for nitrate removal in flow reactors using mild steel [27] and zero-valent iron [28] electrodes, respectively. Further, basic studies are necessary for evaluating of the role of ER and EC pathways in EDN process. The main objective of the present research work is to identify experimental conditions under which the 100 mg L^{-1} of nitrate-N can be removed from aqueous solution containing 100 mg L^{-1} NaCl by EDN process and also to elucidate the respective role of ER and EC in nitrate removal.

2. Materials and methods

2.1. Denitrification experiments

Electrochemical denitrification experiments were performed at room temperature in an open undivided batch electrolysis cell (500 mL glass beaker) containing 300 mL electrolyte, as depicted in Fig. 1. Graphite (Gr), aluminium (Al) and iron (Fe) plates were employed as electrode materials. Anode and cathode with an inter electrode distance of 2 cm were connected to a regulated DC power supply (ApLab C3202). Synthetic nitrate contaminated water was prepared using analytical grade potassium nitrate (KNO_3, 99% Himedia, India) and sodium chloride (NaCl, 99% Merck Chemicals India). The salts were dissolved in double distilled water. Electrolyte pH was found to be in the range of 7 ± 0.1. The electrolyte was continuously stirred magnetically at a constant speed (300 rpm) during electrolysis and then allowed to settle for 2 h. The solution was filtered through Whatmann filter paper and the filtrate was used for analysis. Triplicate runs were carried out for every experiment to ensure reproducibility.

2.2. Data analysis

Nitrate-N (NO_3^--N) concentration in the solution before and after EC was analyzed by UV spectrophotometer (JASCO V-650). 1 N HCl was used for the acidification of samples to prevent the interference from hydroxide or carbonate anions. Chloride and sulfate have no effect on the estimated value [29]. Ammonia-N (NH_4-N) concentration in residual solution was estimated colorimetrically by Nesslerization method [29]. All the experiments were performed at 25 ± 2 °C. The sludge samples obtained after EDN process was washed with distilled water and dried overnight at 40 °C. The scanning electron microscope (SEM) and X-ray diffraction (XRD) pattern of the dried sludge was obtained using JEOL JSM-6390 and SHIMADZU XPERT-PRO diffractometer, respectively.

For the estimation of nitrate-N content, the sludge (100 mg) was dissolved in 3–5 mL of concentrated H_2SO_4 to obtain a clear solution. The solution was then made up to 100 mL. The nitrate-N

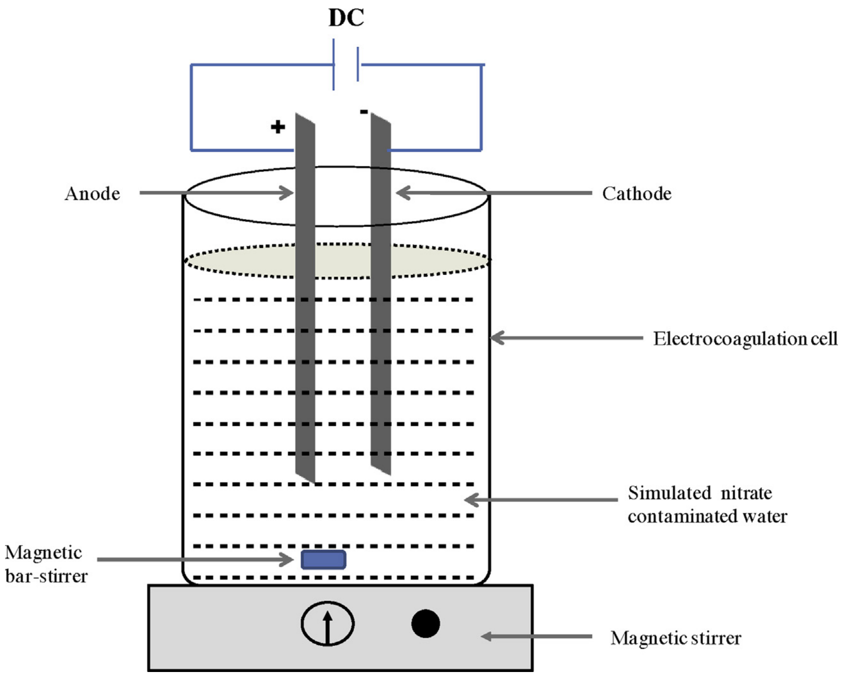

Fig. 1. Schematic representation of electrochemical denitrification (EDN) cell.