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Review

# A monograph on the remediation of hazardous phthalates

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## HIGHLIGHTS

- Historical development of phthalates to its current applications.
- Impact of phthalates on the environment and health hazards.
- Illustrated the bioremediation of phthalates with combined pathways.
- Latest developments to alleviate phthalate pollution.

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## ABSTRACT

Phthalates or phthalic acid esters are a group of xenobiotic and hazardous compounds blended in plastics to enhance their plasticity and versatility. Enormous quantities of phthalates are produced globally for the production of plastic goods, whose disposal and leaching out into the surroundings cause serious concerns to the environment, biota and human health. Though *in silico* computational, *in vitro* mechanistic, pre-clinical animal and clinical human studies showed endocrine disruption, hepatotoxic, teratogenic and carcinogenic properties, usage of phthalates continues due to their cuteness, attractive chemical properties, low production cost and lack of suitable alternatives. Studies revealed that microbes isolated from phthalate-contaminated environmental niches efficiently bioremediate various phthalates. Based upon this background, this review addresses the enumeration of major phthalates used in industry, routes of environmental contamination, evidences for health hazards, routes for *in situ* and *ex situ* microbial degradation, bacterial pathways involved in the degradation, major enzymes involved in the degradation process, half-lives of phthalates in environments, *etc*. Briefly, this handy module would enable the readers, environmentalists and policy makers to understand the impact of phthalates on the environment and the biota, coupled with the concerted microbial efforts to alleviate the burden of ever increasing load posed by phthalates.



**Contents**



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## 1. Introduction

The word plastic is sprouted from *plasticos* (Greek), which means capable of moulding into different shapes. By dint of the swift advancement in technology and the geometric progression of the global population growth, plastic materials have found versatile applications in every aspect of modern human life. Different substances are blended in plastics at various proportions to improve their performance and reduce cost [1]. Phthalates or esters of phthalic acid are a class of xenobiotic organic compounds widely employed to make plastic goods more flexible. Some of the commonly used phthalates are described in Table 1 [2,3], which are not chemically bound to the polymer mesh, and hence, they would easily migrate from plastic products into the surrounding environments [4–6]. Many experimental studies (*in silico*, *in vitro* mechanistic, pre-clinical and clinical) have shown that phthalates act as endocrine disruptors *in vivo*, apart from causing various health problems including hepatomegaly, osteoporosis, peroxisome proliferation, feminization of boys, reduction in body weight, skin and breast cancers, *etc.* [7–10]. Humans are normally exposed to phthalates *via* dermal, inhalation, oral, and intravenous routes [11]. Upon ingestion, phthalates in mammals rapidly metabolized to form monophthalate by intestinal lipases or esterases, and subsequently into oxidative metabolites, which would be glucuronidated before excretion through urine [12,13]. Diester phthalates have accelerated biological effects, when they are hydrolyzed to monoester, the monophthalates [14].

In the environment, phthalates are degraded by abiotic process like photo-degradation at sluggish rates. However, microbial intervention – especially by bacteria and fungi – is the best known method for the complete mineralization of these hazardous pollutants. Thus, this review makes an in-depth analysis on phthalates *vis-à-vis* health implications associated with phthalates in biological system, based on the available *in silico* computational, *in vitro* mechanistic, pre-clinical animal and human epidemiological evidences. Connected to this, the following major questions are addressed in this review: description of the common phthalates, description of the biodegradation process, *in situ* or *ex situ* mechanism of phthalate utilization, description of the enzymes involved in the degradation process, the favourite substrates (among phthalates) for these enzymes and details of products formed, the resistance of phthalates in the environment (half-life), and the mechanism of microbial action on phthalates.

## 2. Phthalates as plasticizer

Castor oil is the first plasticizer used for making cellulose nitrate in 1856; later in 1870, it was replaced by camphor. To overcome the odor released from volatile camphor, phthalates were introduced in 1920s as an alternative. Synthesis of polyvinyl chloride (PVC) in 1931, followed by the introduction of DEHP in 1933 (a suitable plasticizer of PVC) drastically changed the world of plastics. A simple chemical reaction between an alcohol and phthalic anhydride results in the formation of phthalates [1].

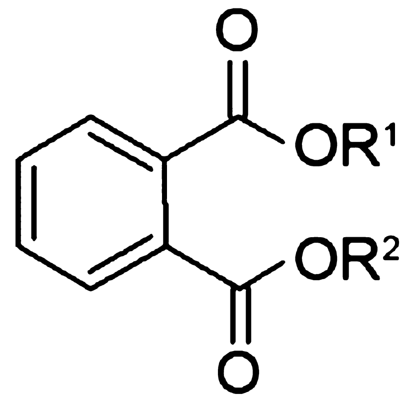


**Fig. 1.** General chemical structure representing phthalic acid esters.

Phthalates are esters of 1,2-benzene dicarboxylic acid (Fig. 1). Their structure varies depending on the number of side chains; dialkyl, alkyl or aryl groups attached to the basic phenyl moiety (Fig. 2). Three isomeric forms (*ortho*, *para* and *meta*) of 1,2-benzene dicarboxylic acid, and corresponding esters constitute the major category of plasticizers (Fig. 2). Phthalic acid, the *ortho* isomer and its esters represent the major share of all phthalates produced globally, especially used as the plasticizer for making PVC plastics. Terephthalic acid, the *para* isomer and its esters and isophthalic acid, the *meta* isomer and its esters are used as monomers mainly for the synthesis of various polyesters in manufacturing industry (Fig. 2). For instance, DMTP and DMIP are used for the industrial production of fibres, electrical capacitors, film, *etc.* [11]. Higher molecular weight (MW) phthalates, such as DIDP, are used as a softener in child care products and toys, and DEHP (the major plasticizer in PVC products) is predominantly used in medical devices; while lower MW phthalates, such as BBP, are used in cosmetics, including nail polishes; DBP in vinyl tile; and DEP in personal care products to enhance fragrance [15], (all the diphthalates mentioned in this article are summarized in Table 1).

PVC plastics represent the largest group of plastics. The attachment of PVC polymer chains are in such a way that it forms a rigid criss-crossed structure (Fig. 3). Plasticizer is an additive for PVC to soften it, or in other words, it facilitates the sliding of chains against each other for manufacturing different products having improved