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## Review

## Recent advances in degradation of chloronitrophenols

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## ABSTRACT

Chloronitrophenols (CNPs) constitute a group of environmental pollutants that are widely distributed in our surrounding environment due to human based activities. This group of chemicals is highly toxic to living beings due to its mutagenic and carcinogenic nature. Examples include 2-chloro-4-nitrophenol, 4-chloro-2-nitrophenol, 2-chloro-5-nitrophenol, 4-chloro-3-nitrophenol and 2,6-dichloro-4-nitrophenol. Several methods including advanced oxidation processes, adsorption and bacterial degradation have been used for degradation of CNPs. Among, bacterial degradation is an eco-friendly and effective way to degrade CNPs. Several bacterial metabolic pathways have been proposed for degradation of CNPs and their genes and enzymes have been identified in bacteria. These bacteria were able to degrade CNPs in broth culture and soil. Therefore, CNPs-degrading bacteria are suitable candidates for bioremediation of CNPs-contaminated sites. Few CNP-degrading bacteria exhibited chemotaxis towards CNPs to enhance their biodegradation. The present review summarizes recent progress in degradation of CNPs.

## 1. Introduction

Chloronitrophenols (CNPs) are aromatic compounds that contain a benzene ring, one hydroxyl group, one or more chloro group(s) and one or more nitro group(s). Examples include 2-chloro-4-nitrophenol (2C4NP), 4-chloro-2-nitrophenol (4C2NP), 5-chloro-2-nitrophenol (5C2NP), 4-chloro-3-nitrophenol (4C3NP), 2,6-dichloro-4-nitrophenol, and 2-chloro-4,6-dinitrophenol (2CDNP) (Fig. 1). These compounds are widely used for synthesis of dyes, drugs, herbicides and pesticides (Min et al., 2014). 2C4NP is considered as a potent fungicide that is an active ingredient of nitrofungin (fungicide) and herbicide dicapthon that is well known for a cholinesterase inhibitor (Liman, 2014). Naturally, 2C4NP is produced by plants as an antifungal substance during their defence mechanism. 2C4NP was also used as a preservative in leather industry to prevent growth of fungus. Many commercial products have been synthesized through conjugation of CNPs with other compounds. Examples are 2-chloro-4-nitrophenyl-4-O-beta-D-galactopyranosylmaltoside, 2-chloro-4-nitrophenyl alpha-L-fucopyranoside and alpha-L-fucosidase (Arora et al., 2014a). These compounds are used as substrates for various enzymatic activities. For example, 2-chloro-4-nitrophenyl-4-O-beta-D-galactopyranosylmaltoside is used for detection of amylase activity (Morishita et al., 2000).

CNPs have been widely distributed in water and soil due to their extensive uses in agriculture fields and various industries (Arora et al., 2012a). 4C2NP has been detected in waste water derived from

pharmaceutical industries. The presence of CNPs in environment is a sign of danger because of their highly toxic nature. When CNPs enter the human body via skin contact, feeding, drinking or inhalation, they transport various organs and tissues through blood and undergo various transformation reactions to produce mutagenic and carcinogenic substances. Like other chlorinated nitroaromatic compounds, CNPs may cause genotoxicity, splenotoxicity, hepatotoxicity, immunotoxicity, nephrotoxicity, hematotoxicity, and carcinogenicity (Arora et al., 2012a). Due to presence of nitro groups, CNPs cause methaemoglobinaemia, reducing blood's capacity to carry oxygen (Arora et al., 2014a). They also effect to natural microbial community due to their antimicrobial and antifungal properties.

Several physicochemical methods and bacterial degradation have been used for removal of CNPs from water and soil (Ji et al., 2016). However, bacterial degradation has advantages over physicochemical methods as they are eco-friendly and cost effective. In this review, we describe recent progress in the degradation of CNPs using both physicochemical methods and bacterial degradation.

## 2. Advances in physicochemical methods for degradation of CNPs

Several physicochemical methods have been used for degradation of CNPs (Arora et al., 2012a). Advanced oxidation process (AOP) is considered as a technology for destruction of a variety of pollutants present in water. AOP is a two step process; First step involves generation of

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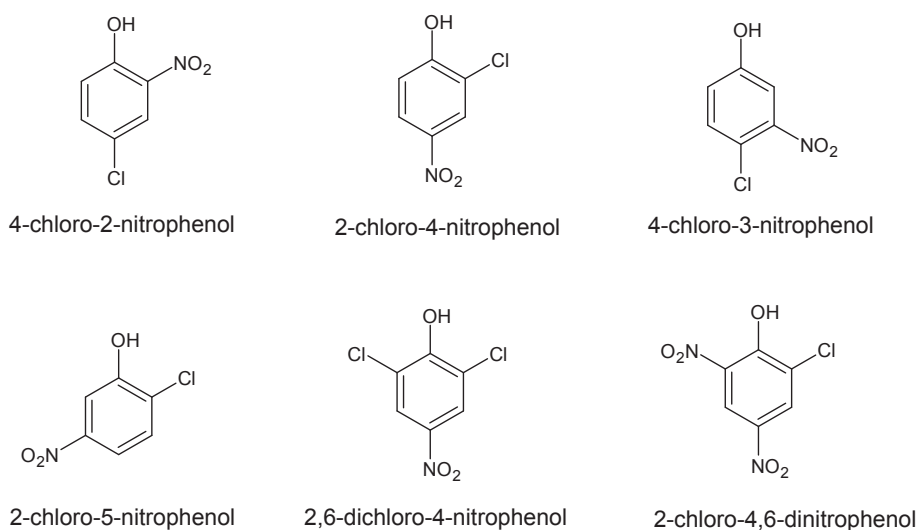


Fig. 1. Chemical structures of various chloronitrophenols.

hydroxyl radical ( $\text{OH}^\cdot$ ) or sulfate radical ( $\text{SO}_4^{\cdot-}$ ) and second step is degradation of all contaminants present in waste water by hydroxyl or sulfate radical. Hydroxyl radical based AOPs include conventional methods such as ozonation, photocatalysis, Fenton,  $\text{H}_2\text{O}_2$  and sonication (Ji et al., 2016). Hydroxyl radicals degrade organic contaminants via radical addition, hydrogen abstraction, electron transfer, and radical combination (Deng and Zhao, 2015). Hydroxyl radicals react with organic pollutants to produce carbon-centered radicals ( $\text{R}^\cdot$  or  $\text{R-OH}^\cdot$ ) which may undergo oxidation to produce organic peroxy radicals ( $\text{ROO}^\cdot$ ) (Deng and Zhao, 2015). Further reactions among all radicals produce more reactive species such as superoxide ( $\text{O}_2^{\cdot-}$ ) which may cause mineralization of the organic compounds to generate carbon dioxide and water (Deng and Zhao, 2015).

Sulfate radical based AOPs involve activation of persulfate or peroxydisulfate by heat, catalysts, transition metals, base and UV radiation (Ghanbari and Moradi, 2017). Sulfate radicals may degrade CNPs through electron transfer, hydroxylation, dehalogenation or denitrification.

4C2NP is considered as a model compound to study the degradation of CNPs by AOPs. Ozonation degraded 4C2NP in aqueous solution with formation of chlorophenol as a major intermediate (Gharbani et al., 2010). The rate of the 4C2NP degradation was faster at alkaline pH than acidic pH. Priya and Madras (2006) studied photocatalytic degradation of various CNPs and reported that the rate of 4C2NP degradation was higher than 2C4NP and 4C3NP. A combination of two or more AOPs is more effective than a single AOP to decontaminate CNPs from waste water. For example; the process of photochemical oxidation degraded 4C2NP more effectively as compared to photooxidation or chemical oxidation (Saritha et al., 2007). Similarly, Verma et al. (2013) studied degradation of 4C2NP by sonolytic, photocatalytic, and sonophotocatalytic processes and the results concluded that sonophotocatalytic process is more effective than sonolytic and photocatalytic processes for 4C2NP degradation. Shokri and Joshagani (2016) used microwave (MW) irradiation, photolysis, and photocatalyst in various combinations for degradation of 4C2NP and reported that the combination of MW, ultraviolet and  $\text{TiO}_2$  degraded 4C2NP more effectively and the rate of the 4C2NP degradation was reported in the following order:  $\text{UV/TiO}_2/\text{MW} > \text{UV/TiO}_2 > \text{MW/UV} > \text{UV} > \text{MW}$ . Verma et al. (2015) reported the 2C4NP degradation via heterogeneous photocatalytic reaction using  $\text{TiO}_2$  slurry and fixed bed reactor. Heterogeneous photocatalysis is a process in which catalyst such as  $\text{TiO}_2$  increased the photooxidation of contaminants, but the process of catalysis is initiated by light.

Gharbani and Mehrizad (2014) investigated heterogeneous catalytic ozonation for removal of 4C2NP from aqueous solution. In this process,

ozone combined with nano-ZnO is used for degradation of 4C2NP and nitrite ions were detected in aqueous solution. They compared catalytic ozonation with ozonation for 4C2NP mineralization. The results showed that ozonation alone showed slow degradation as compared to ZnO-catalyzed ozonation that degraded 99% 4C2NP. It is due to the fact that ZnO in water increased catalytic reaction on the surface of ZnO; therefore, the rate of 4C2NP degradation was increased. This reaction was pH dependent; maximum degradation was observed at low pH (pH = 3) as compared to the high pH (pH = 9) due to decreased active sites on the surface of ZnO at high pH.

Sulfate radical based oxidation of 4C2NP has also been studied recently (Ji et al., 2016). Zhou et al. (2015) studied transformation of 4C2NP by sulfate radicals which were generated by co-mediated peroxydisulfate activation. In this reaction, chloride and nitrite ions were released as results of dechlorination and denitrification, respectively. Rechlorination was also observed as evidenced by detection of polychlorophenols; however, there is no evidence for the renitrification. The process of renitrification was observed during the study of heat activated persulfate oxidation of 4C2NP and 2NP (Ji et al. 2016). In this study, polynitrophenols such as 4-chloro-2,6-dinitrophenol, 2,4-dinitrophenol and 2,6-dinitrophenol were formed as results of process of renitrification (Ji et al., 2016). Therefore, it concludes that renitrification and rechlorination are common during sulfate radical oxidation of CNPs.

Another process of the CNPs removal is adsorption of CNPs onto the surface of adsorbent (Pan and Xing, 2016). Adsorption is a rapid, effective, inexpensive and non-destructive method for removal of contaminants from waste water. This process is generally used as a final step in the treatment of industrial waste water for the removal of recalcitrant chemical molecules (Lemus et al., 2012). It is a process of capturing of the pollutant (adsorbate) by adsorbent via physicochemical interactions (Perreault et al., 2015). Various kinds of physicochemical interactions such as van der Waals force, hydrophobic effect, hydrogen bonds,  $\pi$ - $\pi$  bonds, covalent and electrostatic interactions are responsible for adsorption of organic compounds on adsorbents, depending on the chemical properties of adsorbent and adsorbate molecules (Yang and Xing, 2010). A variety of adsorbents, including activated carbon, alumina, flyash, soya cake, chitosan, zeolite, sphagnum moss peat, sea weeds have been used for the removal of various pollutants from wastewater and industrial effluents (Sharma et al., 2009). Nanomaterials and nanostructured materials have been emerged as more effective adsorbents due to their small sizes, large surface area and having a greater number of active sites for interaction of different adsorbate molecules (Sharma et al., 2009). Examples are carbon nanomaterials, nanosized metallic oxides and graphene. Carbon

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