Removal of sodium azide from aqueous solution by Fenton-like process using natural laterite as a heterogeneous catalyst: Kinetic modeling based on nonlinear regression analysis

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A B S T R A C T

Treatment of sodium azide aqueous solution by heterogeneous Fenton process in the presence of natural laterite as catalyst was studied. Influence of initial pH, dosages of laterite and H_2O_2, sodium azide concentration and reaction time on removal efficiency was investigated. Optimized experimental conditions were as pH = 3, 1 g/L laterite, 3 mmol/L H_2O_2. Under optimal conditions, removal efficiency of sodium azide was 97% after 60 min. Laterite sample was characterized by XRD, SEM and BET analysis. XRD pattern presents that laterite is source of iron. Also, experimental results demonstrated that laterite was a suitable alternative for typical ferrous salts. A kinetic model based on nonlinear regression analysis was developed to calculate the pseudo-first order rate constant (k_{app}) as a function of initial pH and concentrations of NaN_3 and laterite. The calculated results were in consistent with the experimental data ($R^2 = 0.975$).

1. Introduction

Sodium azide is a white, odorless, tasteless and highly water-soluble crystalline powder with smooth, rapid thermal decomposition characteristics. It has also other features including: the high specific nitrogen content (65 mol%), long shelf-life and hexagonal crystal structure [1–7]. Recently because of high demand for using sodium azide as an inflator propulsion in car airbag systems, industrial manufacture of this product has increased dramatically [3,8,9]. During an automobile collision, sodium azide instantly explodes and yield N_2 gas according to following reaction [3,9]:

$$3NaN_3 \rightarrow 3Na + 2N_2 \quad T \geq 300\,°C \tag{1}$$

Moreover, in the inflator production process, additives like potassium nitrate and silica or iron oxide utilized to generate nitrogen and scavenge the metallic sodium respectively [8,9]. Sodium azide has other uses. Due to intensive antiseptic property of sodium azide, it is used as chemical preservative in laboratories, clinics and hospitals [4,10,11]. It is also used in agriculture as pesticide component and as an antihypertensive because of its vasodilatory effects [3,7]. Metal azides such as lead and silver azide are used as explosives detonators in military industry [1,12].

Sodium azide is a water soluble salt with pKa of 4.6. In the aqueous solution, the reaction of NaN_3 with water yields hydrozaic acid ($HN_{3(aq)}$) [4]. Because the Henry's law constant of hydrazoic acid is very low ($K_H = 12$ mo1/atm at 25 °C) so, HN_3 is a volatile compound [8,9,12]. In this way, there is an equilibrium between $HN_{3(aq)}$ and hydrazoic acid in vapor phase ($HN_{3(gas)}$). The partition of hydrozaic acid to gas phase depends on pH.

For instance, as the pH of aqueous solution becomes acidic, not only the concentration of $HN_{3(aq)}$ is raised but also the vapor pressure of $HN_{3(gas)}$ is increased too [4,12]. Moreover, hydrozaic acid can be protonated in relatively low values of pH (Eq. (2)) [12].

$$HN_3 \leftrightarrow H^+ + N^{3-} \quad pKa = 4.65(25\,°C) \tag{2}$$

Exposure to sodium azide induces several symptoms such as irritation of eyes, skin, headache, vomiting, tachycardia, cough, shortness of breath, trembling of hands and extra [1,10].

However, the main concern is high toxicity of sodium azide especially about environmental issues. Sodium azide is a broad spectrum biocide that is as poisonous as cyanide. According to U.S. Environmental Protection Agency maximum allowable concentrations for NaN_3 in water and workplace are 0.15 mg/L and 2×10^{-4} mg/L, respectively [8,9]. On the other hand, metal azide

complexes are result of combining metals with azide when sodium azide comes in contact with or dries on metal surfaces. Sodium azide can also react with metal pipe in laboratory sinks, traps, drains and with metal spatulas or lab equipment to form shock sensitive salts. For instance, reaction of sodium azide with lead or copper-containing fixtures in drain of laboratories causes explosion [3]. So developing an effective method for removal of sodium azide from wastewaters is inevitable.

To the best of our knowledge, relatively very little work performed for the removal of sodium azide in aqueous solution. Lin et al. [8] investigated the adsorption of hydrazoic acid from aqueous solution by macroreticular resin. In this work, the complex adsorption resin column has been used with different equipment and regeneration processes for removal of hydrazoic acid. The reported method is time-consuming and may not be an economical procedure for removal of sodium azide. Moreover, the low removal efficiency of approximately 35% in 60 min for each adsorption cycle, make it necessary to find an economical and suitable method for treatment of solutions containing NaN_3.

In other works, Hoigné et al., Pryor et al. and Betterton and Craig, investigated the kinetics and mechanism of the reaction of sodium azide with ozone in aqueous solution. Also, they have indicated that hydrazoic acid is transformed to various nitrogenous compounds, including N_2, NO_2^-, NO_3^- during ozonation process [9,13,14]. However, it is essential to mention that ozonation process needs expensive equipment for ozone generation. Also, obtaining alkaline solution (pH = 12) in this process, is difficult and leads to rise in the operation costs.

In recent years advanced oxidation processes (AOPs) have received great attention for removal of toxic, recalcitrant chemicals, dyes and other contaminants from sewerages and wastewaters [15–23]. Among various AOPs, heterogeneous Fenton process is a proper choice by reason of great oxidation power of hydroxyl radicals formed from Fenton reaction (Eq. (3)) and unique properties of iron-rich catalysts [16,17,24–29].

$$Fe(II) + H_2O_2 + H^+ \rightarrow Fe(III) + {}^\bullet OH + H_2O \qquad (3)$$
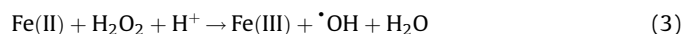
By employing iron-rich catalysts in Fenton process, disadvantages of homogenous Fenton procedure such as a narrow pH range, the formation of iron-containing sludge and catalyst deactivation by the produced intermediate, can be obviated [17]. Furthermore, iron catalysts have advantages including: stability in thermal and chemical processes, no harm for environment, sustainability and reusability [24–27,30,31].

Laterite is one of the important and novel catalysts which is source of iron and can be utilized in Fenton process [28,29]. The term laterite includes a variety of materials. Swanson define laterite as essentially a mixture of ferric hydroxide, aluminum hydroxide, titanium, rarely manganese and free silica in varying proportions [32]. However, there are a number of different catalysts that can be used in Fenton-like process including clays, hydrotalcites (anionic clays), zeolites and silicas [33–36]. It is essential to note that the mentioned catalysts are not as sufficient as laterite for Fenton process. Laterite in spite of other catalysts belongs to the natural mesoporous catalysts which contain mesopores of 2 nm to 50 nm with narrow spherical particles. This feature provides a large specific surface area that allows for a faster reaction. This is because the reaction between the different types of molecules such as NaN_3, H_2O_2, and ${}^\bullet OH$ molecules, in the case of the heterogeneous Fenton process, takes place on the surface of a solid catalyst. Also, in comparison with other solid catalysts such as natural clays, resin supports and zeolites, laterite possesses higher content of Fe ions (see Table 1) [35]. In fact, due to the lack of iron in composition of the aforementioned catalysts, sophisticated methods such as impregnation, hydrothermal and ion exchange are employed to achieve suitable percentage of Fe ions in final

Table 1
Elemental composition of laterite soil.

SiO_2	38–43%
Al_2O_3	25–28%
Fe_2O_3	26–30%
TiO_2	3–4%
K_2O	1–2%
CaO	0.5%
C	0.2%

catalysts [33,35,37]. The other motive can be that degradation of pollutants in presence of laterite is accomplished in ambient temperature. Whereas in contrast, some of the Fenton-like processes using heterogeneous catalysts based on clays and zeolites are fulfilled in more than 60 °C [35,38–41]. Also laterite is stable in thermal and chemical processes and has no toxicity for environment [42,43]. Moreover, other main privileges of laterite are as follows: abundance, considerable low cost and a proper alternative to the traditional ferrous salts applied in homogenous Fenton process [25,43,44].

In the present study, removal of sodium azide from aqueous solution by heterogeneous Fenton process was considered. To the best of our knowledge, no previous literature has reported using of Fenton procedure for treatment of sodium azide in water. The novel laterite catalyst was employed as a source of iron in this work. The physical and chemical properties of laterite characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and BET analysis. Additionally, influence of initial pH, dosages of laterite and H_2O_2, sodium azide concentration and reaction time was investigated and optimized for the maximum removal of sodium azide. Also, the pseudo-first order rate constant (k_{app}) was calculated by a kinetic model (based on non-linear regression analysis) as a function of initial sodium azide concentration, initial laterite dosage and pH.

2. Experimental

2.1. Materials

All chemicals used in this study were of analytical grade and were utilized without further purification. Sulfuric acid (H_2SO_4, 98% purity), hydrochloric acid (HCl, 37% purity), hydrogen peroxide (H_2O_2, 30% purity) and iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were purchased from Merck, Germany. Sodium azide (NaN_3) was purchased from Lobo Chemie, India. Stock sodium azide aqueous solution (1000 mg/L) was prepared gravimetrically from NaN_3. Also natural laterite catalyst was acquired from Kan Azar, Tabriz, Iran. The characteristics of laterite and sodium azide are given in Tables 1 and 2, respectively.

2.2. Characterization instruments

To determine the crystal phase composition of the laterite sample, XRD characterization was carried out at room temperature (PANalytical x'pert PRO diffractometer, Eindhoven, The Netherlands). The surface morphology and the structure of the prepared sample were obtained with the aid of a SEM (S-4200, Hitachi, Japan) at an acceleration voltage of 10 kV. Moreover, nitrogen sorption analyses were obtained with a sorptometer (Micrometrics, ASAP-2010). The surface area was calculated according to the BET analysis.

Table 2
Characteristics of sodium azide.

Chemical structure	Molecular formula	λ_{max} (nm)	Mw (g/mol)
$N^-=N^+=N^-$ Na^+	NaN_3	460	65