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Persistent organic pollutants management and remediation

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Abstract

Persistent organic pollutants (POPs) are toxic chemicals that originate from man-made sources associated with the production, use, and disposal of certain organic chemicals. Many of the chemicals were produced commercially for pest and disease control, crop production and industrial use. Some of the POPs such as pesticides and polychlorinated biphenyls (PCBs) are intentionally produced, while others such as dioxins and furans are unintentional by-products of industrial processes or result from the combustion of organic chemicals. Over the last six decades, the unsustainable management of chemicals through their life cycles has resulted in widespread and massive contamination of the environment, biota and humans with POPs and other persistent toxic substances. Many techniques had been used for treating POPs. However, these techniques did not prove to be highly efficient due to the high operational costs involved. Recent studies found that, Guar gum and Xanthan gum are highly recommended as an option for treating POPs, because it is a biodegradable biopolymer, non-toxic, involved low treatment cost, easily available and is produced in abundance.

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1. Introduction

Persistent Organic Pollutants (POPs) are organic compounds that can persist in the environment for a very long time as they resist photolytic, chemical and biological degradation (Buccini, 2003). POPs are major global issue due to their persistency, long range transportability, ability to bio accumulate in fatty tissue, and are highly toxic even at low concentration (Tang, 2013). POPs can be found all over the world even at arctic region as it can travel far away from

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the source and with high stability (Brown & Wania, 2008). POPs can exist in gaseous form and attach to the solid particle surface or water sediments (El-Shahawi et al., 2010). POPs reached the ground surface through rain or deposition of the flying ashes (El-Shahawi et al., 2010). Figure 1 shows the chemical structures of common POPs.

The sources of POPs are mainly from anthropogenic activities and can be introduced into the environment through many pathways (Doong et al., 2008). POPs are able to reach the environment through agricultural runoff, industrial effluent, urban runoff, drainage system, deposition from the atmosphere and landfill leachate (Blanchard et al., 2004).

Environmental contamination by organochlorine insecticides is commonly found in conventional farm and agricultural area for rice paddy (Revathi & Jennifer, 2006). The residue level of most organochlorine insecticides in river or sediments are found in much higher concentration at agricultural area as compared to other area which do not involve farming activities (Zuriati et al., 2003). Vector control, household insecticides and structural pest management are some of the other sources of POPs pesticides contamination. However, these studies have not been conducted and lead to large gap in identifying the actual source of POPs contamination other than in agricultural areas.

The main source of polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) is waste incinerator (USM, 2004). However, POPs originated from natural sources as well. Volcanic activities and vegetation fires contributed to the levels of dioxins and furans in the environment (Jacob & Cherian, 2013). Polychlorinated biphenyls (PCBs) are still found in old transformers and capacitors in use that contain PCB-contaminated oil (Hashim, 2001). According to Agamuthu & Narayanan (2013), POPs might be found in the waste stream due to activities from industrial, residential and commercial area. Waste disposal practices can be one of the cumulative sources of POPs through uncontrolled landfilling and open burning especially in developing countries (Agamuthu & Narayanan, 2013).

In 1970s, POPs have been banned in Europe and USA due to their persistency against biological/chemical degradation, long range transportability, tendency to bio accumulate in fatty tissue, and detrimental impacts to living organisms (Pandit et al., 2001). However, POPs are still widely used in many countries until Stockholm Convention (SC) came into force (Pandit et al., 2001). SC is a global treaty that aims to protect human and environment from POPs by controlling and eliminating the introduction of POPs into the environment (Xu et al., 2013).

According to Xu et al., (2013), currently there are 22 POPs listed in SC. Table 1 shows the POPs listed in SC amendment. Twelve POPs known as the “dirty dozen” including aldrin, dieldrin, endrin, chlordane, heptachlor, HCB, mirex, toxaphene, DDT, PCBs, PCDDs, and PCDFs are listed in the initial Stockholm Convention in 2004. In 2009, chlordecone, lindane, α-HCH, β-HCH, hexabromobiphenyl, tetra-BDE, penta-BDE, hexa-BDE, hepta-BDE, PFOs and its salts, PFOSF, and pentachlorobenzene were added in an amendment and came into force one year later. In 2011, endosulfan became the 22nd POP. From the 22 POPs listed in SC, 15 are pesticides.

However, this number could increase as more than 800 compounds appear likely to meet the criteria for POPs (Brown and Wania, 2008). Phenol,2,4-bis(1,1-dimethylethyl) and DEHP can be considered as POPs as they meet the main criteria of POPs such as persistence, long range transportability, ability to bioaccumulate and high toxicity (Davı and Gnudi, 1999; Wang et al., 2003; Bakir et al., 2014; Net et al., 2014). Several studies found that phenol 2,4-bis(1,1dimethylethyl) and DEHP were among the chief POPs found in agricultural farm (Kong et al., 2012; Gushit et al., 2013). Pesticide has been widely used in agricultural activities since many decades ago to augment the crop production in many countries. Over use of pesticide has been a threat for public health and environment (Gushit et al., 2013).

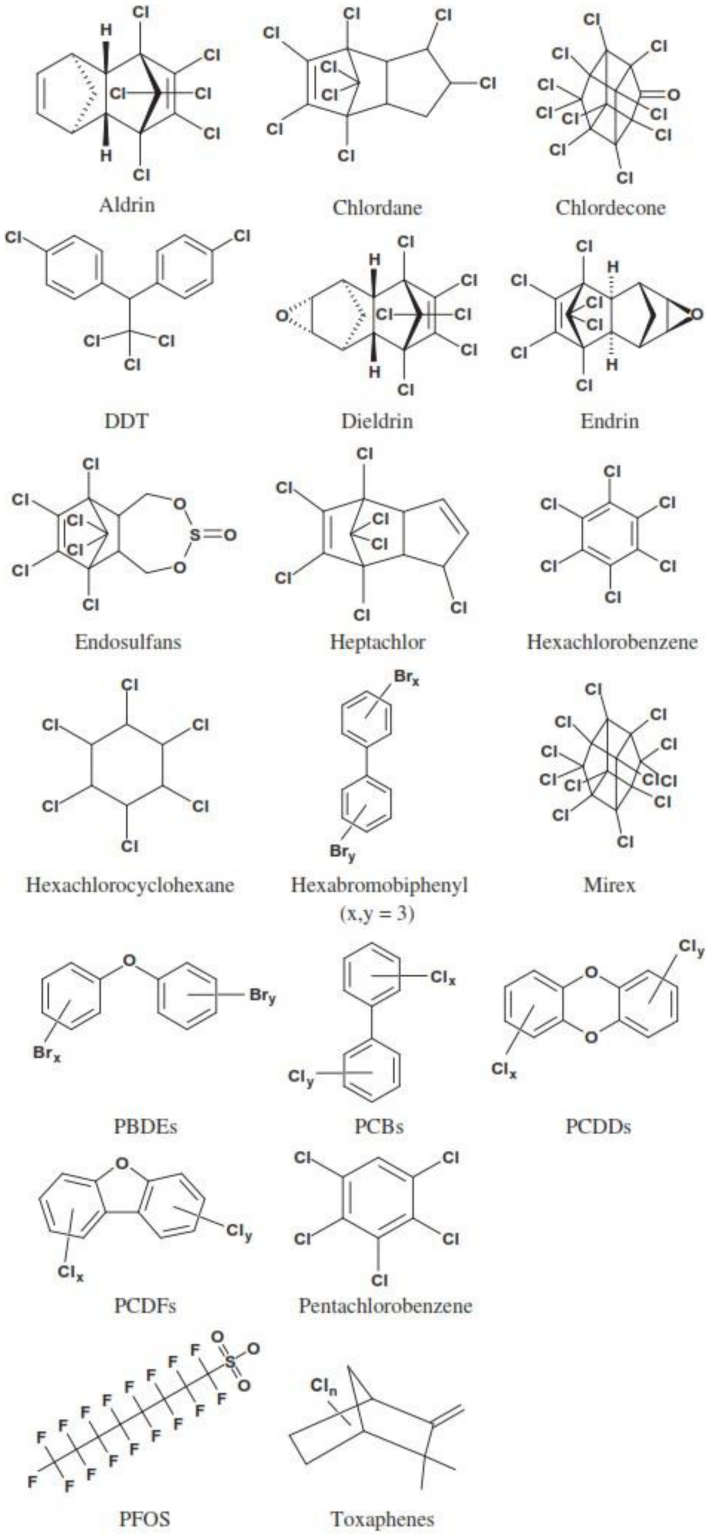

Fig.1. Chemical structures of common POPs (Tang, 2013).

Table 1. POPs listed in Stockholm Convention amendment (Xu et al., 2013).

Item	Chemicals	Type
2001 amendment		
1	Aldrin	Pesticide
2	Dieldrin	Pesticide
3	Endrin	Pesticide
4	Chlordane	Pesticide
5	Heptachlor	Pesticide
6	HCB	Pesticide
7	Mirex	Pesticide
8	Toxaphene	Pesticide
9	DDT	Pesticide
10	PCBs	Industrial and by-product
11 and 12	PCDDs and PCDFs	By-product
2009 amendment		
13	Chlordecone (Kepone)	Pesticide
14	Lindane	Pesticide
15	α- HCH	Pesticide and by-product
16	B- HCH	Pesticide and by-product
17	Hexabromobiphenyl	Industrial
18	Tetra-BDE and penta-BDE	Industrial
19	Hexa-BDE and hepta-BDE	Industrial
20	PFOs and its salts PFOSF	Industrial
21	Pentachlorobenzene	Pesticide, industrial and by-product
2011 amendment		
22	Endosulfan	Pesticide

2. Challenges in POPs Management

Reviewing the first 10 years of the Stockholm Convention implementation by the alternative approach of assessing reductions of global POPs inventories and progress with the management of POPs stockpiles better demonstrates the practical challenges of POPs legacies. There has only been very slow progress with the destruction of POPs pesticides and polychlorinated biphenyl (PCB) stockpiles especially in developing countries and countries with economies in transition. These countries often have few or no adequate destruction facilities. They face huge challenges with the end-of-life management of PCB and pesticide stockpiles and increasing e-waste containing PBDEs. Their problems are often magnified by exports of POPs in waste and products from industrial countries (Breivik et al., 2011). Even in industrial countries most 'remediation' undertaken to date involves containment rather than the 'destruction or irreversible transformation' required by the Stockholm Convention for POPs wastes. This approach leaves pollutants for future generations to manage and is not consistent with sustainable development.

Most of the pesticides were found to be reduced in the environment after they were banned except for lindane and endosulfan (Ibrahim, 2007). Studies showed that high concentration of POPs are still found in several rivers and sediments in the country after the prohibition of pesticides usage (Leong et al., 2007; Zakaria et al., 2003). This revealed that POPs pesticides might still be used illegally in the country. Previous research also found that the main sources for OCPs are from agricultural activities such as vegetable cultivation and paddy field (Zakaria et al., 2003). However, there is very limited research done on non-pesticide sources of POPs. More research on POPs in different types of wastewater such as agricultural farm effluent and landfill leachate should be carried out to obtain quantitative data for better management of POPs.

The danger of POPs was only known after large amount of these chemicals had been widely spread all over the world. In Malaysia, not much data are available on POPs especially for levels of POPs in ambient air, levels of dioxins and furans. Lack of expertise and laboratory facilities to measure very low concentration of POPs are likely the main reasons of scarce data available (Ibrahim, 2007).

3. Remediation/ Treatment Technologies

Due to human activities and rapid development, large amount of POPs are contributing to environmental pollution. Organic chemicals substances such as phthalate ester, petroleum hydrocarbon, pesticides and halogenated compounds are contaminating the soil and aquatic system (Megharaj et al., 2011). Bioremediation is one of the methods commonly used for POPs treatment. Bioremediation is a relatively efficient and cost effective method that involved the usage of microorganism in treating POPs (Megharaj et al., 2011). It is often selected as an option for treating POPs because of the ubiquitous nature of microorganism, ability to work in extreme conditions, effective catalytic mechanism and wide diversity (Mishra & Lal, 2001; Paul et al., 2005). However, there are some limitations in using bioremediation such as poor capabilities of microbial, lesser bioavailability of contaminants on temporal and spatial scales, and lack of bench-mark values for efficacy testing of bioremediation (Megharaj et al., 2011).

The continuous release of POPs into the environment has raised a need to come out with effective treatment method. Coagulation and flocculation process is widely used for treating POPs in wastewater due to its simple operation (Rui et al., 2012). According to Aziz et al. (2007), coagulation and flocculation process is very effective for removing high concentration of organic pollutants. Coagulant destabilizes the colloidal particles in coagulation process. Then it followed by flocculation process which increase the unstable particle size into larger flocs and encourage flocs formation. This process enables the removal of colloid particles and suspended solids from the solution. pH adjustment and addition of coagulants are common approaches used to overcome the repulsive forces between the particles (Ayoub et al., 2001).

Aluminium sulphate (alum) is a commonly used inorganic salt for treating wastewater. Alum is chosen for treating organic contaminants due to the low cost involved and easily available (Renault et al., 2009). However, alum is not environmental friendly as it produces large amount of sludge and possible to be toxic. In addition, the effectiveness of alum is highly dependent on pH and the flocs are not very mechanically resistant when formed in cold water (Renault et al., 2009). Thus, extensive research on biopolymers as an alternative option for POPs remediation should be carried out. There are many factors that can affect the effectiveness of POPs removal using coagulation and flocculation process such as pH, mixing speed, dosage of coagulant/ flocculants, temperature and retention time (Rui et al., 2012). Previous study found that phthalic acid esters (PAEs) were not effectively removed using coagulation and flocculation process (Zheng et al., 2009). Similarly, only 6.7% of DEHP was removed using polyferric sulfate (PFS) by coagulation and flocculation (Zolfaghari et al., 2014).4. Online license transfer

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4. Role of Green Technology

Natural coagulants are better options as compared to chemical coagulants in treating POPs in landfill leachate and agricultural wastewater due to the minimal coagulant dosage requirement, efficiency at low temperature and produce small volume of sludge. Chemical coagulants are generally more expensive, toxic and with low biodegradability (Verma et al, 2012). Guar gum and Xanthan gum have been investigated for removing POPs from farm effluent and landfill leachate.

Recent studies found that 4.0 mg/L of Guar gum at pH 7 could remove 99.70% and 99.99% of phenol,2,4-bis(1,1-dimethylethyl) and DEHP, respectively (Kee et al., 2015). The zeta potential of the raw effluent is -24.6 mV and after addition of Guar gum it decreases to -25.1 mV. Hence, it can be said that charge neutralization did not contribute towards coagulation–flocculation; rather polymer bridging by Guar gum was responsible for POPs removal. Beyond the optimum point, the percentage of removal started to decrease, possibly due to increased negative interaction between the flocculant and the suspended particulate matters, inhibiting floc formation (Mishra and Bajpai, 2005; Mukherjee et al., 2013). The lowest removal of phenol,2,4-bis(1,1-dimethylethyl) was observed at 5.0 mg/L. Removal of POPs by alum was less efficient as compared to Guar gum. Highest POPs removal by alum was achieved at 1 g/L after which it significantly decreased at 1.5 g/L. Excess alum beyond optimum value did not aid in flocs formation, it instead stayed in the sample as impurity decreasing POPs removal (Sen Gupta and Ako, 2005). Higher dosage of alum was required to remove POPs as compared to Guar gum. Study also revealed that more voluminous sludge was produced by alum. The flocs formed by Guar gum were more compact which reduces disposal cost. SEM micrograph indicated that numerous void spaces in Guar gum enabled it to remove POPs more effectively as compared to alum. From economic point of view, the cost of treatment for one million gallon of wastewater using alum (at 1 g/L) will be 96 times higher than Guar gum (at 4 mg/L). Recent studies conducted also proved that the efficiency of Xanthan gum was 5% better than alum in removing POPs. Natural coagulant is highly recommended as a substitute to chemical coagulant in treating POPs due to its non-toxic and biodegradable characteristics.

5. Conclusion

There is a growing priority for the management and remediation of POPs since POPs are one of the toxic groups of chemical pollutants and listed under the Stockholm Convention for global elimination. They are potentially hazardous to living organism because of their higher degree of halogenations, inclination to bioaccumulate in the lipid component and their resistance to natural degradation. Contamination by POPs is widespread because POPs are chemically stable, bioaccumulate, and circulate globally via the atmosphere, oceans, and other pathways. To address the threat posed by this widespread POPs contamination, remediation technologies continue to be developed to treat these pollutants. Natural coagulant such as Guar gum and Xanthan gum were very effective in treating POPs and are highly recommended as an option for treating POPs because it is a biodegradable biopolymer, non-toxic, involved low treatment cost, easily available and is produced in abundance.

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