Microbial Degradation of Nitroaromatic Pesticide: Pendimethalin

20

Prasad Jape, Vijay Maheshwari, and Ambalal Chaudhari

20.1 Introduction

Agriculture is recognized as the main engine to drive the economy in Indian subcontinent, where 60–70% of the population has relied on agriculture for food. India's population is expected to reach approximately 1.3 billion by 2020 (Kanekar et al. 2003), while world population will increase to 12 billion before 2050 (Pimentel 1995). The weeds, insects, and microorganisms are the main competitors the moment humans settled to agriculture cropland, ravaging crops, food, and feed stores. Unfortunately, the worldwide crop losses have been estimated approx. 50% by pestilent, 13–16% by insect pest, 12–13% by phytopathogens, and 10–13% by weeds which cost to $ 244 billion loss of revenue per year (Pimentel 1997). For this purpose, intensive agricultural strategies are adopted to increase food grain production and prevent crop loss (Shroff 2000). For these tribulations, more emphasis is accorded to (i) use quality seeds, (ii) increased chemical fertilizer inputs for more crop productivity, and (iii) protection of crops against various plant pests that adversely affect crop productivity (Ahemad and Khan 2011). To ameliorate the enormous crop losses caused by pests, more use of chemically synthesized pesticides is promoted. Pesticide application to control plant pest was adopted as an effective regime to increase crop productivity, which promoted more production of pesticide widespread usage and spillage in the soil environment disposed or washed out in water, aquifers, etc. In recent years, a variety of pesticides of wide diversity chemical groups (>500) have been extensively employed for protection of the crop plants (Ahemad et al. 2009), large amount of which are lost in application process, and meager amount of pesticides reaches to the target pest (Pimentel 1995). The demand for pesticide in India is 3.75% of the total world consumption (Jogdand

---

P. Jape · V. Maheshwari · A. Chaudhari (✉)
School of Life Sciences, Kavayitri Bahinabai Chaudhari North Maharashtra University, Jalgaon, India

D. P. Singh et al. (eds.), *Microbial Interventions in Agriculture and Environment*,
https://doi.org/10.1007/978-981-13-8391-5_20

2000). The most commonly used pesticides are categorized as (i) organophosphate, (ii) organochlorine, (iii) carbamate, (iv) pyrethroids, (v) neonicotinoids, (vi) nitroaromatics, and (vii) biopesticides. Among these, organophosphates and nitroaromatics are extensively used in the agriculture. Despite the benefits, the haphazard application of pesticides in the last two to three decades caused (i) serious environmental pollution; (ii) bulk of the residue (80–90%) was deposited on nontarget areas, such as soil, water, sediments; (iii) caused loss of vital plant pollinators; (v) threatened nontarget life forms; (vi) obligated public health issues; and (vii) damage loss to the tune of 100 billion every year (Sakata 2005; Parte et al. 2017). Of these, plethora of nitroaromatic compounds are manufactured for intended application, and tons of them finally come into water, retained in the soil, affect oil fertility, and impact various life forms in the ecosystem (Parte et al. 2017). Nitroaromatics are (i) stable to biotic and abiotic attack, (ii) persistent in the environment for prolonged time, (iii) synthesized in great volume and differ in chemical structure, (iv) used as chemical feedstock material for the synthesis of variety of pesticides, explosives, herbicides, dyes, etc. Indiscriminate application of nitroaromatics has caused inexorable amount of environmental pollution and was recognized as recalcitrant compound and priority hazardous type of pollutant by various regulatory systems. The recalcitrance nature of nitroaromatics is due to (i) unusual substitution, (ii) condensed aromatic ring, (iii) insolubility in aqueous phase, and (iv) resistance to abiotic and biotic degradation. Majority of them are identified as potent neurotoxin, endocrine disruptor, carcinogenic, mutagenic, teratogenic, toxic, and designated as a major priority pollutant by various regulatory systems. Moreover, the growing attention to public health hazards, environmental awareness, and legal requirement on the release of pesticides are becoming more complex, strict, and warranting for their removal. Hence, removal of nitroaromatic pesticide from contaminated environment is realized as peremptory art. Several conventional cleanup methods such as (i) incineration, (ii) volatilization, (iii) hydrolysis, (iv) photo-oxidation, (v) adsorption, (vi) percolator filters, (vi) advance oxidation, (vii) and photo-catalysis with TiO_2 are available for the removal of pollutant (Timmis et al. 1994). The cost-effective and eco-friendly biological system is also emerged out as effective alternative for removal of pesticides from contaminated areas either by (i) bioaugmentation, (ii) biostimulation, (iii) natural attenuation, (iv) biosparging, (v) in situ, (vi) ex situ, (vii) land farming, or (viii) composting. The physical cleanup methods (i) generate toxic (NO_x) nonintermediates that end up with enormous estimated cost of 3000–4000 USD per ton (Kanekar et al. 2003; Ortiz-Hernandez et al. 2011), (ii) cant handle complex chemistry of pesticides producing equally or even more toxic intermediates, and (iii) proved inefficient (Parte et al. 2017), while biological system follows biphasic mode of pesticide degradation but few of them may require prolonged time to recuperate the contaminated sites (Shaer et al. 2013; Ishag et al. 2017). Among the pesticides, a strategy to control weeds from crop area for more crop yield with herbicides has spurt the interest in world market as a profitable business, which is evidenced from steep rise in worldwide market demand for herbicide by 39% and projected to grow more by 11% (Gianessi 2013).

Presently, herbicides are grouped into 29 different classes on the basis of mechanism of action and generally applied either by (i) foliar spray, (ii) soil contact, (iii) broadcast, or (iv) spot contact (Singh and Singh 2014). The most commonly used herbicides in agriculture include (i) atrazine, (ii) metolachlor, (iii) glyphosphate (GP), (v) pendimethalin (PND), (vi) 2,4-dichlophenoxy acetic acid (2,4-D), (vii) clodinafop propargyl, and (viii) diuron (Singh and Singh 2014). Excess use of herbicides in the last two to three decades has caused (i) great concern to the environment, (ii) enormous water and soil pollution (Juhler et al. 2001), (iii) reduced biodiversity, (iv) lowered soil heterotrophic bacterial load, (v) and threat to nontarget life forms due to bioaccumulation risk in human, animal, and crop plants and disrupting the ecosystem through food chain, bioaccumulation, biomagnification, etc. (Singh and Singh 2014). Inadequate management and indiscriminate application of wide variety of chemical herbicides are the major root cause of contamination and irreparable damage to the ecosystem. Moreover, chemical properties, quantum of herbicide load, and its persistence determine the extent of impact. The necessity to remove the recalcitrant herbicides in an economical and eco-friendly manner constitutes the major objective (Singh and Singh 2014). The present review provides an overview of an attempt made for microbial removal of the third most frequently used herbicide in the world, pendimethalin (PND).

20.2 Pendimethalin: A Nitroaromatic Pesticide for Crop Protection

Pendimethalin (PND) (CAS registry number 40487-42–1); [N-(1-ethylpropyl)–2,6-dinitro-3,−4xylidine] is a dinitroaniline herbicide that has nitrated aromatic ring structure consisting of hydroxyl (-OH) and nitro (-NO_2) groups with molecular mass of 281.312 Da with empirical formula $C_{13}H_{19}N_3O_4$ and hydrophobic, sparingly soluble in 0.275 ppm water (Richardson and Gangolli 1992; Strandberg and Scott-Fordsmand 2004). PND is widely applied to soil as a selective preplant, preemergence, and sometimes postemergence herbicide in variety of crop plants including cotton, soybean, maize, wheat, rice, peas, and vegetable crops to control annual grasses, certain broad leaf weeds of dryland crops and non-crop areas, and also for plant growth promotion under tropical, subtropical, as well as temperate conditions (Ni et al. 2016a; 2018). PND is also recommended for use on fruit, grapes, vegetable, oil seeds, cereals, tobacco, and ornamental plants at 2 kg/ha in the European Union (EU) and at 6.7 kg/ha in the USA (European Community 2003).

Besides glyphosphate and parquet, PND is the third most frequently used selective herbicide throughout the world and has been on the market for almost 35 years (Ni et al. 2016b; Vighi et al. 2017). The demand for PND in crop protection raised from 9 to 114.3 tons, with more than 12-fold increase (Choudhury et al. 2016), and the northern part of India alone utilized almost 11.8 tons of PND a year for protection of cotton crop alone (Choudhury et al. 2016). PND is available in 30% EC or granule for manual application through spray method to pre- and postemergence or directs own crop plants.

20.3 Hazardous Implications of PND

PND has relatively (i) low volatility due to vapor pressure of 3×10^{-3} mmHg at 25 °C, and some meagre amount (10%) is lost through volatilization from surface soil; (ii) persist longer time in soil because of low leaching potential; (iii) hydrophobic nature assists to form strong physical bond with organic matter of soil and clay minerals (Walker and Bond 1977; Singh and Singh 2014); (iv) has high geometric mean (GM) with half-life of 76–98 days and 20 days in agriculturally relevant soils and sediment water under aerobic and anaerobic condition, respectively; (v) and there was a strong inhibitory action on mitotic cell division in developing root shoot system (Singh and Singh 2014). Although these attributes make PND a selective herbicide, it enters the surface water mainly as runoff from new application area due to heavy rains, which results in 2–134 μg l^{-1} residue to water sediments (Keese et al. 1994), and accumulates in onion up to 1 $mgkg^{-1}$ (Tsiropoulos and Miliadis 1998) making it a threat to the ecosystem. The major concern to herbicide use is that only meager amount of PND reaches the target and the remaining accumulates into the environment, where it adversely affects crop, animal, and public health (Pimentel 1995). PND contamination majorly occurred due to improper guidance on handling of herbicides on farm with moisture condition, temperature, and cultivation practices aiding the long-time persistence in the soil (Swarcewicz and Gregorczyk 2012). The widespread usage and contamination are an alarming environmental concern, and hence PND is listed as a persistent bioaccumulative toxin and a possible human carcinogen (group C) by US EPA (Ahmad et al. 2016). Excessive use of pendimethalin has further shown toxicity effects onto (i) onion and maize roots (Promkaew et al. 2010), (ii) the growth of funnel plants by inhibiting the tubulin production during mitosis (Engebretson et al. 2001; Fennell et al. 2006; El-Awadi and Hassan 2011), (iii) fish and other aquatic invertebrates on bioaccumulation, (iv) root knot nematode, (v) and humans through the food chain (Abd-Algadir 2011). Kidd and James (1991) observed oral LD_{50} of 1050–5000 $mgkg^{-1}$ in rats. Pendimethalin is (i) relatively nontoxic to humans by ingestion; (ii) slightly toxic by skin exposure, with dermal LD_{50} of ≥2000 $mgkg^{-1}$ in rats; (iii) and mildly irritant to the eye of rabbits.

20.4 Rationale Necessity for Removal of PND

PND is registered for herbicide use in several countries since two to three decades ago as the most effective, efficient, and economical entity to abate weed growth, but excessive application has raised these various concerns about potential environmental hazards. The environment fate of PND indicates that only 10% reaches to the target weed pest, 10–20% vaporizes in the first week after application, and the rest may dissipate via biological or chemical process with DT_{50} values between 30 and >200 days, suggesting (i) phytotoxicity to nontarget plant crops; (ii) enough time for physical adhesion to soil, organic fraction, sediment, and clay particles (Strandberg and Scott-Fordsmand 2004); (iii) more chances for entry into the food chain and lesser possibility for degradation; and (iv) decomposition to toxic NO_x. Consequently, PND (i) affects symbiosis between legume and *Rhizobium*; (ii) reduced nodulation by >25%; (iii) lowers VAM colonization by 36–69%; (iv) drops overall heterotrophic microbial activity for the initial 4–10 weeks; (v) suppresses rhizosphere nutrient cycling by microbes; (vi) exerts toxicity to plants, microbes, and also fish with LC_{50} (96 h) for rainbow trout and blue gill sunfish of 0.14 and 0.2 mgL^{-1} (Kidd and James 1991); (vii) reduces soil nematode by 35–36%; and (viii) inhibits roots and shoots in seedlings (Strandberg and Scott-Fordsmand 2004). Extensive use of PND as a preferred herbicide has now posed adverse toxicological impacts on flora and fauna through direct and indirect exposure. PND exposure in the agriculture health study had shown (i) increased incidences of lung, rectal, and pancreatic cancers (Ahmad et al. 2016), (ii) genotoxic effects on the fish species *Oreochromis niloticus* and aquatic invertebrate (El-Sharkawy et al. 2011), and (iii) mild hemotoxic effect in female rats after administration of dosage for 90 days (Ayub et al. 1997). As a result, PND is classified as a (i) persistent bioaccumulative toxic agent (Roca et al. 2009), (ii) possible human carcinogen (group C), and (iii) slight acute toxic compound (toxicity class III) (Ni et al. 2016b). Extensive exposure of PND for prolonged time can (i) cause cytotoxicity to living CHO cells (Patel et al. 2007); (ii) disrupt the endocrine, reproductive, and immune system; (iii) cause neurobehavioral disorders (Ritter et al. 1995); (iv) cause thyroid follicular cell adenoma; and (v) inhibit mitotic cell division in growing root system (Singh and Singh 2014). Overall, the forgoing discussion suggests the necessity for removal of PND from the contaminated environment.

20.5 Pendimethalin Degradation by Abiotic and Microbial Route

Until now, various abiotic avenues have been employed for removal of PND, but they have either lacked specificity or haven't proved to be reliable. Environmental parameters, such as reluctant species (complex structure, volatility, water solubility), pH, and dissolved oxygen matter (DOM), determine the PND degradation in the nature. DOM increase nitro group reduction in liquid solution of sulfide in anoxic black carbon-amended sediments (Gong et al. 2016). PND is sensitive to different wavelengths of UV light in water and soil-water suspension causing dealkylation of amino group (Scheunert et al. 1993), reduction into diamines by zero valent iron powder (Keum and Li 2004), and degradation which is achieved using TiO_2 (Pandit et al. 1995), nanoparticles of $BaTiO_3/TiO_2$ in the presence of peroxide, and per sulfate species by crystalline gel conversion methods (Gomathi Devi and Krishnamurthy 2008). Combination of ultraviolet light and sunlight had shown degradation of 99% PND (Dureja and Walia 1989; Moza et al. 1992), while electrolytic and electro-irradiated methods based on diamond anodes help to remove PND from soil washing effluents (Almazan-Sanchez et al. 2017). The abiotic mode of degradation (i) causes decomposition to toxic fumes of NO_x, (ii) separates unwanted compounds without destruction, (iii) generates toxic intermediates, and (iv) poses several issues for on-site or off-site treatment system. Hence, abiotic degradation route is obsolete and less preferred alternative in the present era.

In biotic degradation, microorganisms are the only tiny entities endowed with inherent abilities to transform complex compound to simple form and appeared as an effective strategy to decontaminate PND from the contaminated sites. Only microorganisms are empowered in the biosphere to bind, thrive, colonize, and metabolically utilize the compound as CorN and energy source for their growth and convert it into simple and nontoxic chemical structure of the target compound due to their involvement in nutrient cycling (Diez 2010; Pinto et al. 2012). This incredible versatility harbored by microbes can help to incorporate the recalcitrant PND into biogeochemical cycle. Bacterial and fungal entities are associated with significant role in transformation of nitroaromatic compounds (Pinto et al. 2012). Hence, applications of microorganisms are the most preferred strategy to degrade nitroaromatic compound, pendimethalin (More et al. 2015). At present, only few microbial systems for degradation of PND have been studied under both aerobic and anaerobic environments (Zheng and Cooper 1996). Collectively, three different mechanisms, namely, (i) oxidative N-dealkylation, (ii) cyclization, and (iii) nitroreduction, have been reported to initialize the PND degradation (Kole et al. 1994). Biodegradation of PND with *Azotobacter chroococcum* adopts N-dealkylation and reduction of more than one nitro group to form six metabolites (S_1, S_2, S_3, S_4, S_5, and S_6). S_1 metabolite is formed through oxidative complete N-dealkylation; further, it undergoes acetylation of the aniline nitrogen to S_3 and S_4 through elimination of nitro group at C-2 without substitution, S_2 by reduction of nitro group at C-6 position, and minor metabolite S_5 formed by aryl methyl group oxidation at C-3; oxidative cyclization reduced the 2-nitro group and N-dealkylation to S_6 (Kole et al. 1994). Likewise, several microbes (Table 20.1) including (i) fungus strain *Lecanicillium saksenae* had shown degradation of 250 ppm PND (Pinto et al. 2012); (ii) *Fusarium oxysporum* and *Paecilomyces variotii* converted PND into two metabolites, namely, N-(1-ethylpro-pyl)-3,4-dimethyl-2-nitrobenzene-l,6-diamine(II) and 3,4-dimethyl-2,6-dinitroaniline by nitroreduction and dealkylation (Singh and Kulshrestha 1991); (iii) *Bacillus circulans* degraded the PND and formed 6-amino pendimethalin and 3,4-dimethyl-2,6-dinitroaniline metabolites (Megadi et al. 2010; More et al. 2015); (iv) *Paracoccus* sp. P13 degrade 100 ppm PND within 2 days by ring cleavage through oxidation to yield 1,3-dinitro-2-(pentan-3-ylamino) butane-1,4-diol, an alkane organic compound (Ni et al. 2018); (v) *Bacillus subtilis* consumed 100 ppm PND within 2 days to form three metabolites, namely, 6-amino pendimethalin by nitroreduction using PND nitroreductase, 5-amino-2-methyl-3-nitroso-4-(pentan-3-ylamino) benzoic acid by nitroreduction at the nitro group connected to C-2, and 8-amino-2-ethyl-5-(hydroxymethyl)-1,2-dihydroquinoxaline-6-carboxylic acid by carboxylation of the aryl methyl group at C-4 (Ni et al. 2016b); (vi) six fungal species, *Aspergillus flavus*, *A. terreus*, *Fusarium solani*, *F. oxysporum*, *Penicillium citrinum*, and *P. simplicissimum*, have shown 66% of 500 ppm PND degradation in 15 days, and *Fusarium solani* alone displayed higher specificity to degrade 62% PND to form three metabolites through partial N-dealkylation to N-propyl-3-methyl-4-hydroxy-2,6-dinitroaniline, subsequent ring hydroxylation

Table 20.1 Summary of PND degrading microbial species isolated from various ecohabitats

Source	Medium	Condition	PND (mgL^{-1})	Degradation (%)	Metabolites	Reference
Bacteria						
Azotobacter chroococcum	N-free MS (pH 7.2)	31 °C in dark at steady state	500	55 (20 days)	2-Methyl-4,6-dinitro-5-[(lethylpropyl)amino] benzylalcohol,2,6-dinitro-3,4-xylidine,2-methyl4,6-dinitro-5-[(1-ethylpropy1) aminolbenzaldehyde,2-nitro-6-amino-(N-ethylpropyl)-3,-4xylidine,2,6-dinitro-3,4-xylidin	Kole et al. (1994)
Bacillus circulans	MS (pH 7)	30 °C at 150 rpm	1000	100	6-Amino pendimethalin by nitroreduction and form 3,4-dimethyl–2,6-dinitroaniline and pantane by oxidative dealkylation	Megadi et al. (2010)
Bacillus megaterium	MS (pH 7)	30 °C at 150 rpm	100	100 (5.6 days)	Undetected	Belal and Hassan (2013)
Bacillus lehensis XJU PUF cells	MS (pH 7)	(30 ± 2 °C) at 150 rpm	2000	100 (4 days)	Reduction to3,4-dimethyl 2,6-dinitroaniline by PND oxidative dealkylation	More et al. (2015)
Bacillus subtilis Y3	MS (pH 7)	30 °C 150 rpm	100	99.9 (2.5 days)	Nitroreductase catalyze nitroreduction of PND to 6-amino pendimethalin	Ni et al. (2016b)
Bacillus subtilis Y3	LB broth or MSM (pH 7.5)	PNR activity at 35 °C	7	100	Reduced the C-6 nitro group of the aromatic ring of PND to 2-nitro-6-amino-N-(1-ethylpropyl)-3,4-xylidine	Ni et al. (2016a)
Bacillus subtilis Y3	MS (pH 7)	30 °C at 150 rpm	100	99.5	Nitroreductase catalyze nitroreduction of PND to 6-amino pendimethalin	
B. safensis FO-36bT, *B. subtilis* subsp. *inaquosorum* KCTC *13429 T*, *B. cereus* ATCC 14579	MS (pH 7)	25 °C at stationary phase	28	90 (30 days)	N-(1-ethylpropyl)-3-methyl-2,6-diaminobenzine	Ishag et al. (2017)

(continued)

Table 20.1 (continued)

Source	Medium	Condition	PND (mgL^{-1})	Degradation (%)	Metabolites	Reference
Paracoccus sp. *P13*	MS (pH 7)	30 °C at150 rpmin (dark)	200	99.8 (5 days)	Oxidative ring cleavage converted PND to 1,3-dinitro-2-(pentan-3-ylamino)butane-1,4-diol	Ni et al. (2018)
			Fungi			
Aspergillus flavus, *A. terreus*, *Fusarium solani*, *F. oxysporum*, *Penicillium citrinum*, *and P. simplicissimum*	Czapek's broth (pH 6.5)	28 ± 2 °C in dark	500	60 (15 days)	N-(1-ethylpropyl)-2-amino-6-nitro-3,4-xylidin, by partial N-dealkylation by ring hydroxylation, N-propyl-3-methyl-4-hydroxy2,6 dinitroaniline by nitro group reduction and 2,6dinitro-3,4-xylidene by complete N-dealkylation	Barua et al. (1990)
Fusarium oxysporum and *Paecilomyces variotii*	Czapek's broth (pH 6.8)	31 ± 2°C (dark with intermittent shaking)	100	100 (6 days)	N-(1-ethylpro-pyl)-3,4-dimethyl-2-nitrobenzene-1,6-diamine (II) and 3,4-imethyl-2,6-dinitroaniline by nitroreduction or dealkylation of substituted amine	Singh and Kulshrestha (1991)
L. saksenae	MS (pH 7)	30 °C at 150 rpm	25	99.5 (10 days)	Metabolites undetected	Pinto et al. (2012)
Phanerochaete chrysosporium	MS (pH 7)	30°at 150 rpm	100	96	Metabolites undetected	Belal and Nagwa (2014)

MS, minimal salt medium

via C-dealkylation to N-(1-ethylpropyl)-2-amino-6-nitro-3,4-xylidine, and finally to 2,6-dinitro-3,4-xylidiene through complete N-dealkylation (Barua et al. 1990); and (vii) polyacrylamide and PUF-immobilized *Bacillus lehensis* XJU degraded the 100 ppm PND in 96 h and 6-amino pendimethalin through reduction reaction to form 3,4-dimethyl-2,6-dinitroaniline metabolites via oxidative dealkylation (More et al. 2015). In brief, the forgoing evidences suggest that more efforts were earlier focused on metabolites formed after nitroreduction reaction and more scope still exists to search for newer microbes with array of metabolic apparatus for effective remediation of PND using microbial system.

20.6 Pathway for Biodegradation of PND

The need for PND removal has been the focus of research more evidently in the recent years. Conventional methodologies used for pesticide treatment with (i) adsorption, (ii) photolysis, (iii) photolysis combined with oxidants, (iv) photo-fenton process, and (v) photocatalysis did not receive much commercial interest as these techniques are (i) just a segregation of pesticides rather than a treatment and (ii) often result into incomplete mineralization and (iii) more toxic residues that may even persist for longer duration in the ecosystem. These conventional physico-chemical approaches have proved to be (i) uneconomical, (ii) unreliable, and (iii) inconclusive due to incomplete conversion and (iv) failure with consequent unintentional damage to environment. On these evidences, microbial degradation to remediate polluted sites appeared as an emerging technology (Samanta et al. 2002). Biodegradation of herbicide using microbial system is (i) economic, (ii) is effective, and (iii) does not produce toxic products (Jiang and Li 2018), (iv) catalyzes either mineralization of compound to form inorganic end products, such as CO_2 and water, or (v) attempts co-dissimilatory nonspecific transformation with enzyme(s) specific for other substrates under aerobic or anaerobic conditions.

Several bacteria and fungi so far explored for degradation of PND have not deciphered the metabolic mechanism (Table 20.2). Ni et al. (2016b) reported the nitroreduction is the first initial degradation and detoxification step for PND and recognized PND nitroreductase (PNR) encoded by *pnr* responsible for initial degradation step of PND from *Bacillus subtilis* Y3. PNR, a functional homodimer with a subunit molecular size of 23 kDa, showed reduction of C-6 nitro group of PND to yield 2-nitro-6-amino-N-(1-ethylpropyl)-3,4-xylidine which showed negligible inhibitory effect on *Saccharomyces cerevisiae* BY4741 during detoxification assay vis-a-vis parent PND, indicating potential role of PNR in detoxification of PND. More studies on such aspect are required to delineate the pathway for microbial mineralization of PND and, therefore, warrant search for robust microbes endowed with inherent capability to not only to degrade PND but also catabolize other toxic pesticides in the presence of metal ions in edaphic conditions to recoup the contaminated soil habitats.

More efforts to search the potent microbes which contain pesticide-degrading gene from the ecological habitat are highly essential for bioaugmentation,

Table 20.2 Metabolic pathway adopted for biodegradation of pendimethalin by various microbes

Microbes	Pathway		Reference
Bacteria			
A. chroococcum	PND	→2,6-Dinitro-3,4-xylidine	Kole et al. (1994)
		→6-Nitro-3,4-xylidine	
	PND	→2,6-Dinitro-3,4-xylidine (2,6-dinitro-3,4-dimethyl) phenyl cetamide	
	PND	→2-Methyl-4,6-dinitro-5-[(l-ethylpropyl) amino] benzyl alcohol	
		→2-Methyl 4,6-dinitro-5-[(1-ethylpropy1) aminol benzaldehyde	
	PND	→2-Methyl-4-nitro-5-N-(1- cyclopropyl)-6-nitrosobenzyl alcohol	
	PND	→N-2,6-dinitro-3,4- dimethyl) phenyl cetamide	
	PND	→2-nitro −6- amino-(N- ethylpropyl)-3, −4 xylidine	
Bacillus circulans	PND	→6-Aminopendimethalin	Megadi et al. (2010)
	PND	→3,4-dimethyl −2, 6- dinitroaniline	
		→Pantane	
Pseudomonas aeruginosa	PND	→*N*-(1-Ethylpropyl)-3-methyl-2, 6 diaminobenzin + CH$_2$O	Shaer et al. (2013)
Bacillus subtilis Y3	PND	→6-Aminopendimethalin	Ni et al. (2016a)
		→5-Amino-2-methyl-3-nitroso-4-(pentan-3-ylamino) benzoic acid	
		→8-Amino-2-ethyl-5-(hydroxymethyl)-1,2 dihydroquinoxaline-6-carboxylic acid	
Paracoccus sp. *P13*	PND	→1,3-Dinitro-2-(pentan-3- ylamino) butane-1,4-diol	Ni et al. (2018)
		→CO$_2$ + H$_2$O	
Fungi			
Fusarium solani	PND	→N-(1- ethylpropyl)-2-amino-6-nitro-3,4-xylidine	Barua et al. (1990)
	PND	→N-propyl- 3-methyl-4-hydroxy 2, 6 dinitroaniline	
	PND	→2,6 Dinitro-3,4-xylidene	
Fusarium oxysporum and *Paecilomyces variotii*	PND	→N-(1-Ethylpropyl)-3,4-dimethyl-2-nitrobenzene-l,6-diamine	Singh and Kulshrestha (1991)
	PND	→Isomeric diamine (N-(1-ethylpropyl)-3, 4-dimethyl-6-nitrobenzene-l, 2 diamine-	
		→3,4-Dimethyl-2,6-dinitroaniline	

biostimulation, or natural attenuation strategy. In bacteria, pesticide-degrading genes often reside on the plasmids (catabolic plasmid) and encode for the pollutant-degrading enzymes (Laemmli et al. 2000). The catabolic plasmids are now recognized from *Alcaligenes*, *Actinobacter*, *Arthrobacter*, *Cytophaga*, *Moraxella*, *Klebsiella*, and *Pseudomonas*. Plasmid-mediated augmentation method could possibly provide an effective solution to remove PND from the environment.

20.7 Conclusion

Ecosystems are under consistent threat due to the exposure to excess use of herbicide pollution. Microbes equipped with biodegradation pathways and response to biotic and abiotic system are providing the tool to design most suitable strategy for on-site or off-site removal of herbicides. Despite the availability of a gamut of microbes from the ecological habitat, the reach of bioremediation to degrade pesticide remains a great challenge. This review on environmentally relevant nitroaromatic pesticides reveals many limitations and future research scopes associated with the current body of knowledge. Effective and indigenous microbial strain or consortia with capability to tolerate and degrade pesticides in edaphic conditions as an effective biofertilizer could minimize chemical fertilizer application by 20–30%. Genetically engineered organism, with multiple nitroaromatic compound-degrading genes or enzyme systems, may play a crucial role in the biodegradation of these otherwise recalcitrant compounds. The development of a system-oriented understanding of natural pesticide attenuation with respect to pesticide degradation at low concentrations and in low-nutrient situations is urgently needed so as to ameliorate the toxicity of herbicide and safeguard the planet Earth.

References

Abd-Algadir M, Sabah Elkhier M, Idris O (2011) Changes of fish liver (*Tilapia nilotica*) made by herbicide (Pendimethalin). J Appl Biosci 43:2942–2946

Ahemad M, Khan MS (2011) Ecotoxicological assessment of pesticides towards the plant growth promoting activities of lentil (Lens esculentus)-specific *Rhizobium sp*. strain MRL3. Ecotoxicology 20:661–669

Ahemad M, Zaidi A, Khan MS, Oves M (2009) Factors affecting the variation of microbial communities in different agro-ecosystems. In: Microbial strategies for crop improvement. Springer, Berlin, p 301–324

Ahmad I, Ahmad A, Ahmad M (2016) Binding properties of pendimethalin herbicide to DNA: multispectroscopic and molecular docking approaches. Phys Chem Chem Phys 18:6476–6485

Almazán-Sánchez PT, Cotillas S, Saez C, Solache-Rios MJ, Martínez-Miranda V, Canizares P, Linares-Hernández I, Rodrigo MA (2017) Removal of pendimethalin from soil washing effluents using electrolytic and electro-irradiated technologies based on diamond anodes. Appl Catal B Environ 213:190–197

Ayub SM, Garg SK, Garg KM (1997) Sub-acute toxicity studies on pendimethalin in rats. Indian J Pharm 29:322

Barua AS, Saha J, Chaudhuri S, Chowdhury A, Adityachaudhury N (1990) Degradation of pendimethalin by soil fungi. Pestic Sci 29:419–425

Belal EB, Hassan NE (2013) Dissipation of pendimethalin by *Bacillus megaterium*. Mansoura J Plant Prot Pathol 5:463–472

Belal EB, Nagwa ME (2014) Biodegradation of pendimethalin residues by *P. chrysosporium* in aquatic system and soils. J Biol Chem Environ Sci 9:383–400

Choudhury PP, Singh R, Ghosh D, Sharma AR (2016) In herbicide recomandation for various crops. Herbicide use in Indian Agriculture ICAR – Directorate of Weed Research, Jabalpur, Bulletin No.22: 25–48

Diez MC (2010) Biological aspects involved in the degradation of organic pollutants. J Soil Sci Plant Nutr 10(3):244–267

Dureja P, Walia S (1989) Photodecomposition of pendimethalin. Pestic Sci 25:105–114

El-Awadi ME, Hassan EA (2011) Improving growth and productivity of fennel plant exposed to pendimethalin herbicide: stress–recovery treatments. Nat Sci 9:97–108

El-Sharkawy NI, Reda RM, El-Araby IE (2011) Assessment of stomp®(Pendimethalin) toxicity on *Oreochromis niloticus*. J Am Sci 7:568–576

Engebretson J, Hall G, Hengel M, Shibamoto T (2001) Analysis of pendimethalin residues in fruit, nuts, vegetables, grass, and mint by gas chromatography. J Agric Food Chem 49:2198–2206

European Community (2003) Review report for the active substance pendimethalin, Report 7477/VI/98-final. European Comission, Health and Consumer Protection Directorate General, Brussels, pp 1–43

Fennell BJ, Naughton JA, Dempsey E, Bell A (2006) Cellular and molecular actions of dinitroaniline and phosphorothioamidate herbicides on *Plasmodium falciparum*: tubulin as a specific antimalarial target. Mol Biochem Parasitol 145:226–238

Gianessi LP (2013) The increasing importance of herbicides in worldwide crop production. Pest Manag Sci 69:1099–1105

Gomathi Devi LN, Krishnamurthy G (2008) Photocatalytic degradation of the herbicide pendimethalin using nanoparticles of $BaTiO_3/TiO_2$ prepared by gel to crystalline conversion method: a kinetic approach. J Environ Sci Health B 43:553–561

Gong W, Liu X, Xia S, Liang B, Zhang W (2016) Abiotic reduction of trifluralin and pendimethalin by sulfides in black-carbon-amended coastal sediments. J Hazard Mater 310:125–134

Ishag AESA, Abdelbagi AO, Hammad AMA, Elsheikh EAE, Elsaid OE, Hur JH (2017) Biodegradation of endosulfan and pendimethalin by three strains of bacteria isolated from pesticides-polluted soils in the Sudan. Appl Biol Chem 60:287–297

Jiang J, Li S (2018) Microbial degradation of chemical pesticides and bioremediation of pesticide-contaminated sites in China. In: Twenty years of research and development on soil pollution and remediation in China. Springer, Singapore, p 655–670

Jogdand SN (2000) Biotechnology for hazardous waste management. In: Environmental biotechnology. Himalaya Publication House, New-Delhi, p 121–140

Juhler RK, Sorensen SR, Larsen L (2001) Analysing transformation products of herbicide residues in environmental samples. Water Res 35:1371–1378

Kanekar P, Daupure P, Sarnaik S (2003) Biodegradation of nitroexplosive Indian. J Exp Biol 41:991–1001

Keese RJ, Camper ND, Whitwell T, Riley MB, Wilson PC (1994) Herbicide runoff from ornamental container nurseries. J Environ Qual 23:320–324

Keum YS, Li QX (2004) Reduction of nitroaromatic pesticides with zero-valent iron. Chemosphere 54:255–263

Kidd H, James DRE (1991) The agrochemicals handbook. The Royal Society of Chemistry, Cambridge, UK

Kole RK, Saha J, Pal S, Chaudhuri S, Chowdhury A (1994) Bacterial degradation of the herbicide pendimethalin and activity evaluation of its metabolites. Bull Environ Contam Toxicol 52:779–786

Laemmli CM, Leveau JH, Zehnder AJ, van der Meer JR (2000) Characterization of a second tfd gene cluster for chlorophenol and chlorocatechol metabolism on plasmid pJP4 in *Ralstonia eutropha* JMP134 (pJP4). J Bacteriol 182:4165–4172

Megadi VB, Tallur PN, Hoskeri RS, Mulla SI, Ninnekar HZ (2010) Biodegradation of pendimethalin by Bacillus circulans. Indian J Biotechnol 9:173–177

More VS, Tallur PN, Niyonzima FN, More SS (2015) Enhanced degradation of pendimethalin by immobilized cells of *Bacillus lehensis* XJU. 3 Biotech 5:967–974

Moza PN, Hustert K, Pal S, Sukul P (1992) Photocatalytic decomposition of pendimethalin and alachlor. Chemosphere 25(11):1675–1682

Ni HY, Wang F, Li N, Yao L, Dai C, He Q, He J, Hong Q (2016a) The nitroreductase PNR is responsible for the initial step of pendimethalin degradation in *Bacillus subtilis* Y3. Appl Environ Microbiol 82:7052–7062

Ni H, Yao L, Li N, Cao Q, Dai C, Zhang J, He Q, He J (2016b) Biodegradation of pendimethalin by *Bacillus subtilis* Y3. J Environ Sci 4:121–127

Ni H, Li N, Qiu J, Chen Q, He J (2018) Biodegradation of pendimethalin by *Paracoccus sp*. P13. Curr Microbiol 75:1077–1083

Ortiz-Hernández ML, Sánchez-Salinas E, Olvera-Velona A, Folch-Mallol JL (2011) Pesticides in the environment: impacts and its biodegradation as a strategy for residues treatment. In: Pesticides-formulations, effects, fate. InTech, China, p 551–574

Pandit GK, Pal S, Das AK (1995) Photocatalytic degradation of pendimethalin in the presence of titanium dioxide. J Agric Food Chem 43:171–174

Parte SG, Mohekar AD, Kharat AS (2017) Microbial degradation of pesticide: a review. Afr J Microbiol Res 11:992–1012

Patel S, Bajpayee M, Pandey AK, Parmar D, Dhawan A (2007) In vitro induction of cytotoxicity and DNA strand breaks in CHO cells exposed to cypermethrin, pendimethalin and dichlorvos. Toxicol in Vitro 21:1409–1418

Pimentel D (1995) Amounts of pesticides reaching target pests: environmental impacts and ethics. J Agric Environ Ethics 8:17–29

Pimentel D, Wilson C, McCullum C, Huang R, Dwen P, Flack J, Cliff B (1997) Economic and environmental benefits of biodiversity. BioScience 47(11):747–757

Pinto AP, Serrano C, Pires T, Mestrinho E, Dias L, Teixeira DM, Caldeira AT (2012) Degradation of terbuthylazine, difenoconazole and pendimethalin pesticides by selected fungi cultures. Sci Total Environ 435:402–410

Promkaew N, Soontornchainaksaeng P, Jampatong S, Rojanavipart P (2010) Toxicity and genotoxicity of pendimethalin in maize and onion. Kasetsart J-Nat Sci 44:1010–1015

Richardson ML, Gangolli S (eds) (1992) The dictionary of substances and their effects. Royal Society of Chemistry, London. (1)

Ritter L, Solomon KR, Forget J, Stemeroff M, O'Leary C (1995) Persistent organic pollutants: an assessment report on: DDT-aldrin-dieldrin-endrin-chlordane-heptachlor-hexachlorobenzene-mirextoxaphene-polychlorinated biphenyls-dioxins and furans 1995. Inter-Organization Programme for the Sound Management of Chemicals (IOMC), Geneva

Roca E, D'Errico E, Izzo A, Strumia S, Esposito A, Fiorentino A (2009) In vitro saprotrophic basidiomycetes tolerance to pendimethalin. Int Biodeterior Biodegrad 63:182–186

Sakata M (2005) Organophosphorous pesticides. In: Suzuki O, Watanabe K (eds) Drugs and poisons in humans. Springer, Verlag, New York, pp 535–544

Samanta SK, Singh OV, Jain RK (2002) Polycyclic aromatic hydrocarbons: environmental pollution and bioremediation. Trends Biotechnol 20:243–248

Scheunert I, Mansour M, Doerfler U, Schroll R (1993) Fate of pendimethalin, carbofuran and diazinon under abiotic and biotic conditions. Sci Total Environ 132:361–369

Shaer IBS, Abdelbagi AO, Elmustafa EA, Ahmed SAI, Osama GE (2013) Biodegradation of pendimethalin by three strains of bacteria isolated from pesticides polluted soils. Univ Khartoum J Agric Sci 21:233–252

Shroff R (2000) Chairman address in pesticide information. Annual Issue. Pesticide Association of India Publication, New Delhi

Singh SB, Kulshrestha G (1991) Microbial degradation of pendimethalin. J Environ Sci Health B 26:309–321

Singh B, Singh K (2014) Microbial degradation of herbicides. Crit Rev Microbiol 42:245–261

Strandberg M, Scott-Fordsmand JJ (2004) Effects of pendimethalin at lower trophic levels-a review. Ecotoxicol Environ Saf 57:190–201

Swarcewicz MK, Gregorczyk A (2012) The effects of pesticide mixtures on degradation of pendimethalin in soils. Environ Monit Assess 184(5):3077–3084

Timmis KN, Steffan RJ, Unterman R (1994) Designing microorganisms for the treatment of toxic wastes. Annu Rev Microbiol 48:525–557

Tsiropoulos NG, Miliadis GE (1998) Field persistence studies on pendimethalin residues in onions and soil after herbicide postemergence application in onion cultivation. J Agric Food Chem 46:291–295

Vighi M, Matthies M, Solomon KR (2017) Critical assessment of pendimethalin in terms of persistence, bioaccumulation, toxicity, and potential for long-range transport. J Toxicol Environ Health B 20:1–21

Walker A, Bond W (1977) Persistence of the herbicide AC 92,553, N-(1-ethylpropyl) 2, 6-dinitro-3, 4-xylidine, in soils. Pestic Sci 8:359–365

Zheng SQ, Cooper JF (1996) Adsorption, desorption, and degradation of three pesticides in different soils. Arch Environ Contam Toxicol 30:15–20