Journal of Hazardous Materials 241–242 (2012) 478–485

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Study on the aerobic biodegradability and degradation kinetics of 3-NP; 2,4-DNP and 2,6-DNP

Zonglian She[a], Tian Xie[a], Yingjie Zhu[a], Leilei Li[a], Gaifeng Tang[a], Jian Huang[b,*]

[a] Key Laboratory of Marine Environmental Science and Ecology, Ministry of Education, College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China
[b] Department of Environmental Ecology, College of Marine Life Sciences, Ocean University of China, Qingdao 266003, China

HIGHLIGHTS

- We assessed the biodegradability of three nitrophenols using four methods.
- We simulated the degradation kinetics model and estimated relevant parameters.
- We compared the kinetics performances of solo substrates and co-substrates.

ARTICLE INFO

Article history:
Received 4 February 2012
Received in revised form 3 October 2012
Accepted 4 October 2012
Available online 13 October 2012

Keywords:
Nitrophenols
Aerobic biodegradation
Kinetics
Co-substrate

ABSTRACT

Four biodegradability tests (BOD_5/COD ratio, production of carbon dioxide, relative oxygen uptake rate and relative enzymatic activity) were used to determine the aerobic biodegradability of 3-nitrophenol (3-NP), 2,4-dinitrophenol (2,4-DNP) and 2,6-dinitrophenol (2,6-DNP). Furthermore, biodegradation kinetics of the compounds was investigated in sequencing batch reactors both in the presence of glucose (co-substrate) and with nitrophenol as the sole carbon source. Among the three tested compounds, 3-NP showed the best biodegradability while 2,6-DNP was the most difficult to be biodegraded. The Haldane equation was applied to the kinetic test data of the nitrophenols. The kinetic constants are as follows: the maximum specific degradation rate (K_{max}), the saturation constants (K_S) and the inhibition constants (K_I) were in the range of 0.005–2.98 mg (mgSS d)$^{-1}$, 1.5–51.9 mg L^{-1} and 1.8–95.8 mg L^{-1}, respectively. The presence of glucose enhanced the degradation of the nitrophenols at low glucose concentrations. The degradation of 3-NP was found to be accelerated with the increasing of glucose concentrations from 0 to 660 mg L^{-1}. At high (1320–2000 mg L^{-1}) glucose concentrations, the degradation rate of 3-NP was reduced and the K_{max} of 3-NP was even lower than the value obtained in the absence of glucose, suggesting that high concentrations of co-substrate could inhibit 3-NP biodegradation. At 2,4-DNP concentration of 30 mg L^{-1}, the K_{max} of 2,4-DNP with glucose as co-substrate was about 30 times the value with 2,4-DNP as sole substrate. 2,6-DNP preformed high toxicity in the case of sole carbon source degradation and the kinetic data was hardly obtained.

1. Introduction

Nitrophenols belong to nitroaromatic compounds which are deemed to be the exclusive pollutants from anthropogenic sources [1–3]. These chemicals are widely spread across the environment due to their extensive use as raw material or synthetic intermediate in the manufacture of pharmaceuticals, wood preservatives, rubber chemicals, pigments, dyes, plastics, pesticides and fungicidal agents, explosives and industrial solvents [2–5]. Nitrophenols pose potential risks to both human health and ecosystem since they are toxic to plants, fish and many other organisms and can accumulate in the food chain [6].

The biodegradability of chemicals is one of the most important criteria to assess their environmental behavior and hazards because a biodegradable substance is expected to cause less ecological problem in the long term than a persistent one [7,8]. For this reason standardized methods have been used by laboratories to determine biodegradability [8–12], which ensure comparable and reproducible results in different laboratories. The OECD (Organization for Economic Co-operation and Development) guidelines and ISO (International Organization for Standardization) biodegradation tests were divided into three categories: tests on ready biodegradability, tests on inherent biodegradability and simulation test [8]. In the last few decades some of these bioassays have been used to check biodegradability of nitrophenols under

* Corresponding author. Tel.: +86 0532 88622632.
E-mail address: jianhuang666@hotmail.com (J. Huang).

0304-3894/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhazmat.2012.10.008

aerobic or anaerobic conditions. Tomei et al. [13] investigated the biodegradation process of 4-nitrophenol (4-NP) in a sequencing batch reactor and found out that acclimated activated sludge had ability to degrade 4-NP both in the presence of a biogenic substrate fraction in the feed and with 4-NP as the sole carbon source. Some static tests indicated that 2-nitrophenol, 3-nitrophnol and 4-nitrophenol can be removed completely at low concentrations under anaerobic conditions [14,15]. Several studies have showed that some pure bacterial strains were capable of metabolizing 4-NP as a sole carbon source by the induction of the synthesis of specific enzymes [16,17]. Previous works on aerobic degradation of nitrophenols are mainly related to 4-NP and 2,4-DNP, including aerobic degradability [18], removal in biomass reactor [13,19,20] and the effect of co-substrate [16], etc. The literature survey shows that there is a lack of information on the aerobic biodegradation of other nitrophenols which are also harmful to human.

Kinetic study of nitrophenols is important in designing an effective biotech strategy for removal of nitrophenols from industrial wastewater. Some authors investigated the kinetic process of 4-NP biodegradation in reactors and described the process mathematically according to substrate inhibition model (the Haldane equation) [13,21,22]. Papers dealing with the effect of operating conditions on the kinetic parameters of 4-NP were recently proposed in the specialized literature. Different proportions of 4-NP and readily biodegradable substrate would influence the kinetic process [23]. Some physico-chemical indexes, such as pH, affected kinetic parameters of 4-NP biodegradation [24]. So far, few researchers have paid attention to the aerobic degradation kinetics and relevant kinetic constants of other nitrophenols.

The objectives of present study were: (1) to evaluate the aerobic biodegradability of 3-NP, 2,4-DNP and 2,6-DNP, (2) to investigate the aerobic degradation kinetics and relevant kinetic constants of the three nitrophenols at different concentrations of nitrophenols and glucose. Experiments have been carried out with a mixed bacterial culture. Four tests were used to assess the biodegradability of nitrophenols. Degradation kinetics, both in the presence and absence of glucose, were investigated in sequencing batch reactors (SBRs).

2. Materials and methods

2.1. Inoculum sludge

A sludge sample taken from the aerobic stage of a full-scale urban wastewater treatment plant in Qingdao (China) was utilized as inoculum. The sludge was cultured in a SBR with synthetic wastewater for 14–30 days in order to obtain high active sludge and was then used in tests discussed below. The synthetic wastewater was composed of glucose (1300 mg L^{-1} COD) and necessary nutrient elements.

2.2. Biodegradability testing

In present study, four kinds of testing methods including (1) BOD_5/COD ratio, (2) the production of carbon dioxide (PCD), (3) the relative oxygen uptake rate (ROUR) and (4) the relative enzymatic activity (REA) were used for the assessment of the aerobic biodegradability of 3-NP, 2,4-DNP and 2,6-DNP.

2.2.1. The test of BOD_5/COD ratio

The BOD_5 and COD of solution samples containing single 3-NP, 2,4-DNP or 2,6-DNP were determined according to the standard method recommended by American Public Health Association (APHA). Nitrophenol concentration in the samples was 100 mg L^{-1}. The experiment tests were carried out in triplicate for each nitrophenol. If the BOD_5/COD ratio was higher than 0.4, the sample could be considered readily biodegradable [12]. When the ratio was lower than 0.2, the sample was believed poorly biodegradable [25]. If the ratio was in the range of 0.2–0.4, the sample could be considered partially biodegradable.

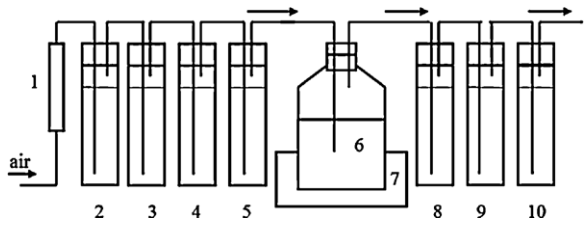

Fig. 1. Scheme of PCD experiment apparatus: (1) gas flowmeter, (2) first NaOH absorption bottle, (3) second NaOH absorption bottle, (4) $Ba(OH)_2$ absorption bottle, (5) pure water wash bottle, (6) reaction bottle, (7) water bath, (8) first $Ba(OH)_2$ absorption bottle, (9) second $Ba(OH)_2$ absorption bottle, (10) third $Ba(OH)_2$ absorption bottle.

2.2.2. The test of the production of carbon dioxide

The test was performed following standard procedures ISO 14852 [26] with modification. It was based on the measurement of the ultimate aerobic mineralization of test substances to carbon dioxide (CO_2) in water. CO_2 was determined by using the apparatus as shown in Fig. 1. Tested nitrophenol solution, inoculum sludge and inorganic nutrients solution were added to the reaction bottle to achieve a total reaction volume of 4000 ml, an initial nitrophenol concentration of 100 mg L^{-1} (as dissolved organic carbon) and a MLSS concentration of 500 mg L^{-1}. Before inoculation, the inoculum sludge was aerated for 10 h to remove organic substance. The experimental temperature was 20 ± 1 °C. The experimental period was 14 days. An endogenous test without nitrophenol was also undertaken simultaneously. Replicates of the tests have been carried out for each nitrophenol and endogenous sample.

During experiments, the amount of CO_2 production from biochemical reaction was determined every two days by titrating with standard HCl solution, and the curve was plotted as the function of time (Fig. 2).

2.2.3. The test of the relative oxygen uptake rate

Biodegradability measurement based on oxygen uptake rate (OUR) was carried out in a series of conical flasks of 200 ml. Tested nitrophenol solution containing inorganic nutrients was added to the flasks. Then inoculum sludge was added to reach a MLSS concentration of 3000 mg L^{-1}. Before inoculation, the inoculum sludge was aerated for 10 h to remove residual organic compounds and attain air saturation conditions. The flasks were sealed with rubber plug equipped with probe of dissolved oxygen (DO) and were put on magnetic stirring apparatus. The DO in the flasks was monitored

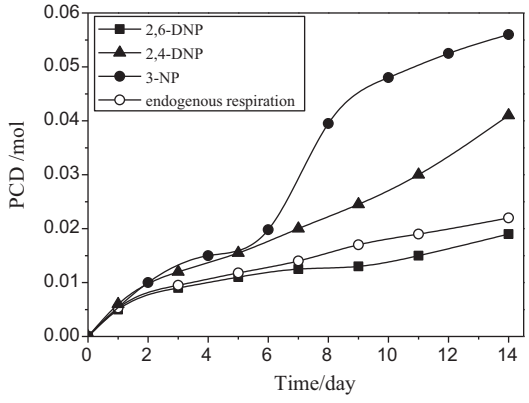

Fig. 2. The cumulative productions of CO_2.