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Kinetics, thermodynamics and isotherm modeling for removal of nitrate from liquids by facile one-pot electrosynthesized nano zinc hydroxide

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ABSTRACT

This study deals with the removal of nitrate from water by electrocoagulation process using zinc and stainless steel as anode and cathode respectively. The optimizations of various experimental operating parameters like effect of electrolyte pH, current density, temperature, and inter-electrode distance on the removal of nitrate were carried out. The effect of co-existing anions such as carbonate, phosphate, silicate and phosphate was studied on the removal efficiency of nitrate. The results showed that the optimum removal efficiency of 69% was achieved. The maximum removal efficiency was achieved at a current density of 0.1 A dm^{-2} and pH of 7.0. First and second-order rate equations were applied to study adsorption kinetics and the adsorption process follows second order kinetics model with good correlation. The Langmuir adsorption isotherm favors monolayer coverage of adsorbed molecules for adsorption nitrate. Thermodynamic parameters, including the Gibbs free energy, enthalpy, and entropy, indicated that the adsorption of nitrate on zinc hydroxide was feasible, spontaneous and endothermic.

1. Introduction

Nitrate in groundwater has become a serious environmental problem globally and it is derived mainly from industrial processes and agricultural runoff, and also from animal wastes, septic systems. Though the nitrate itself is relatively less-toxic, but nitrite and ammonia (derived by reduction of NO_3) can cause health problems like methemoglobinemia, liver damage, and even cancers [1,2]. Therefore, the NO_3 concentration in the drinking water needs to be limited to drinking water standards. World Health Organization [3] set the drinking water guidelines value of 50, 0.5 and 0.5 mg/L for nitrate, nitrite and ammonia respectively. Thus, remediation of groundwater system contaminated with nitrate has been extensively studied over last decades. Recent methods for the nitrate removal from ground water are limited to physiochemical and biological methods [4–7]. The physiochemical processes include ion exchange, reduction and membrane separation methods. Ion exchange is a process in which the target ion replaces another less well adsorbed ion on a resin. This process is a promising technology for nitrate removal because of its simplicity, effectiveness, and relatively low cost but it is nonspecific for the ions of interest and yields copious amounts of concentrated brines containing sulfate, chloride, and NO_3^- which must be disposed off separately. Membrane based separation techniques yield concentrated brines, and are cost-prohibitive on large scales. Biological denitrification is widely used for the treatment of municipal and industrial wastewater by degradation of microorganisms, but is less commonly used in drinking water applications. In recent days, metallic iron and aluminum as powder were used to reduce nitrate in water; however this reduction process is highly dependent on the solution pH. Most current NO_3^- removal process has various limitations and is particularly not suitable for small communities.

Recent research has demonstrated that, electrochemical processes offer an attractive alternative to traditional methods for treating nitrate contaminated water [8–15]. Due to formation of by-products like nitrite and ammonia during treatment, the application existing processes are limited in practice [16–18]. The nitrite and ammonia by-products are subsequently oxidized to nitrate and nitrogen, respectively by oxidants either generated by in-situ or ex-situ methods before further use [19]. The challenge is to find suitable process to limit the formation of byproducts in treated water. The ultimate objective of this work is to examine the adsorption of NO_3^- by coagulant, generated by in-situ, by anodic dissolution of aluminum alloy and to find effective conditions to avoid the formation of nitrite and ammonia in electrocoagulation process. The main reactions taking place in electrocoagulation process are,

At the cathode:

$$2H_2O + 2e^- \rightarrow H_2\ (g) + 2OH^- \quad (1)$$

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At the anode,
(when zinc as sacrificial anode)

$$Zn \rightarrow Zn^{2+} + 2e^- \quad (2)$$

$$Zn^{2+}(aq) + 2H_2O \rightarrow Zn(OH)_2 + 2H^+ \quad (3)$$

The main disadvantage in case of aluminum electrode (conventionally used) is the residual aluminum (The USEPA guidelines suggest that maximum contamination is 0.05–0.2 mg L^{-1}) present in the treated water due to well known cathodic dissolution. This will create health problems like cancer. In the case of zinc electrodes, there is no such disadvantage like aluminum electrodes. The USEPA guidelines suggest that the maximum guideline value of zinc in water is 5 mg L^{-1}.

The present work provides a critical study on the adsorption of nitrate by one-pot electrochemically synthesized nano zinc hydroxide. The various operating parameters on the removal efficiency of nitrate were investigated, such as initial pH, current density, inter-electrode distance, co-existing ions and temperature. First- and second-order rate equations were applied to study adsorption kinetics. Adsorption isotherms of nitrate on $Zn(OH)_2$ were determined and correlated with isotherm equations such as Langmuir, Freundlich, D–R and Temkin models. Thermodynamic parameters, such as standard Gibb's free energy (ΔG^o), standard enthalpy (ΔH^o), and standard entropy (ΔS^o), were also evaluated by Van't Hoff equation.

2. Experimental section

2.1. Cell construction and electrolysis

The experiments were carried out in a mono polar batch reactor using 1.0-L Plexiglas vessel that was fitted with a polycarbonate cell cover with slots to introduce the electrodes, pH sensor, a thermometer and the electrolytes. Zinc (commercial grade, India) electrode of surface area (0.02 m^2) acted as the anode. The cathode was stainless steel (commercial grade, India) sheets of the same size as the anode is placed at an inter-electrode distance of 0.003 m. The temperature of the electrolyte was controlled to the desired value with a variation of ±2 K by adjusting the rate of flow of thermostatically controlled water through an external glass-cooling spiral. A regulated direct current (DC) was supplied from a rectifier (10 A, 0–25 V; Aplab model). The required concentration of nitrate was prepared by dissolving sodium nitrate (Aldrich, USA) in doubled distilled water. The solution of 0.90 L was used for each experiment as the electrolyte. The pH of the electrolyte was adjusted and measured by a pH meter (DKK-TOC, Japan) at the beginning and during the experiment. After adjusting the initial solution pH to the desired value, the current density was set. Magnetic stirring at 250 rpm provided a homogeneous solution in the batch reactor. During the electrolysis, pH of the solution was monitored and at specified time intervals, samples were taken for analysis. Temperature studies were carried at varying temperature (303–343 K) to determine the type of reaction. To study the effect of co-existing ions, in the removal of nitrate, sodium salts (Analar Grade) of phosphate (2–50 mg L^{-1}), silicate (5–15 mg L^{-1}), carbonate (2–250 mg L^{-1}) and sulfate (2–50 mg L^{-1}) were added to the electrolyte.

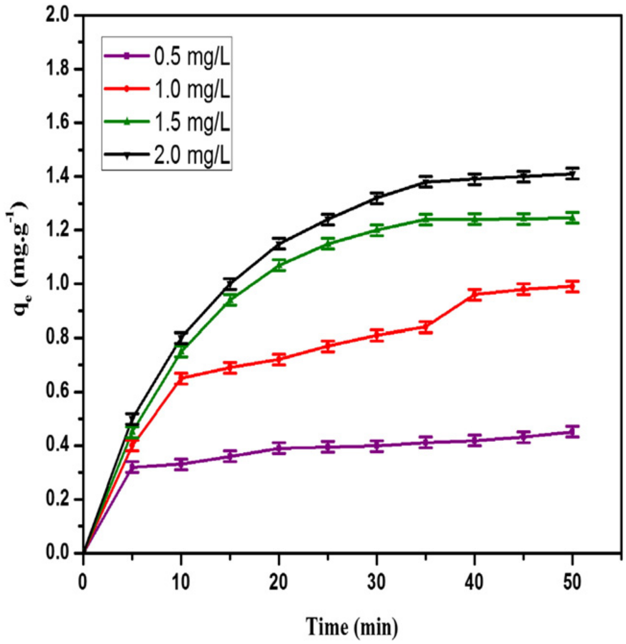

Fig. 1. Effect of time and initial concentration of nitrate ions for the adsorption on zinc hydroxide. Experimental conditions: pH of the electrolyte: 7.0; Temperature: 303 K.

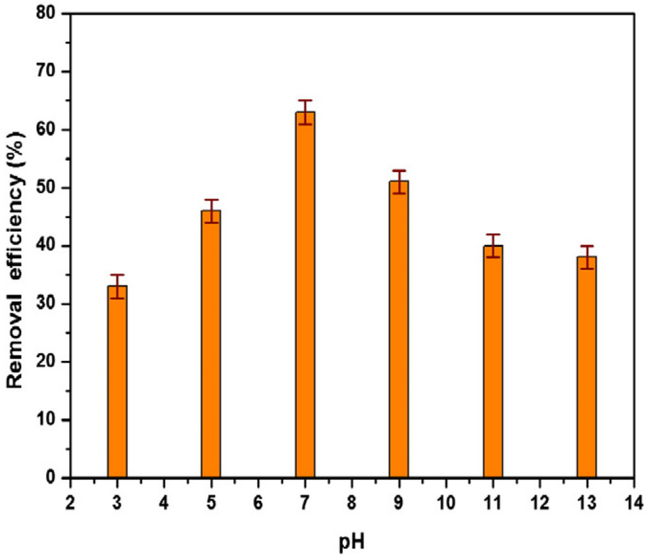

Fig. 2. Effect of pH of the electrolyte on the removal efficiency of nitrate ion, electrolyte concentration: 2.0 mg L^{-1}; current density: 0.1 A dm^{-2}, temperature: 303 K, time: 35 min.

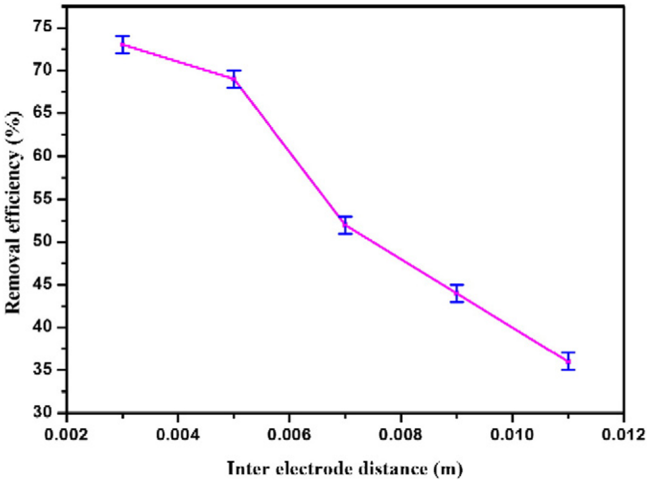

Fig. 3. Effect of inter electrode distance between anode and cathode on the removal efficiency of nitrate ion, electrolyte concentration: 2.0 mg L^{-1}; current density: 0.1 A dm^{-2}, temperature: 303 K, time: 35 min.