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Review

Recent strategies for removal and degradation of persistent & toxic organochlorine pesticides using nanoparticles: A review

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A B S T R A C T

Organochlorines (OCs) are the most hazardous class of pesticides, therefore, banned or restricted in several countries. The major sources of OCs include food industries, agriculture and sewage wastes. Their effluents discharged into the water bodies contain extremely high concentration of OCs which ultimately causes environmental concern. Because of their high persistence, toxicity and potential to bio-accumulation, their removal from wastewater is imperative. The degradation techniques are now advanced using nanomaterials of various kinds. During the last few years, nanoparticles such as TiO_2 and Fe are found to be excellent adsorbents and efficient photocatalysts for degrading more or less whole OCs as well as their toxic metabolites, which opens the opportunities for exploring various other nano-particles as well. It is noteworthy that such methodologies are economic, fast and very efficient. In this review, the detailed information on different types of OC pesticides, their metabolites, environmental concern and present status on degradation methods using nanoparticles have been reviewed. An attempt has also been made to highlight the research gaps prevailing in the current research area.

Contents

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1. Introduction

Pesticides are substances used by human beings to kill undesirable organisms (pests) to preserve agricultural produce (EPA, 2009). Based on their action towards targeted pests, the largest used pesticides are insecticides and herbicides followed fungicides, acaricides, nematicides, molluscicides and rodenticides (London and Meyers, 1995; EPA, 2009). Pesticides can be chemically classified as: (i) organochlorines (OCs) (ii) organophosphates (iii) carbamates and (iv) substituted urea. Among all, OCs are the most hazardous persistent organic pollutants (POPs) and poses serious risk to the environment.

OC pesticides (mainly insecticides) are chlorinated hydrocarbons used extensively from the 1940s through the 1980s in agriculture and mosquito control (Choi et al., 2016). Representative compounds are DDT, methoxychlor, dieldrin, chlordane, lindane, and benzene hexachloride. These are endocrine disrupter chemicals (EDCs) with high chronic, developmental toxicity which resulted in poisoning cases numbered about 1 million per year (WHO, 1990; Igbedioh, 1991; Forget, 1993). Possibility of health hazards during pesticide manufacturing and formulation are even higher (Varma and Varma, 2005). Moreover, many pesticides persist for long periods of time in the environment (upto many years) e.g. the predicted half-life of γ-HCH in water is 191 days (Kafilzadeh, 2015) and the average half-life of γ-HCH and α-HCH around the Great Lakes region ranged from about 3 to 4 years (Cortes and Hites, 2000). Hence, the use of a number of OCs, including DDT, has been banned or restricted around the world (Beard, 2006). Due to high persistence and bio-accumulative nature (high Ko/w: range) (WHO, 2003), they are still widespread and detected in coastal environments (Arienzo et al., 2013), seafood (Moon et al., 2009), marine mammals (Robinson et al., 2015), birds (Hong et al., 2014), and humans (Moon et al., 2012). Moreover, they exhibit long range transport properties, as a result of which they can be carried to long distances by means of air or water (Cortes and Hites, 2000). For example, HCH and Endosulfan were predominantly transported from farmland to estuary under tropical regime, which ultimately causes a serious risk to the aquatic biota (Leadprathom et al., 2009). Fig. 1 lists all the major OC pesticides synthesized so far and Table 1 describes their physiochemical properties.

Nowadays, the transformation products (TP) of various pesticides have also gained attention worldwide because of their higher concentration and toxicity than the parent ones (Pozo et al., 2001; Patsias et al., 2002; Nawab et al., 2003) e.g., the by-products of DDT i.e. DDE and DDD are very toxic and even dieldrin is the toxic by-product of Aldrin (Tian et al., 2009; Bandala et al., 2002). In 1997, the European Directive 91/414/EEC and its subsequent amendments established that, before a new pesticide is launched in the market, its complete environmental data must be provided for all amounts of metabolites, and degradation and reaction products, which account for more than 10% of the amount of the active substance (Barcelo and Hennion, 1997).

1.1. Worldwide consumption/production of pesticides

Europe is now the largest pesticide consumer in the world, followed by Asia. As for countries, China, USA, France, Brazil and Japan are the largest pesticide producers or traders in the world (Zhang et al., 2011). In 2007, 44.75% of the total pesticide sale was contributed only by USA alone (Zhang et al., 2011). Atrazine is a widely used pesticide especially in the developed countries. In 2005 its consumption reached 57.39 million pounds (Zhang et al., 2011). The worldwide consumption of pesticides is depicted in Table 2 (Singh et al., 2014). If we look for developing countries like India which is an agricultural land due to its biodiversity, role of pesticides is very important. The pesticide production in India started in 1952 and India is now the second largest manufacturer of pesticides in Asia after China and ranks twelfth globally (Mathur, 1999). There has been a steady growth in the production of technical grade pesticides in India, from 5,000 metric tons in 1958 to 102,240 metric tons in 1998. In 1996–1997 the demand for pesticides in terms of value was estimated to be around Rs. 22 billion (USD 0.5 billion), which is about 2% of the total world market (Mathur, 1999).

1.2. Need for removal

Extensively used OCs are persistent i.e., extremely long half-lives in soil and water (upto many years), toxic, high potential to bioaccumulation, and high resistant to microbial attack (Lal and Saxena, 1982; Nagata et al., 1999; Sahu et al., 1992; Martijn et al., 1993; Smith et al., 1994; Cortes and Hites, 2000; Barcelo and Hennion, 2003; Cahill et al., 2011). Several OCs were detected in water (0.068–0.098 ppb), foodstuffs (0.027–0.045 ppb) and human breast milk (Gilliom, 2001; Sudaryanto et al., 2006; Shoiful et al., 2013; Zhenwu et al., 2013). These factors lead to their immediate eradication from the environment (Nemerow and Dasgupta, 1991; Tchobanoglous and Franklin, 1991; Ali and Aboul-Enein, 2004).

1.3. Pesticide removal techniques

Several disadvantages of using pesticides (Gilliom, 2001; Zhenwu et al., 2013) encouraged to develop and design efficient methods for the removal of different harmful pesticides, particularly OCs from waste water reservoirs. Several physical, chemical as well as biological methods involving adsorption, oxidation, catalytic degradation, membrane filtration and biological treatment have been developed (Li et al., 2010; Rodante et al., 1992; Lin and Lin, 2007; Smith et al., 2004; Zinovyev et al., 2005). Due to the recalcitrant structures of the OCs, only specific bacterial and fungal species have been reported to be capable of degrading them (Kwon et al., 2005; Bhalerao and Puranik, 2007; Navaratna et al., 2010). Adsorption was found as the most popular technique because of its simplicity and economical approach (Gupta and Ali, 2008; Paknikar et al., 2005; El-Temsah et al., 2016). Because of unique properties (large specific surface area, small diffusion resistance, higher adsorption capacity, and faster adsorption equilibrium) nanomaterials have gained attention for the removal of several contaminants from waste water reservoirs (Buzea et al., 2007; Ma et al., 2011; Jassal et al., 2015a, 2015b, 2015c; Jassal et al., 2016a, 2016b; Shanker et al., 2016). Most of the nanomaterials are semiconducting in nature and can easily degrade OC pesticides photocatalytically (Fig. 2). More efforts are required in this field in order to achieve efficient results which can be employed at industrial scale. Therefore, it was considered worthwhile to write this review in order to summarize and address the advancements in this field of removal of OC pesticides using nanoparticles. One of the main driving forces in the writing of this article is to organize all the scattered information in this particular field. Table 3 describes list of various OC pesticides degraded using nanoparticles, respectively.

2. Degradation of various OC pesticides

2.1. DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane)

It was used massively worldwide in 1940–70s as an insecticide for agricultural purposeand public health to check malaria and other mosquito bornediseases (yellow fever, encephalitis). After