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Analytical expressions of concentration of nitrate pertaining to the electrocatalytic reduction of nitrate ion

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ABSTRACT

A theoretical model of an electrochemical reduction of nitrate ion is presented. Analytical expressions pertaining to the concentration of nitrate, nitrite, ammonia, and nitrogen are obtained in terms of reaction rate constant. Simple and closed expression of current is also derived. In this paper, a powerful analytical method, called Homotopy Analysis Method (HAM) is used to obtain approximate analytical solutions for a nonlinear ordinary differential equation. The main objective is to propose an analytical method of solution, which do not require small parameters and avoid linearization and physically unrealistic assumptions. The obtained analytical solution in comparison with the numerical ones is found to be in satisfactory agreement.

1. Introduction

Interest in the electrochemical reduction of nitrate and nitrite ions has increased in the past several years [1–5]. It is to decrease the concentration of the contaminants in drinking water. At present, the major health concern for nitrate in water is that it can lead to methemoglobinemia and gastric cancer in humans and animals. The uptake of nitrate in the human body causes oxygen-deficiency such as cyanosis and breathing problems. In particular, infants are seriously affected, and this disease in infants is known as blue-baby syndrome. Such toxicity is not due to nitrate itself but to nitrite formed from it. The nitrite oxidizes hemoglobin to methemoglobin, resulting in loss of the capability of carrying oxygen. The most common problem of the reduction of nitrate is the formation of side-products such as nitrite, ammonia and hydroxylamine, which are more toxic than the removed nitrate [6,7]. It is also believed that N-nitrosamines formed from nitrite and amines cause an increased possibility of cancer and diabetes. Despite this concern, investigations of nitrate electroreduction have been limited to acidic or alkaline systems without consideration of neutral pH solutions that may well reflect typical drinking water. Several of the reported investigations were carried out in either acidic or alkaline concentrated nitrate and nitrite ion solutions for environmental reasons [3,5,8].

Lu et al. [2] used different hydrogen storage cathodes to reduce nitrate to ammonia in alkaline media and found that the efficiency of ammonia production depended on the nitrate ion concentration, electrode type and applied current density. Both galvanostatic and potentiodynamic electroreduction were investigated. The reduction of nitrate ion has received considerable attention over the last four decades, mainly because of the possibility of utilizing abundant and inexpensive sources for the production of useful chemicals [9–14]: nitrous oxide (N_2O), a compound used as an anesthetic in medical applications; ammonia (NH_3), a nitrogen source in fertilizers; hydroxylamine (NH_2OH), a material very important in the manufacture of caprolactam. Numerous efforts have been made so far, concerning the electrochemical reduction of nitrate on various metallic electrodes [15–18] and graphite. This method is applicable when nitrite, nitrogen and ammonia are the only products of the reduction of nitrate. The reduction of nitrate also gives other products such as hydroxylamine and nitrous oxide.

An area in which the conversion of nitrate into NH_3 may also find application is the recycling of strongly alkaline solutions used in the neutralization of nitric acid waste clean-up solutions in the nuclear industry [19]. Moreover, the increasing interest in the reduction of nitrate is also connected with environmental problems and the increasing cost of the purification of drinking water [20]. Several water treatment methods for nitrate removal are available [21], but R&D work is still needed to improve both process performances and economics [22–24]. In fact the challenge between different technologies depends on desired water quality, plant capacity, process automation or access to manpower of suitable technical skill.

Electro-catalytic reduction of nitrate has been experimentally studied in the last 30 years [1,3,4,14,25–28]. Moreover, the

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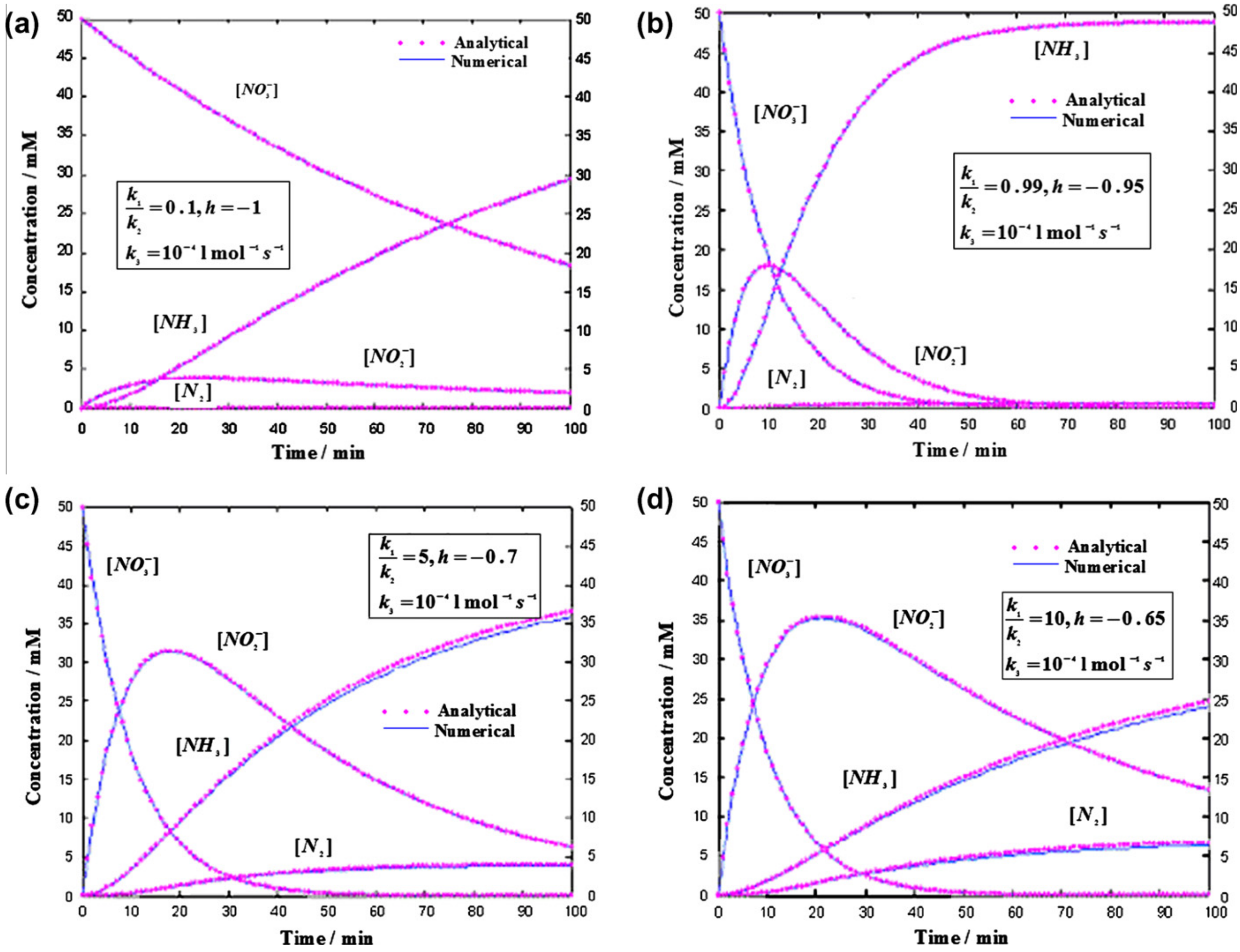

Fig. 1. Concentration profiles for the nitrate $[NO_3^-]$, nitrite $[NO_2^-]$, ammonia $[NH_3]$ and nitrogen $[N_2]$ against the electrolysis time t for $C_0 = 50$ mM. (a) $k_1 = 10^{-2}\,s^{-1}$, $k_2 = 10^{-1}\,s^{-1}$, $k_3 = 10^{-4}\,lmol^{-1}s^{-1}$ and $h = -1$. (b) $k_1 = 0.99 \times 10^{-1}\,s^{-1}$, $k_2 = 10^{-1}\,s^{-1}$, $k_3 = 10^{-4}\,lmol^{-1}\,s^{-1}$ and $h = -0.95$. (c) $k_1 = 10^{-1}\,s^{-1}$, $k_2 = 2 \times 10^{-2}\,s^{-1}$, $k_3 = 10^{-4}\,lmol^{-1}\,s^{-1}$ and $h = -0.7$. (d) $k_1 = 10^{-1}\,s^{-1}$, $k_2 = 10^{-2}\,s^{-1}$, $k_3 = 10^{-4}\,lmol^{-1}\,s^{-1}$ and $h = -0.65$.

concen tration of nitrate can influence the rate of the reduction and the distribution of the products, as it has been previously reported [29–34]. To our knowledge, no general analytical expressions for the concentration of nitrate, nitrite, ammonia and nitrogen against the electrolysis time t and current have been reported for all values of the rate constants k_1, k_2 and k_3 [10]. The purpose of this paper is to derive an analytical expression for the concentration of nitrate, nitrite, ammonia, nitrogen and current for all values of the rate constants k_1, k_2 and k_3 using Homotopy Analysis Method (HAM).

2. Mathematical formulation of the problem

The first order kinetics for both nitrate and nitrite was performed assuming the following reduction scheme [10]:

$$NO_3^- \xrightarrow{k_1} NO_2^- \xrightarrow{k_2} NH_3$$

$$2NO_2^- \xrightarrow{k_3} N_2 \tag{1}$$

The nonlinear differential equations for the concentrations of the various products in (1) may be written as follows [10]:

$$\frac{d[NO_3^-]}{dt} = -k_1[NO_3^-] \tag{2}$$

$$\frac{d[NO_2^-]}{dt} = k_1[NO_3^-] - k_2[NO_2^-] - 2k_3[NO_2^-]^2 \tag{3}$$

$$\frac{d[NH_3]}{dt} = k_2[NO_2^-] \tag{4}$$

$$\frac{d[N_2]}{dt} = k_3[NO_2^-]^2 \tag{5}$$

Here $[NO_3^-], [NO_2^-], [NH_3]$ and $[N_2]$ denote the concentration of nitrate, nitrite, ammonia and nitrogen against the electrolysis time t. k_1, k_2 and k_3 are the rate constants. An appropriate set of initial conditions are given by:

$$[NO_3^-] = C_0\text{ mM}, \quad [NO_2^-] = 0, \quad [NH_3] = 0 \quad \text{and } [N_2] = 0 \tag{6}$$

where C_0 is the initial concentration of $[NO_3^-]$. The Eqs. (2)–(5) can be combined to yield $\frac{d}{dt}([NO_3^-] + [NO_2^-] + [NH_3] + 2[N_2]) = 0$. Using the initial conditions (6), we can obtain,

$$[NO_3^-] + [NO_2^-] + [NH_3] + 2[N_2] = C_0 \tag{7}$$

Total current is the sum of the partial currents of all the electrolysis products and can be expressed as follows [10]: