

Sonochemical Oxidation of Cyanide Ion Using Potassium peroxydisulfate as an Oxidizing Agent

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1. Introduction

Cyanide is a singly-charged anion containing unimolar amounts of carbon and nitrogen atoms triply-bonded together: $C\equiv N^-$ or CN^- . It is a strong ligand, and is capable of complexing at low concentrations with virtually any heavy metal. Because the health and survival of plants and animals are dependent on the transport of these heavy metals through their tissues, cyanide is very toxic. The mean lethal dose for the human adult is between 50 and 200 mg [1]. The U.S. EPA standards for drinking and aquatic-biota waters regarding total cyanide are 200 and 50 PPb, respectively, where there are total cyanides [2]. Free cyanide refers to the most toxic forms of cyanide: cyanide anion and hydrogen cyanide. Weak-acid dissociables (WADs) refer to cyanide complexes with metals such as cadmium, copper, nickel and zinc. Although thiocyanate (SCN^-) is a WAD it is often considered in its own category. Strong-acid dissociables (SADs) refer to cyanide-complexes with metals such as cobalt, gold, iron and silver.

The advanced oxidation process (AOP) using ultraviolet (UV) radiation in combination with various oxidants such as H_2O_2 , Fenton's reagent and ozone, is a highly promising technology for the treatment of toxic compounds which are refractory in nature and difficult to oxidize completely by conventional methods [3,4]. Among the different advanced oxidation processes (AOPs) such as sonochemical and peroxydisulfateion (PDS), mediated oxidation also plays an important role because it can decompose most organic and inorganic compounds. However, under the conditions of water treatment, mineralization of organic compounds is not likely to occur. The rate of chemical oxidation with PDS is relatively slow at room temperature [5], whereas PDS can readily be decomposed into sulfate anion radicals by sonochemical, photolysis or thermal decomposition [6]. Moreover, when $\cdot SO_4^-$ ($E=3.1V$) is compared to the most common oxidant, hydroxyl radical, $\cdot OH$ ($E= 2.72 V$), an active interest is currently being taken in the sulfate radical based AOPs [7]. Sonochemistry has attracted attention among the different AOP methods used in remediation processes because of its simple operational requirements and its ability to be used along with simple oxidants [8]. Sonochemical oxidation has the advantage that it can operate under

ambient conditions and is a safer technique than UV and ozonation. To date, no study has been conducted reporting on the PDS assisted oxidation of cyanides using the sonochemical method. In this study, the KCN and KSCN oxidation of PDS by ultrasonic irradiation were investigated.

2. Materials and methods

The reactor was made up of a glass cup-horn type with a 1 L capacity equipped with an ultrasonic cup-horn type transducer (MEGA-100 MIRAE ULTRASONIC, 450 kHz, maximum power 100 w) which consisted of a single piezoelectric transducer (PZT; Tamura). The diameter of each transducer is 10 cm, and when using all the solution the diameter is 500 mL. The probe compound, reagent grade potassium cyanide (KCN) in 0.1% NaOH, was obtained from Alfa Aear^R, while for the remaining reagents, potassium thiocyanate (KSCN) was obtained from Aldrich chemical company, Inc., and Potassium peroxydisulfate (PDS, $K_2S_2O_8$) is a Sigma-Aldrich product of Germany, (Purity, $\geq 99\%$). The TOC concentration of cyanide and thiocyanate was monitored with a TOC analyzer (GE Sievers 5310C and Sievers 900 Autosampler).

Cyanate concentration was determined by hydrolyzing it to ammonia at acidic pH (1.5-2.0) and ammonia was measured by Nesslerisation.

The amount of sulfate and nitrate released in the solution was determined by ion chromatography (IC), using a Dionex, DX500.

3. Results and discussion

3.1. Reaction kinetics of US/PDS oxidation of free cyanide and thiocyanate

The combination of US and PDS can create a very fast and efficient process for water treatment by producing hydroxyl and sulfate anion radicals. The complete oxidation mechanism of free cyanide (CN^-) and thiocyanate (SCN^-) using different radicals formed during the sonolysis process is described in the following reaction:

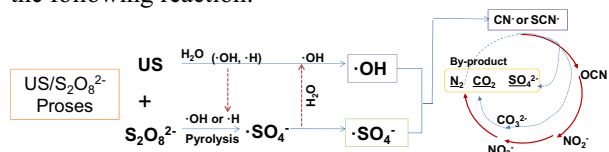


Fig.1. CN^- and SCN^- treatment mechanisms diagram with a US/PDS process

The results are shown in Fig. 2. The reaction kinetics of cyanide and thiocyanate oxidation were found to be pseudo-first order and the rate constant has been determined for different PDS concentrations. Results show a cyanide and thiocyanate TOC kinetic constant of 0.03, 0.031, 0.063, 0.064 and 0.0016, 0.024, 0.048 and 0.062 min^{-1} for the US, US/PDS20, US/PDS40 and US/PDS60 processes in respectively.

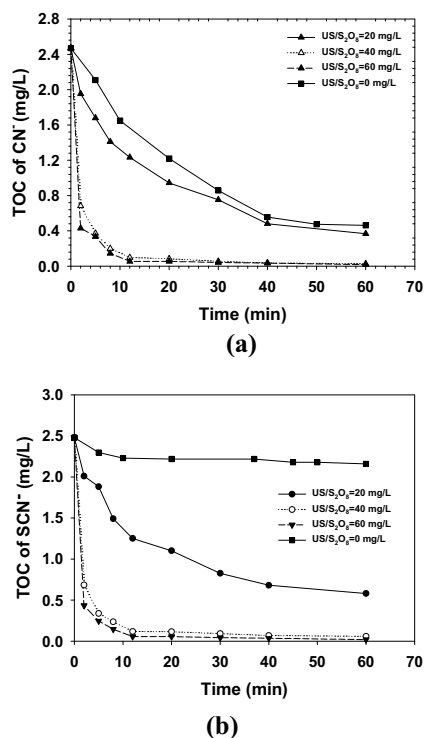


Fig.2. Effect of different initial concentrations of PDS on the oxidation kinetic of cyanide and thiocyanate. (a) kinetic of CN⁻(b) kinetic of SCN⁻. Excrement condition CN⁻: 20 mg/L, Frequency: 450 kHz, power density: 35.5 W/L.

3.2. Reaction pathways of cyanide and thiocyanate oxidation

Cyanide and thiocyanate concentrations were determined quantitatively in both chemical oxidation as well as sonochemical oxidation. Results are shown in Fig. 3(a). Cyanate concentration increased at a reaction time of 10 minutes and oxidized at 50 minutes to the decrement at 0. It was seen that cyanate did not completely hydrolyse to NO₂⁻ and NO₃⁻ in the case of sonochemical oxidation with the by-product which creates NO₂⁻ and NO₃⁻ or the part volatilized with N₂ and CO₂ gas. Results are shown in Fig. 3(b). Cyanate concentration increased at a reaction time of 12 minutes and oxidized in time with the decrement. The SO₄²⁻ concentration increased at a reaction time of 60 minutes by 10 mg/L with the by-product which creates NO₂⁻ and NO₃⁻.

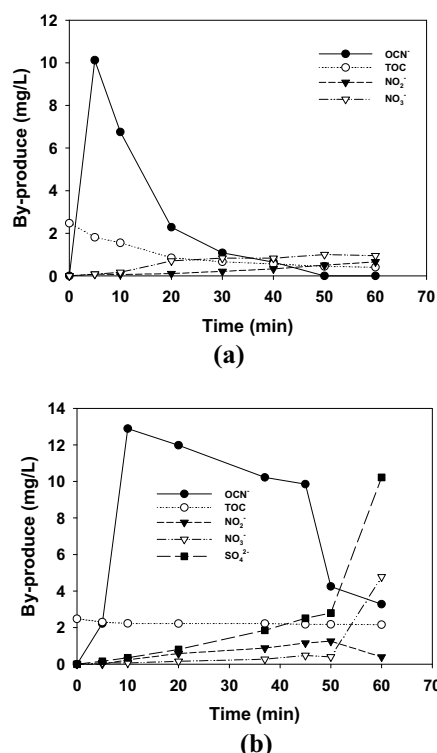


Fig.3. By product concentration profile during US oxidation of CN⁻ and SCN⁻(a) oxidation of CN⁻ by-product (b) oxidation of SCN⁻ by-product.

4. Conclusion

The reaction kinetics of cyanide and thiocyanate TOC were found to be pseudo-first order and the rate constant has been determined for different PDS concentrations.

The advantage of sonochemical oxidation of cyanide and thiocyanate is that neutralization after treatment is not required.

Acknowledgement

This study was supported by the Korea Ministry of Environment as "The GAIA Project No: 173-111-039".

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