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Review

Bacterial degradation of nitrophenols and their derivatives



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HIGHLIGHTS

- This review presents the current scenario of bacterial degradation of nitrophenols.
- Biochemical characterization of degradation of nitrophenols is described.
- Genetic characterization of degradation of nitrophenols is discussed.
- Bioremediation and chemotaxis potentials of nitrophenols-degrading bacteria are discussed.

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ABSTRACT

This review intends to provide an overview of bacterial degradation of nitrophenols (NPs) and their derivatives. The main scientific focus is on biochemical and genetic characterization of bacterial degradation of NPs. Other aspects such as bioremediation and chemotaxis correlated with biodegradation of NPs are also discussed. This review will increase our current understanding of bacterial degradation of NPs and their derivatives.

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1. Introduction

Nitrophenols (NPs) are nitrated aromatic ring structures consisting of benzene rings, hydroxyl (–OH) and nitro (–NO₂) groups. These include mononitrophenols, halonitrophenols, polynitrophenols, methylnitrophenols and aminonitrophenols (Fig. 1). These compounds are widely used for manufacturing of dyes, drugs, pesticides, herbicides, fungicides, paints and explosives [1–5]. The various applications of NPs are summarized in Table 1.

NPs have been discharged into the environment in large quantities through improper waste disposal practice, agriculture uses, medical applications and domestic activities. These compounds have been detected in agriculture soil, ground water, surface water, rain water, active sludge, air and industrial effluents [19–25]. People may be exposed to NPs in the environment by (i) breathing contaminated air, (ii) drinking substances containing NPs, (iii) eating substances containing NPs and (iv) from skin contact with NPs [3,8]. NPs can pass into the blood stream (i) through our lungs by breathing, (ii) from the stomach if swallowed and (iii) through skin via absorption [3,8]. When NPs enter inside our body, blood can carry them to various organs and tissues including kidney, liver, brain, eyes where they may undergo transformation process (via reduction and oxidation) and conjugation with glucuronic and sulfuric acids [3,8]. The toxic effects of NPs have been studied in living beings and summarized in Table 2.

NPs have gained attention due to their toxic profiles and their widespread occurrence throughout the environment. The United States Environmental Protection Agency has listed several NPs as "priority pollutants". A number of physico-chemical methods have been used for the removal of NPs from the wastewater [30–33], but none of them could achieve the complete mineralization of NPs. Bacterial remediation may be used as an effective technology to remove NPs from the environment since several bacteria have ability to use NPs as their sole carbon and energy sources.

Over the last several years, several reviews have addressed bacterial degradation of nitroaromatic compounds, chlorinated nitroaromatic compounds and chlorophenols [2,5,34]. The present review focuses on the bacterial degradation of various derivatives of NPs. We hope that this review will increase our understanding of biochemical and genetic characterization of bacterial degradation of various NPs.

2. Mechanisms of bacterial degradation of NPs

Numerous NPs-degrading bacteria have been isolated and some can utilize NPs as their sole carbon and energy sources [35–73]. The biochemical pathways for the bacterial degradation of NPs such as mononitrophenols [36,39,40,55,59,61], halonitrophenols [2,14,37,38,44,45,67] and polynitrophenols [4,50,56–58,68] have been well investigated. The bacterial degradation of NPs may be initiated by one of the following mechanisms: (a) Monooxygenation in which a monooxygenase catalyzes the removal of the nitro group as nitrite ion by adding one oxygen atom [2,4]; (b) Dioxygenation in which a dioxygenase catalyzes the insertion of two hydroxyl groups with subsequent removal of the nitro group as nitrite ion [2,4]; (c)

Reduction of the nitro group in which a nitroreducatase catalyzes the reduction of nitro group to a hydroxylamine or a amino group [4]; (d) Formation of Meisenheimer complex in which the addition of a hydride ion to the aromatic ring of a polynitrophenol take places to form a Meisenheimer complex and subsequently nitro groups eliminate as nitrite ions [4]; (e) Reductive dehalogenation from a halonitrophenol in which a reductive dehalogenase removes a halogen atom from a halonitrophenol and further degradation occurs via oxidative removal of nitro group [2].

3. Bacterial degradation of various NPs

Several bacteria catalyze mineralization or biotransformation of NPs under aerobic conditions [35–43,50,51]. In the process of mineralization, bacteria use NPs as their sole carbon and energy sources by transforming NPs into inorganic compounds like CO₂ via a series of enzymatic reactions [2]. The degradation of NPs by NPs-mineralizing bacteria is summarized in Table 3. Another process of bacterial degradation is biotransformation that involves the conversion of NPs into other organic compounds [2]. In this section, we have described aerobic pathways for mineralization and biotransformation of NPs in bacteria.

3.1. Mononitrophenols and their degradation

Mononitrophenols are the simplest form of the NPs, which exist in three isomeric forms: (i) *p*-nitrophenol (PNP) or 4-nitrophenol (4NP), (ii) *o*-nitrophenol (ONP) or 2-nitrophenol (2NP), and (iii) *m*-nitrophenol (MNP) or 3-nitrophenol (3NP).

3.1.1. Bacterial degradation of 4NP

4NP is the most common isomer of mononitrophenol and several bacteria have been isolated with their ability to utilize 4NP as the sole carbon and energy source [1,36,39–41,43,51,55,62–66,70]. Simpson and Evans [73] provided the first evidence of 4NP degradation in a *Pseudomonas* sp. that mineralized it with the release of nitrite ions. Raymond and Alexander [74] isolated a soil bacterium, *Flavobacterium* sp., which accumulated nitrocatechol (NC) as a metabolite when the resting cells were treated with 0.1% chloroform. Another 4NP-mineralizing bacterium, *Pseudomonas* sp. 8P isolated from a parathion adapted microbial consortia degraded 4NP via hydroquinone (HQ) [63].

Metabolic pathways of 4NP degradation have been studied in several bacteria [1,36,39–41,43,51,55,62–66,70] and two major pathways have been proposed for bacterial degradation of 4NP: (i) HQ pathway and (ii) NC pathway. The HQ pathway was well characterized in a number of Gram-negative bacteria including *Moraxella* sp. [55], *Pseudomonas* sp. WBC-3 [64] and *Pseudomonas* sp. 1-7 [63]. The enzymes of the HQ pathway have also been purified and characterized from *Pseudomonas* sp. WBC-3 [64] and *Pseudomonas* sp. 1-7 [63]. The first step of this pathway is conversion of 4NP into 1,4-benzoquinone (BQ) by an enzyme 4-nitrophenol-4-monooxygenase (EC=1.14.13.167) which requires one mole of NADPH for oxidation of one mole of 4NP [55,64]. The second step involves the reduction of the BQ to HQ by a

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