## IRON WASTE BASED POINT-OF-USE DEVICE TO TREAT PESTICIDES IN WATER

A Dissertation Submitted to the Graduate Faculty of the North Dakota State University of Agriculture and Applied Science

By

Tauqeer Abbas

In Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major Department: Civil and Environmental Engineering

July 2019

Fargo, North Dakota

# North Dakota State University Graduate School

### Title

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Tauqeer Abbas

The Supervisory Committee certifies that this disquisition complies with North Dakota

State University's regulations and meets the accepted standards for the degree of

### DOCTOR OF PHILOSOPHY

SUPERVISORY COMMITTEE:

Eakalak Khan

Chair

John McEvoy

Om Yadav

Craig Stockwell

Approved:

December 10, 2019

Date

David R. Steward

Department Chair

#### ABSTRACT

Organochlorine pesticide (OCP) contamination in groundwater is a problem worldwide, more severely in rural areas that normally cannot afford centralized water treatment systems. Iron nanoparticles have shown their ability to degrade a number of chlorinated organic pollutants in water. However, their practical application as a point-of-use filtration medium is not possible because of their mobility, high cost and unknown/potential toxic effects to human health. In this study, iron turning waste, a common waste material which has the same valence as iron nanoparticles but is ubiquitous and affordable, was experimented to remove individual (batch wise) and mixture of six OCPs (batch and continuous systems) including lindane, heptachlor, endosulfan, dieldrin, endrin, and dichlorodiphenyltrichloroethane from water. The effects of iron turning dose, water pH and initial pesticide concentration, and common minerals in groundwater such as magnesium, sodium, calcium, and nitrate on the removal of the pesticides were examined. Results indicate that pesticide removal increased with the increase of iron dose. Acidic pH favored the removal of the pesticides except endosulfan. Low pH restricted the formation of rust on iron surface resulting in better interaction between iron surface and the pesticides. For endosulfan removal, both hydrolysis and reductive dehalogenation were involved under basic conditions. Common minerals in groundwater had minimal effect on the removal of pesticides. Iron turning waste removed the pesticides more efficiently at higher pesticide concentrations. Iron turning waste media worked better in combination with sand in a filtration column at long empty bed contact time. Iron turning waste first dechlorinated the pesticides followed by ring cleavage and formation of aldehydes. Degradation by-products of all pesticides were far less toxic than the parent pesticides. Shewanella oneidensis, a non-pathogenic environmental bacterium successfully regenerated the exhausted iron turning waste, and the

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pesticide removal efficiencies of microbially regenerated iron turning were comparable to virgin iron turning waste. This research provides an efficient and affordable method to treat OCPs in water and for the first time elucidates degradation pathways through the identified degradation products and demonstrates utilization of microbially regenerated iron turning waste for OCPs removal.

#### ACKNOWLEDGEMENTS

First and foremost, I would like to thank God Almighty for his countless blessings. My deepest gratitude goes to my adviser, Dr. Eakalak Khan, for providing me the opportunity to work under his supervision. I would like to thank him for his consistent guidance, immeasurable support, and encouragement throughout the course of this dissertation. He not only gave me the freedom to think and explore but also supported me with immeasurable time and guidance when my steps faltered. I explicitly appreciate his assistance to make me an independent researcher and guide me all the time. Thank you for sharing your profound knowledge, thoughtful ideas and experience in the field of engineering. Throughout the years, I learned so much about both technical and non-technical writing, and science which will be greatly beneficial in my future practical life. I am highly indebted to him for the financial support at times of need, which gave me peaceful mind to finish this work.

I would like to thank my co-advisor Dr. John McEvoy for his support and allowing me to work in his lab. He always helped me whenever Dr. Khan was out of his office. I would like to acknowledge my committee members Drs. Om Parkash Yadav and Craig Stockwell. Without their help, this dissertation would not have been possible. I would like to thank Dr. Yadav for his time and guidance on statistical analysis. I acknowledge the US State Department and National Academy of Sciences, Engineering, and Medicine, Washington DC for the financial support throughout this research. I would like to thank current and past members of the NDSU Environmental Engineering Laboratory for having a friendly environment.

Last but not least I would like to thank my lovely wife, Noor Fatima who sacrificed her golden period of life just for my Ph.D. My words would not justify the love, support and encouragement she gave me throughout this journey.

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## DEDICATION

To my beloved wife, Noor Fatima

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## LIST OF ABBREVIATIONS

[OCP]	Organochlorinated pesticides
[nZVI]	Nanozerovalent iron
[mZVI]	Microzerovalent iron
[mZVIM]	Zerovalent iron microparticles
[ORP]	Oxidation reduction potential
[AC]	Activated carbon
[DDT]	Dichlorodiphenyltrichloroethane
[DDD]	Dichlorodiphenyldichloroethane
[DDE]	Dichlorodiphenyldichloroethylene
[HCH]	Hexachlorocyclohexane
[MF]	Microfiltration
[UF]	Ultrafiltration
[NF]	Nanofiltration
[RO]	Reverse osmosis
[Fe <sup>0</sup> ]	Zerovalent iron/metallic iron
[Fe <sup>2+</sup> ]	Ferrous ions
[Fe <sup>3+</sup> ]	Ferric ions
[XRD]	X-ray diffraction
[XPS]	X-ray photoelectron spectroscopy
[EDS]	Energy dispersive X-ray spectroscopy
[SPME]	Solid-phase microextraction
[PDMS]	Polydimethylsiloxane
[HPLC]	High performance liquid chromatograph
[DI]	Deionized

[TiO <sub>2</sub> ]	Titanium dioxide
[O <sub>3</sub> ]	Ozone
[H <sub>2</sub> O <sub>2</sub> ]	Hydrogen peroxide

#### **1. GENERAL INTRODUCTION**

#### 1.1. Background

Pesticide contamination of water resources through agricultural activities is a worldwide environmental problem. Pesticides are indispensable agents for the high-quantity production of food. Traces of them are frequently detected in surface water and groundwater. Pesticide contamination in natural waters is one of the major environmental problems worldwide (Plakas and Karabelas, 2012). There are four major groups of pesticides: (i) organochlorines (ii) organophosphates (iii) carbamates, and (iv) substituted urea. Among them, organochlorinated pesticides (OCPs) are the most hazardous persistent organic pollutants and pose serious risk to the environment and human health (Rani et al., 2017). Representative OCPs include lindane, heptachlor, endosulfan, endrin, dieldrin, dichloro-diphenyl-trichloroethane (DDT) and methoxychlor.

OCPs have been effectively used in reducing crop damages from insects, disease and weed and for increasing crop yield. Despite the benefits of OCPs, their toxic effects are evident (Khan et al., 2010). The characteristics of OCPs, such as high lipophilicity, bioaccumulation, long half-life and potential of long-range transport, have increased the chances of water contamination. Due to high persistence and bioaccumulative nature of OCPs (Moon et al., 2009), they are widespread and detected in coastal environments (Arienzo et al., 2013), seafood, and humans (Moon et al., 2009). Although several OCPs are banned in different parts of the world such as lindane, DDT and endosulfan in the U.S. due to their health effects, but they are still being used in developing countries such as India and Pakistan, Southeast Asia, and Africa due to their low costs and wide range of toxicity against pests (Ali et al., 2014; Rani et al., 2017). Their residues are detected in soil and water even after years of last application (Embrandiri et al.,

2012; Yadav et al., 2015). OCPs in surface and groundwater of agricultural communities of Southeast Asia (Ali et al., 2014), China (Xu et al., 2007), India (Yadav et al., 2015), and Pakistan (Ali et al., 2016) were often found to be more than drinking water standards set by the United States Environmental Protection Agency (USEPA). In Europe particularly Ireland and Scandinavian countries such as Denmark and Norway, they were detected in freshwater at levels higher than the European Union (EU) standards (McGarrigle et al., 2010).

Once ground water is polluted with toxic chemicals such as OCPs, it may take many years for the contamination to dissipate or be cleaned up (EPA, 2001). Cleanup may also be very costly and complex, if not impossible (Agarwal et al., 2015; Aktar et al., 2009). OCPs are one of the most refractory contaminant groups and are not effectively removed by a conventional water treatment plant. According to the Office of Pesticide Program, USEPA, coagulation-flocculation, sedimentation, and conventional filtration are not effective in removing or transforming OCPs in drinking water (EPA, 2001). Moreover, developing countries and/or rural communities of developed nations do not have proper centralized water treatment and distribution systems. Therefore, removal of pesticide in water is a challenge for both developed and developing countries.

#### **1.2. Research Problem Statement**

OCPs contamination in groundwater is a global concern for public health (Yadav et al., 2015). Advanced water treatment options including activated carbon and membrane processes are effective in removing pesticides. People living in poor agricultural communities cannot afford these expensive advanced water treatment technologies. Moreover, these technologies are only effective in removing these pesticides without degrading them into less toxic compounds

resulting in hazardous waste such as exhausted activated carbon and brine that need to be managed.

Photodegradation as a pesticide removal technique has been proven to work effectively (Vela et al., 2017). Photolysis using solar radiation, while effective, takes considerably more time when compared to ultraviolet (UV) light. Most of the OCPs by their design are photo-stable so that high intensity lamps are required and this increases energy consumption and operating costs (Ananpattarachai and Kajitvichyanukul, 2015). The incorporation of a catalyst (photocatalysis) improves the efficiency of the removal technique (Ananpattarachai and Kajitvichyanukul, 2015). The most commonly used catalyst is titanium dioxide (TiO<sub>2</sub>). It is less costly compared to other photocatalysts but still expensive for agricultural communities, and its availability is a concern. Moreover, the drawback of this technique is again the energy consumption required for the UV lamps. Solar photocatalysis is not viable for most of the OCPs, and in every country due to local weather conditions.

Recently, metal nanoparticles such as nano-zero valent iron (nZVI) have shown their ability to degrade a variety of chlorinated organic pollutants in water (El-Temsah et al., 2016; Tian et al., 2009). In aqueous environment,  $Fe^0$  presents in nZVI, is rapidly oxidized to ferrous ( $Fe^{2+}$ ) and ferric ( $Fe^{3+}$ ) ions, and removes contaminants/pesticides mainly via reduction. Similar to  $Fe^0$ ,  $Fe^{2+}$  is also capable of removing pesticides, however, it is not clear which one ( $Fe^0$  vs  $Fe^{2+}$ ) is more potent for pesticide/OCP removal. The rapid oxidation of  $Fe^0$  to  $Fe^{2+}$  and  $Fe^{3+}$  in water environment results in a shorter life of nZVI resulting in less contaminant removal. Moreover, there have been limited information regarding OCPs degradation mechanism and degraded by-products in water using nZVI and iron-based materials. The practical application of nZVI as point-of-use filtration media is not possible because of their mobility, high cost and unknown fate and transport in the environment and potential toxic effects to human health. Rural communities are more vulnerable to OCPs contaminated water. They do not have access to centralized water treatment facility and need inexpensive and easily available water filtration media to treat OCPs.

Therefore, it is indispensable to develop, validate, and present an economical and sustainable solution for treating OCPs in water. The problem may be solvable using a waste of iron industry known as iron turning waste, which has the same valence as  $Fe^{0}$ . Iron turning waste is readily available at lower prices compared to other filtration options. Shorter life of filtration media (rapid oxidation of  $Fe^{0}$  to  $Fe^{2+}$  and  $Fe^{3+}$ ) may be addressable with the application of bacteria capable of regenerating  $Fe^{2+}$  through reduction reaction. The performance comparison of virgin iron turning waste and microbially regenerated  $Fe^{2+}$  will reveal their potency to degrade OCPs in water.

#### **1.3. Research Objectives**

- 1. To investigate the degradation kinetics of individual and mixture of OCPs including dieldrin, endrin, endosulfan, heptachlor, lindane and DDT in water provided by iron turning waste.
- 2. To examine the effects of water pH, initial pesticide concentration and minerals in water on removal of individual and mixture of OCPs by iron turning waste.
- To identify the degradation by-products and removal mechanism of individual OCPs by iron turning waste.
- 4. To examine the effect of empty bed contact time (EBCT) on the removal of individual OCPs and service period of filtration media in a continuous flow system.
- 5. To evaluate the ability of a non-pathogenic bacterial strain to regenerate  $Fe^{2+}$ , and the reusability of microbially regenerated  $Fe^{2+}$  for OCPs degradation.

#### **1.4. Hypotheses**

- 1. The degradation rates of individual and mixture of OCPs increase with increasing dose of iron turning waste.
- 2. Iron turning waste degrades OCPs more efficiently in acidic than basic conditions.
- 3. In the presence of dissolved oxygen and water, iron turning waste first degrades/ dechlorinates OCPs into benzene/phenolic compounds followed by ring cleavage.
- Iron turning waste degrades OCPs and is oxidized to Fe<sup>2+</sup> and Fe<sup>3+</sup>. Biologically regenerated Fe<sup>2+</sup> dechlorinates OCPs in water.

#### **1.5. Dissertation Organization**

This dissertation is divided into 7 chapters. This chapter includes background, research problem statement, research objectives and hypotheses and dissertation organization. Chapter 2 provides a literature review on physiochemical properties of OCPs and the removal technologies in water. Chapters 3-5 address the first three objectives. Each chapter covers a pair of pesticides that are similar in properties. Chapter 3 is derived from a manuscript titled "Iron Turning Waste as Efficient Point-of-Use Water Filtration Media for Removal of Endrin and Dieldrin." This manuscript has been submitted for publication in a peer reviewed journal. Chapter 4 is based on a manuscript titled "Iron Turning Waste Media for Treating Endosulfan and Heptachlor Contaminated Water." This manuscript has been published in *Science of the Total Environment*. Chapter 5 is based on a manuscript titled "Elucidation of DDT and Lindane Degradation in Water using Iron Waste." This manuscript will be submitted for publication in a peer reviewed journal. In Chapter 3-5, the degradation kinetics of OCPs, and effects of water pH, initial pesticide concentration, and minerals in water on the removal of OCPs by iron turning waste are presented and discussed. Effects of media dosage and EBCT on the removal of OCPs in a

continuous flow system are included. Based on identified degradation by-products, degradation mechanisms of OCPs are proposed in these chapters. Chapter 6 is aligned with the last objective and is based on a manuscript titled "Iron Turning Waste Media for Treating Chlorinated Pesticides in Water and its Microbial Regeneration with *S. oneidensis*." This chapter addresses the abilities of fresh iron turning (Fe<sup>0</sup>) and bio-regenerated Fe<sup>2+</sup> to degrade a mixture of OCPs. This manuscript will be submitted for publication in a peer reviewed journal. Conclusions and recommendations for future work are presented in Chapter 7.

#### **2. LITERATURE REVIEW**

### **2.1. Introduction**

Pesticide are used to kill insects and boost crop production. Pesticides used in agriculture are transported by diffuse pathways to surface water and groundwater. The contamination of surface water and groundwater by pesticides impairs the water quality and restricts their use for water supply. OCPs have been identified as a major group of water contaminants in various countries due to their persistence in aquatic environments and potential adverse effects on human health (Yang et al., 2018). OCPs exposure could cause allergies, reproductive and neurologic disorders and cancer (Faniband et al., 2014; Ledirac et al., 2005). Water contamination with OCPs has been associated with health effects, such as endocrine disorders, effects on embryonic development, lipid metabolism, and hematological and hepatic alterations (Nicolopoulou-Stamati et al., 2016). Different treatment methods such as adsorption, membrane filtration, and photolysis are available to remove them in water; however, each method has advantages and disadvantages.

#### 2.2. Characteristics and Biochemical Effects of OCPs on Human Health

OCPs are highly persistent and semi volatile pesticides which have low water solubility and high lipid solubility. They can enter the environment through different ways such as after field application, accidental spill, industrial discharge, and polluted waste buried in landfills. Most of the OCPs are stable in sunlight and can attach to the soil and remain in the air for longer periods resulting in enduring exposure to both animals and humans. Table 1 provides physiochemical properties of major OCPs along with the details of the countries that ban their applications.

OCPs	Mol. Wt	Water solubility (mg/L)	Log Kow	Vapor pressure 20–25 °C (mm Hg)	t <sub>1/2</sub> (days)	Log Koc (cm <sup>3</sup> /g)	Status (Banned)
Lindane	290.8	8.35	3.72	4.2×10 <sup>-5</sup>	1095- 1460	3.6	USA
Dieldrin	380.9	0.11	5.4	5.89×10 <sup>-5</sup>	369	6.7	Southeast Asia
Endosulfan	406.9	0.32	4.7	9.0×10 <sup>-3</sup>	50	4.0	India
Endrin	380.9	0.20	3.21– 5.34	2.0×10 <sup>-7</sup>	2190	5.2	Southeast Asia
Heptachlor	373.3	0.18	5.44	3×10 <sup>-4</sup>	250	5.3	USA
DDT	354.5	0.025	6.91	1.6×10 <sup>-6</sup>	1460– 10,950	5.2	USA, Canada, Singapore

Table 1. Physiochemical properties of various OCPs (Rani et al., 2017).

Although most of the OCPs are banned in the U.S., they are being used in developing countries. For instance, lindane is banned in the U.S. but is being used in India. The human exposure to OCPs can cause serious health issues ranging from mental confusion to cancer. Table 2 shows the biochemical effects of OCPs on human health.

OCPs	Biochemical effects
Lindane	Damage human liver, kidney, neural and immune systems, and induces birth defects cancer, cause neurotoxicity, reproductive toxicity and hepatotoxicity
Heptachlor	Convulsions, tremor, mental confusion and incoordination
Dieldrin and endrin	Neurotoxic, reproductive, developmental, immunological, genotoxic, tumerogenic- effects, nausea, vomiting, muscle twitching and aplastic anemia
DDT	Prickling sensation of the mouth, nausea, dizziness, confusion, headache, lethargy, incoordination, vomiting, fatigue, tremors in the extremities, anorexia, anemia, muscular weakness, hyperexcitability, anxiety, and nervous tension
Endosulfan	Decrease of white blood cell count and macrophage migration, adverse effects on humoral and cell-mediated immune system, semen quality, sperm count, spermatogonial cells, sperm morphology and other defects in male sex hormones, deoxyribonucleic acid damage and mutation

Table 2. Biochemical effects of OCPs on human health (Jayaraj et al., 2016).

#### 2.3. Water Contamination with OCPs

Mishra and Sharma (2011) studied DDT and lindane contamination in both surface and groundwater of Dibrugarh and Nagaon districts of Northeast India. The mean lindane contamination levels in groundwater were higher (5.16 and 5.65  $\mu$ g/L) than in those in surface water (4.40 and 4.91  $\mu$ g/L) from Dibrugarh and Nagaon districts, respectively. Surface and groundwater of Nagaon district have higher DDT contamination (6.12 and 6.90  $\mu$ g/L) than Dibrugarh district (5.41 and 6.54  $\mu$ g/L). According to the World Health Organization (WHO),

the allowable/safe concentration of both pesticides in drinking water is 2  $\mu$ g/L, which shows that the drinking water for both districts is not safe and poses serious health risks.

Another study (Sankararamakrishnan et al., 2005) conducted in Kanpur, India, has shown the presence of high concentrations of OCPs in both surface and groundwater samples. In the surface water of River Ganges in Kanpur, the highest concentration of lindane was 0.26  $\mu$ g/L. The highest concentration of lindane in groundwater of agricultural and industrial area of Kanpur was 0.47 and 0.90  $\mu$ g/L, respectively. In addition to lindane, dieldrin was detected in groundwater of an industrial area of Kanpur and its concentration was 29.84  $\mu$ g/L. The concentrations of both pesticides were higher than the drinking water standards set by USEPA (0.2  $\mu$ g/L for both pesticides).

Mutiyar et al. (2011) studied the occurrence of OCPs in a drinking water well-field of Delhi region during pre and post-monsoon periods. The groundwater samples were taken from 5 Ranney wells and 21 borewells. Among the OCPs, lindane, endosulfan, DDT and aldrin were detected in the well-field. The concentrations of these OCPs were 1  $\mu$ g/L and close to 0.5  $\mu$ g/L in Ranney wells and borewells, respectively. The concentrations were above the drinking water standards set by USEPA. According to the Indian national regulatory agency, the contamination levels of OCPs in borewell water were within their national permissible limit. However, drinking water contaminated with low concentrations of OCPs can cause long term health effects such as metabolic disorders, if it is consumed for longer periods (Mutiyar et al., 2011). In India, 58% of drinking water samples drawn from various hand pumps and wells around Bhopal were contaminated with OCPs above the USEPA standards (Kole and Bagchi, 1995).

China is the leading consumer of pesticides in the world (Wu et al., 2014). After the ban of DDT and technical grade hexachlorocyclohexane (HCH) in 1983, lindane (almost pure  $\gamma$ -

HCH) and dicofol (chemically related to DDT) have been continuously and extensively used in China for agricultural applications (Li et al., 2006; Yang et al., 2008). OCPs are still normally detected in air, soil, water and even foodstuff in some regions of China (Fang et al., 2007; Feng et al., 2003; Qiu et al., 2004; Wu et al., 2014). Wu et al. (2014) studied the presence of different OCPs in shallow groundwater of the Taihu Lake region. Fourteen different OCPs were found in 27 collected samples of shallow groundwater of the region. HCHs ( $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ -isomers) and DDTs (dichlorodiphenyldichloroethylene (DDE), dichlorodiphenyldichloroethane (DDD) and DDT) were the most important contaminant as compared to other OCPs due to their higher contamination level in that area. The mean concentrations of the HCHs and DDTs were 43.71 ng/L and 52.46 ng/L, respectively. HCH and DDT were mainly from the historical use of DDT and lindane in the shallow groundwater. In addition to historical residues, the findings suggested that there was fresh input of endrin, heptachlor and aldrin in the shallow groundwater as well. Cancer risk values for dieldrin, aldrin, heptachlor and α-HCH in the shallow groundwater of the Taihu Lake region were more than 10<sup>-6</sup>, posing a serious cancer risk to those who consume the water for drinking purpose.

Zhou et al. (2008) studied the occurrence of OCPs in Qiantang River, flowing through agricultural areas of east China, an is a typical drinking water source. A total of 270 river water samples were collected in 2005-2006, and analyzed for OCPs. The total concentration of OCPs was  $0.007-0.62 \mu g/L$  and the major OCPs in the surface water were heptachlor,  $\delta$ -HCH, aldrin, heptachlor epoxide, and  $\beta$ -HCH. Soil erosion significantly contaminated the water with OCPs, and the OCPs dry and wet deposition to water body was estimated at 0.49 and 0.86 ton/year, respectively.

In Pakistan, limited studies have been conducted to investigate the occurrence and distribution of OCPs in surface water and groundwater (Eqani et al., 2012). Groundwater from the cotton growing regions of Punjab, Pakistan were found to be contaminated with endrin (0.1 to 0.2  $\mu$ g/L), endosulfan (0.13  $\mu$ g/L), dieldrin (0.06  $\mu$ g/L), lindane (0.09 to 0.11  $\mu$ g/L), heptachlor (0.02 to 0.17  $\mu$ g/L), and DDT (0.017 to 1.0  $\mu$ g/L) (Ahad et al., 2001; Ahad et al., 2010; Asi et al., 2008; Eqani et al., 2012). Iram et al. (2009) studied the occurrence of OCPs in the freshwater of Rawal and Simbly lakes, Pakistan. Rawal and Simbly lakes are the major water sources for the residents of twin cities, Rawalpindi and Islamabad. The concentrations of endosulfan and 2,4-DDT in Rawal lake were 0.72 and 2.14  $\mu$ g/L, respectively. In Simbly lake, the detected OCPs were  $\alpha$ -HCH (0.84  $\mu$ g/L), endosulfan (0.66  $\mu$ g/L), 2,4-DDT (0.96  $\mu$ g/L), and 4,4-DDT (0.80  $\mu$ g/L). The contamination levels of all detected OCPs in lakes exceeded the USEPA drinking water standard (0.2  $\mu$ g/L) and the EU limit of 0.1  $\mu$ g/L.

Dalvie et al. (2003) showed the evidence of consistently low-level endosulfan in rural water sources in the Western Cape, South Africa. Out of 382 groundwater samples, 37% contained endosulfan above the EU limit of  $0.1 \mu g/L$ . The influence of intensive horticulture practices on groundwater quality of Portugal was assessed during a two-year period (Gonçalves et al., 2007). Based on the total number of samples analyzed, lindane (53%), endosulfan sulfate (44%), and endosulfan (38%) were often detected. Moreover, 12% and 11% of the samples contained endosulfan and endosulfan sulfate, respectively, above the 0.1  $\mu g/L$  EU limit. Surface and groundwater contaminations with OCPs in Iran, Southeast Asia, Portugal, Mexico, and USA have also been reported (Ali et al., 2014; Cerejeira et al., 2003; Gilliom, 2007; Rodríguez et al., 2018; Shakerkhatibi et al., 2014).

#### 2.4. OCP Removal Technologies

Several physical, chemical as well as biological methods such as adsorption, membrane filtration, oxidation, and biological treatment have been investigated for OCPs removal (Li et al., 2010; Lin and Lin, 2007; Rodante et al., 1992; Smith et al., 2004; Zinovyev et al., 2005). Adsorption is advantageous to other methods because of affordability and design simplicity (Ahmad et al., 2010; Gupta and Ali, 2008). Due to the refractory nature of OCPs, only specific bacteria and fungus are capable of degrading them (Bhalerao and Puranik, 2007; Kwon et al., 2005). Recently, nanomaterials have been investigated for treating different organic contaminants in water including OCPs at laboratory scales because of their large surfaces area and higher adsorption capacities (Rani et al., 2017). The advantages and disadvantages of different pesticide removal technologies are summarized in Table 3.

Treatment technologies	Advantages	Drawbacks
Adsorption	Design simplicity. Ease of operation	Regeneration and disposal of spent adsorbent which require further treatment. Unable to degrade pesticides
Membrane filtration	Operated without phase changes or chemical conditioning	Production of concentrate, which requires further treatment. Unable to degrade pesticides
Advanced oxidation	Capable of treating multiple pesticides in a single step	Formation of by products (chlorine or hypochlorite). High energy costs for large scaling applications
Photolysis	Capable of degrading pesticides	Photocatalyst, and extra energy sources may be needed (solar or UV)
Biological process	Feasible in treating a wide range of pesticides	Large areas for treatment and biomass separation units required. Low degradation rates (days, weeks, or years)

Table 3. Advantages and drawbacks of pesticide removal technologies (Cara and Jitareanu, 2015; Foo and Hameed, 2010).

## 2.4.1. Adsorption

Adsorption is the physical and/or chemical process in which a substance is accumulated at an interface between phases (liquid-solid interface or solid-gas interface). The adsorption process mainly depends on the surface area of adsorbent, its porosity and surface chemistry (Ahmad et al., 2010). There are two major categories of adsorbents: carbonaceous and agricultural. The removal of OCPs using different adsorbents are summarized in Table 4.

Adsorbent category	Adsorbent	OCP	Concentration	Removal/ Capacity	Reaction time	Reference
Carbonaceous	Granular activated carbon	Lindane,	10 mg/L	99%	180 min	(Sotelo et al., 2002)
Carbonaceous	Wood charcoal	Endosulfan	5-50 mg/L	1773 µg/g	24 h	(Yedla and Dikshit, 2008)
Agricultural	Chitosan	Dieldrin, heptachlor, endrin, endosulfan	2.8 ng/L	Peaks area not detected	30 min	(Lu et al., 2011)
Agricultural	Acid treated date stones	Aldrin, dieldrin and endrin	0.5-10 mg/L	90% aldrin and dieldrin 78% endrin	12 h	(El Bakouri et al., 2009)
Industrial waste	Carbon slurry	Endosulfan	3×10 <sup>-6</sup> M	34.11 mg/g	90 min	(Gupta and Ali, 2008)
Industrial waste	Bagasse fly ash	Lindane	0-10 μg/L	0.0025 μg/g	60 min	(Gupta, 2002)
Agricultural	<i>Rhizopuso ryzae</i> biomass	Lindane	20-1000 µg/L	87%	5 h	(Ghosh et al., 2009)

Table 4. Adsorbents for the treatment of OCPs in water.

### 2.4.1.1. Carbonaceous adsorbents

Carbonaceous adsorbents have a special place among the main adsorbents, as they are known, for a long time to be capable of adsorbing various organic compounds (Ahmad et al., 2010). Activated carbon (AC) is one of the most widely used carbonaceous adsorbents to treat pesticides in aqueous environments (Foo and Hameed, 2010). There are two main types of AC: granular activated carbon (GAC) and powdered activated carbon (PAC). Foo and Hameed (2010) reviewed the use of both types of AC to treat pesticides in water. Surface area and pore size of AC play a major role in pesticide removal from water (Foo and Hameed, 2010).

Lin et al. (2015) evaluated the performance of PAC for removing chlorinated aromatics including hexachlorobenzene. The amount of PAC and initial concentration of hexachlorobenzene used in the experiments were 20 mg/L and 5  $\mu$ g/L, respectively. Eighty to ninety five percent of equilibrium adsorption capacity was achieved within 10-30 min, and the equilibrium adsorption capacity for hexachlorobenzene was 1.78 mg/g.

Kouras et al. (1998) studied the adsorption of lindane on PAC with and without the presence of coagulants (ferric chloride and polyaluminium chlorosulfate). In the absence of coagulants, more than 20 mg/L of PAC was required to reduce the initial concentration of lindane from 10 mg/L to 0.1 mg/L within 1 h. However, when coagulants were added to the solution after the addition of PAC, decrease in lindane removal was observed. In that case, double dose of PAC (40 mg/L) was required to achieve the above-mentioned removal. Due to non-ionizable and non-polar nature of lindane, there was no noticeable change in its adsorption onto PAC, when the solution pH ranged between 4 and 10.

Ninkovic et al. (2010) studied the removal of 10 different OCPs in water using a column packed with commercially GAC. The concentration of each pesticide in the influent water was 2  $\mu$ g/L with a flow rate of 0.15 mL/min. Based on breakthrough experiments, it was found that halogenated aromatic hydrocarbons (DDT and DDD) were strongly adsorbed and the cyclodienes (endosulfan, heptachlor, and dieldrin) were fairly adsorbed. However, the OCPs from the group of HCH ( $\alpha$ -HCH,  $\beta$ -HCH, and  $\gamma$ -HCH) were poorly adsorbed.

Seyhi et al. (2014) investigated the removal of heptachlor from aqueous solution by AC produced from wheat straw. Increasing the amount of adsorbent (1 to 2 g/L) resulted in better

heptachlor removal (92% to 97%). After 3 h, more than 97% heptachlor removal was achieved at an initial concentration of (1 mg/L) under neutral and acidic conditions, and adsorption equilibrium was achieved. The maximum adsorption capacity was found 2.22 mg/g.

AC has two drawbacks: reusability and disposal. Once AC is exhausted/saturated with OCPs, it will need to be regenerated and/or replaced, adding to the cost. The disposal and handling of spent AC are an environmental issue because AC only adsorbed pesticides on its surface or within the pores without degrading them requiring safe disposal (secured landfill) or further treatment (i.e. incineration) prior to disposal.

### 2.4.1.2. Agricultural adsorbents

Agricultural waste and byproducts can be used as adsorbent to treat pesticides in water. This type of adsorbent is mainly plant biomass that is composed of cellulose, hemicellulose and lignin. Due to the abundance of agricultural waste, they are cheaper than AC. The removal of pesticides is achieved through their interactions with the hydroxyl and carboxyl groups found in polysaccharides and lignin (Ofomaja, 2008).

Date stones were used as an adsorbent for the removal of aldrin and dieldrin in water (El Bakouri et al., 2009). More than 90% removal of both pesticides was achieved from 100 mL of pesticide solution (0.5 mg/L) using 0.1 g of adsorbent in 3.5 h. The findings suggested that pesticides first rapidly adsorbed onto macropores of date stones due to their hydrophobic nature followed by slow diffusion of pesticides into the smaller pores of adsorbent. The main disadvantage of this study is the requirement of acid for treating the date stones prior to its use as an adsorbent.

The abilities of two different agricultural adsorbents (wood saw dust and cork waste) were investigated to treat 4,4-DDT from aqueous solution (250 mL, 4 mg/L) (Boussahel et al.,

2009). The removal efficiencies of these two agricultural adsorbents were also compared with commercial PAC. Their findings suggested that the adsorption capacities of wood saw dust, cork waste, and PAC were 69.44 mg/g, 19.08 mg/g, and 163.90 mg/g, respectively. Natural organic matter in water decreased the adsorption capacities of these two agricultural adsorbents due to pore blockage of adsorbent that interferes with the pesticide adsorption. Both surface adsorption and the intraparticle diffusion were the rate-controlling mechanisms.

El Bakouri et al. (2008) studied seven different agricultural adsorbents for the removal of endosulfan sulfate in water. The adsorbents used in their study were peanut shells, olive stones, bamboo canes, date stones, avocado stones, wood sawdust, and straw. One-half g of each adsorbent was used to remove endosulfan sulfate ( $0.5 \mu g/L$ ) in 50 mL of aqueous solution. Among the studied adsorbents, the removal capacity of bamboo canes was the highest (82%). Their findings suggested that the removal efficiency of endosulfan sulfate decreased with increasing pH (2-10) and temperature of the solution (10-35 °C).

Pink bark as an alternative to AC for the removal of lindane and heptachlor in water was investigated (Ratola et al., 2003). In batch experiments, 0.5 g of pine bark was used to treat 100 mL of water contaminated with lindane and heptachlor. The concentration of each pesticide in aqueous solution was 20  $\mu$ g/L. Under the same experimental conditions, pine bark removed heptachlor (93.6%) better than lindane (80.6%) in 24 h, suggesting that the structures of pesticides play an important role in their removal by adsorbents.

Although agricultural adsorbents have been used as low-cost adsorbents and alternatives to AC for treating OCPs contaminated water, some pretreatment is needed for most adsorbents to treat OCPs effectively. Depending upon on the nature of agricultural by-products/waste, these

pretreatment varies from simple drying (Ratola et al., 2003) to chemical treatment (Tang et al., 2014), adding to the cost of removal.

Other adsorbents such as industrial waste was also investigated as alternatives to AC to treat OCPs in water. Chemically treated carbon slurry produced in fuel-oil-based industrial generators was used for the removal of endosulfan and methoxychlor from water (Gupta and Ali, 2008). The adsorption capacities of endosulfan and methoxychlor were 34.11 and 36.06 mg/g in batch systems and 32.62 and 33.52 mg/g in continuous flow systems, respectively. Bagasse fly ash was used to remove lindane from water; however, this industrial waste adsorbent offered a very low removal capacity of 0.0025 mg/g (Gupta et al., 2002), and is therefore not suitable for commercial applications.

#### 2.4.2. Membrane Processes

Membrane is a selective barrier between two phases, and this semi-permeable barrier is used to separate the components of a solution or a suspension by using one or more gradients as the driving force. In membrane processes, the feed stream is separated into two fractions known as permeate, and concentrate. Permeate or product is the fraction that diffuses through the membrane, and the fraction containing components that does not pass through the membrane called concentrate or retentate or brine. An overview of membrane filtration based on the driving gradient is presented in Table 5.

Membrane process	Driving gradient	Membrane process	Driving gradient
Microfiltration (MF)	Pressure	Dialysis	Concentration
Ultrafiltration (UF)	Pressure	Electrodialysis	Electrical potential
Nanofiltration (NF)	Pressure	Forward osmosis	Concentration
Reverse osmosis (RO)	Pressure		

Table 5. Membrane processes based on driving gradient.

Pressure driven membranes are widely used to treat pesticides in water (Plakas and Karabelas, 2012). The pressure driven membranes are primarily divided based on their pore size and/or the type of components that they are used for separation. In Figure 1, an overview of the different applications for the four types of pressure driven membranes is illustrated. Among the pressure driven membranes, RO and NF membrane are of the main interest for the removal of pesticides in water (Plakas and Karabelas, 2012).



Figure 1. Applicability range for MF, UF, NF and RO membranes (Madsen, 2014). Reprinted from Chemistry of Advanced Environmental Purification Processes of Water, Copyright (2014), with permission from Elsevier.
Chian et al. (1975) investigated the removal of OCPs such as aldrin, lindane, dieldrin, heptachlor, heptachlor epoxide, DDT, and DDE at a pressure of 48.4 atm using two types of RO membranes: cellulose acetate and cross-linked polyethylenimine membranes. The pesticide concentrations used in the study ranged from 42 to  $321.3 \mu g/mL$ . More than 99% OCPs rejection was achieved by both membranes. It was reported that considerable amounts of OCPs (76-100% for all studied OCPs except lindane (12-68%)) adsorbed onto the membrane material because of hydrophobic bonding between pesticide molecules and the polymeric material of membranes and van der Waals- London forces.

Malaiyandi et al. (1980) studied the separation of lindane (6.8-7.0 mg/L) from its aqueous solution using cellulose acetate RO membrane. It was found that 60% of lindane in the feed remained in the product water whereas the remaining lindane (40%) was assumed to adsorb on the membrane. The amount of adsorbed lindane leached in the water wash was  $1.9 \mu g$  at 9.9 mL/min flush flow rate. Only ten percent of adsorbed lindane was recovered from a membrane of 12.6 cm<sup>2</sup> effective area with 3.7 L of wash water. Malaiyandi et al. (1980) concluded that an impractically large amount of time and water would be required to leach all the sorbed lindane on or in the membrane. Abron and Osburn (1973) also found that large concentrations of DDT and aldrin retained on hollow nylon fiber RO membranes. Any membrane that adsorbs or desorbs contaminant such as OCPs could not be used for their removal from water unless further treatment for contaminant followed the membrane (Duranceau et al., 1992).

Pang et al. (2010) studied the removal of DDT in synthetic water using a NF pilot unit at 35 L/h flow rate and 0.24 MPa pressure. The rejection of DDT was 95% to 85%, when the initial concentration ranged from 5 to 20  $\mu$ g/L. It was found that higher flux can lead to low rejection of DDT. Higher flux promotes to stronger hydrodynamic shear resulted in release of entrapped

DDT molecules in the pores of membrane. Water pH (2-12) had minimal effect on DDT removal. The presence of inorganic matter reduced the pore size of NF membrane resulted in better DDT removal (Pang et al., 2010).

From economic and practical perspectives, it is desirable to have more permeate (water) and less concentrate. However, high recovery of water as permeate resulted in more concentration of pesticide in concentrate, and this may lead to fouling and scaling of membrane (Pang et al., 2010). Even though membrane treatment removes pesticides, there is still an issue of liquid waste (pesticides in brine) disposal which needs further treatment.

#### 2.4.3. Photolysis

Transformation of organic compound as a result of transfer of light energy is called direct photolysis (Schwarzenbach, 2005). The photolysis rate is influenced by light adsorption properties and reactivity of the compound, and the intensity of sun light (Speight, 2016). Natural photodegradation is achieved through the transformation of a chemical resulting from the direct absorption of a solar photon. However, the absorption spectra of some chemicals differ from the spectrum of sunlight, and as a consequence they are resistant to direct photolysis. For the degradation of some of these chemicals, indirect photolysis can be effective which uses reactive intermediates such as hydroxyl radical generated from other light absorbing molecules. The light sources used for photolysis of pesticides has been investigated mainly using UV light (Katagi, 2018).

Lindane remains stable during direct photolysis in soil, air, and water environments because it does not contain chromophores that absorbs light (Vega et al., 2016). Similarly, DDT is resistant to photodegradation as it absorbs very little energy in the solar wavelength (Boul,

1995; Miller and Narang, 1970). Under intense sunlight or UV light, heptachlor is degraded to its photoisomer which is more toxic than heptachlor (Podowski et al., 1979). Photolysis of endosulfan occurs upon exposure to sunlight and generates endosulfan diol and endosulfan  $\alpha$ -hydroxy ether (ATSDR, 2000). Under sunlight, approximately 50% of endrin is degraded to endrin ketone within 7 ± 2 days (IPSC, 1992).

# 2.4.3.1. Photodegradation with photocatalysts

Photolysis is generally too slow and inefficient to be useful in water treatment and so the addition of a photocatalyst is required. Photocatalysts are materials that change the rate of chemical reaction on exposure to light (Ameta et al., 2018). This phenomenon is known as photocatalysis (Ameta et al., 2018). Photocatalysts can be applied as suspension or through media support. One of the main benefit of using supported photocatalytic systems is the ability to reuse catalyst without any post-treatment filtration step (Parra et al., 2004). TiO<sub>2</sub> is one of the widely used photocatalysts in environmental applications due to its non-toxic and chemically stable nature, efficient photoactivity, and low cost (Moma and Baloyi, 2018).

Lindane which is resistant to photolysis under both UV and sunlight, was completely removed in distilled water, when  $TiO_2$  was used as a photocatalyst under UV light (Senthilnathan and Philip, 2009). Ananpattarachai and Kajitvichyanukul (2015) studied photocatalytic degradation of DDT under UV and visible light using interstitial N-doped  $TiO_2$ . Under visible light, 100% degradation of DDT was achieved and the pseudo first order rate constant of DDT degradation using N-doped  $TiO_2$  under visible light (0.1282 min<sup>-1</sup>) was ten-fold higher than that under UV light (0.0121 min<sup>-1</sup>) in the presence of N-doped  $TiO_2$ . Miguel et al. (2012) studied photocatalytic degradation of different OCPs in natural water using  $TiO_2$  alone and in the presence of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as an oxidant. The removal efficiencies of different OCPs is shown in Table 6. The removal efficiencies of DDT and lindane are much lower than what other studies reported (Ananpattarachai and Kajitvichyanukul, 2015; Senthilnathan and Philip, 2009) using  $TiO_2$  as a photocatalyst because Miguel et al. (2012) studied OCPs removal in natural water instead of distilled water (Ananpattarachai and Kajitvichyanukul, 2015; Senthilnathan and Philip, 2009) which means that organic matter, turbidity or other contaminants may affect the performance of the photocatalyst.

Group	OCPs	Removal after TiO <sub>2</sub> /radiation (%)	Removal after TiO <sub>2</sub> /H <sub>2</sub> O <sub>2</sub> /radiation (%)
HCHs	α-HCH	20	20
	β-ΗCΗ	15	15
	γ-HCH (lindane)	15	20
	δ-НСН	15	15
Heptachlors	Heptachlor	50	50
	Heptachlor	30	30
	epoxide A		
	Heptachlor	30	30
	epoxide B		
Endosulfans	$\alpha$ -Endosulfan	90	100
	Endosulfan-	5	10
	sulfate		
Drins	Endrin	50	50
	Dieldrin	30	30
	Isodrin	60	100
	Aldrin	55	95
DDTs	pp'-DDE	40	70
	pp'-DDD + op'-	35	80
	DDT		
	pp'-DDT	20	70

Table 6. Photocatalytic degradation of various OCPs in natural water (Miguel et al., 2012).

# 2.4.4. Advanced Oxidation Processes

Advanced oxidation processes are considered clean technologies for the treatment of polluted waters that are characterized by the production of hydroxyl radicals (OH•), which attack

organic pollutants (Ribeiro et al., 2015). Ozone (O<sub>3</sub>) and O<sub>3</sub> + H<sub>2</sub>O<sub>2</sub> (peroxone) are the most common advanced oxidation processes. O<sub>3</sub> molecules and/or OH• react with pesticides and transform them to primary oxidation products, which often undergo either spontaneous transformation or further oxidation by O<sub>3</sub> and/or OH•(Ikehata and Gamal El-Din, 2005). The efficacy of advanced oxidation processes mainly depends upon the rate of generation of free radicals and extent of their contact with the contaminant molecules (Ranade and Bhandari, 2014).

Yao and Haag et al. (1991) reported that the reaction of lindane with  $O_3$  was so slow that degradation rate could not be calculated. Degradation of lindane increased only up to 21% with the addition of  $H_2O_2$  (2 mg  $H_2O_2/L$ ) as compared to negligible degradation in the presence of  $O_3$  (5 mg applied  $O_3/L$ ) alone (Roche and Prados, 1995). No significant reaction of endosulfan with  $O_3$  was reported in the literature (Ohashi et al., 1993; Reynolds et al., 1989). Even the addition of  $H_2O_2$  along with  $O_3$  (applied  $O_3$  dose = 5 mg/L, and 2 mg  $H_2O_2/L$ ) resulted in only 50% conversion/degradation of 8.65 mg/L of endosulfan (Roche and Prados, 1995). However, extended ozonation (applied  $O_3$  dose = 4 mg/min) degraded/converted 94% of 0.3 mg/L of endosulfan (Yazgan et al., 2003).

Miguel et al. (2007) studied the effectiveness of advanced oxidation processes with  $O_3$ and  $O_3+H_2O_2$  for OCPs degradation. They found that in the case of HCH, heptachlor, endosulfan, dieldrin, endrin, and DDT, degradation yields achieved by  $O_3+H_2O_2$  are less than or similar to with  $O_3$  only. Therefore, the addition of  $H_2O_2$  decreased the effectiveness of  $O_3$  with these pesticides. Improvements in aldrin and isodrin degradation were observed by the addition of  $H_2O_2$ , regardless of the concentration of  $H_2O_2$  applied. Although ozonation can affectively remove OCPs, the cost associated with ozone generation and proper handling because of its poisonous nature are the main constraints in adoption of this technology. Little information is available about degradation by-products of OCPs using ozonation (Ikehata and Gamal El-Din, 2005).

Shah et al. (2013) investigated the ability of UV based advanced oxidation processes for the degradation of endosulfan in water. At a [peroxide]<sub>0</sub>/[endosulfan]<sub>0</sub> molar ratio of 20, 91% of endosulfan removal was achieved by  $UV/S_2O_8^{2-}$  compared to 86%, and 64% by  $UV/HSO_5^-$ , and  $UV/H_2O_2$  processes, respectively, at an initial endosulfan concentration of 2.45 M. Five degradation products of endosulfan were detected: endosulfan sulfate, endosulfan alcohol, endosulfan ether, endosulfan lactone, and 1,2,3,4,5,5-hexachloro-1,3-cyclopentadiene.

Among the well-known advanced oxidation processes, Fenton's reagent is used for the treatment of refractory pollutants (Neyens and Baeyens, 2003). It consists of H<sub>2</sub>O<sub>2</sub> and ferrous salt which react leading to the formation of hydroxyl radicals (Varela, 2003). Begum et al. (2017) investigated the removal of lindane and endosulfan in aqueous phase using Fenton's reagent. The degradation efficiencies of lindane and endosulfan were 84% and 83% using 50 mg/mL and 20 mg/L of FeSO<sub>4</sub>, respectively, at an initial concentration of 7.5 mg/L for both pesticides. Both pesticides were degraded to 1-hexene, and no partially chlorinated intermediates were detected (Begum et al., 2017). Barbusiński and Filipek (2001) studied the removal of OCPs including  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH (lindane),  $\delta$ -HCH in industrial wastewater using Fenton's reagent. All four HCHs were degraded with efficiency of more than 90%. The optimum ratio of [Fe<sup>2+</sup>] to [H<sub>2</sub>O<sub>2</sub>] was from 1:3 to 1:2 while the optimum pH was from 3.0 to 3.5. Although Fenton's reagent has shown its ability to degrade OCPs. However, the costs of the chemicals (FeSO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>) are very high making the process uneconomical for large scale applications (Ranade and Bhandari, 2014).

#### **2.4.5. Metal Nanoparticles**

Nanomaterials have gained attention for the removal of several contaminants including OCPs from water because of their large surface area, higher adsorption capacity, small diffusion resistance, and faster adsorption equilibrium (Rani et al., 2017). The bimetallic Ni/Fe nanoparticles were also found efficient in the degradation of DDT in aqueous solution under weakly acidic or alkaline conditions (Tian et al., 2009). The acidic medium promotes the degradation of DDT more effectively because of production of protons helps in generating hydrogen. El-Temsah et al. (2016) used nZVI for the effective degradation of DDT in water and soil. Higher DDT degradation (92%) was observed in water than in soil (22.4%) due to aging of soil and thus low DDT diffusion rates (Yang et al., 2010). nZVI degraded lindane completely and quickly within 24 h with generation of g-3,4,5,6-tetrachlorocyclohexane (unstable intermediate) which ultimately was reduced into smaller benzene (Elliott et al., 2009). Iron sulfide nanoparticles stabilized by biopolymers successfully degraded lindane with an efficiency of 94% in 8 h (Paknikar et al., 2005). The efficiency of Fe-Pd bimetallic nanoparticles (0.5 g/L) was enhanced in anaerobic medium with 100% degradation of lindane (initial concentration = 1 mg/L) in 300 min. The reason behind that is the reduction process which facilitates the degradation (Joo and Zhao, 2008).

Rani et al. (2017) comprehensively reviewed the application of nanoparticles for pesticide degradation and revealed lack of data on degradation of heptachlor, endrin, dieldrin and endosulfan using nanoparticles. Moreover, the use of nanoparticles at large scale water treatment applications is not economically viable in the near future and controversial due to potential toxic effects of nanoparticles (Rani et al., 2017).

# 2.4.6. Biodegradation

Biodegradation is the breakdown of a substance that occurs when microorganisms such as fungi or bacteria use an organic substance as a source of carbon or energy (Poznyak et al., 2019). *Aspergillus niger* degraded 40% and 98.6% of  $\beta$ -endosulfan by day 1 and day 15, respectively at an initial concentration of 20 µg/10 mL of nutrient medium (Mukherjee and Gopal, 1994). *Achromobacter xylosoxidans* CS5 degraded 10.5 mg/L  $\beta$ -endosulfan and 24.8 mg/L of  $\alpha$ -endosulfan after 8 days in aqueous medium. Endosulfan ether and endosulfan diol were detected as the major metabolites (Li et al., 2009). Kafilzadeh et al. (2015) reported that *Klebsiella, Acinetobacter, Alcaligenes, Flavobacterium,* and *Bacillus* degraded endosulfan into endosulfan diol, endosulfan lactone, and endosulfan ether. The fungal strains, *Chaetosartorya stromatoides, Aspergillus terricola*, and *Aspergillus terreus* degraded 75% of both  $\alpha$  and  $\beta$  endosulfan in the broth within 12 days at an initial concentration of 100 mg/L (Hussain et al., 2007). Mukherjee and Mittal (2005) reported that endosulfan diol and endosulfan sulfate are the major metabolites when active bacteria and fungi were used for endosulfan degradation.

*Stenotrophomonas* sp. DDT-1 was used to degrade DDT in minimal salt medium. The degradation rate of DDT at three concentrations of 0.1, 1.0, and 10.0 mg/l was 0.004, 0.038, and 0.086 mg/l/d, respectively after 21 days of incubation (Pan et al., 2016). It was reported that DDT was converted sequentially to DDE/DDD, 1-chloro-2,2-bis(4' -chlorophenyl)ethylene, 2,2-bis(4' -chlorophenyl)ethanol, bis(4' -chlorophenyl)acetate, and mineralized to carbon dioxide (Pan et al., 2016). *Pseudomonas aeruginosa and Flavimonas oryzihabitans* (in broth media) and *Rhodococcus* sp. IITR03 (in minimal media) could also transform DDT into DDE, DDD, and 1-chloro-2,2-bis(4' -chlorophenyl)ethylene (Bajaj et al., 2014; Barragan-Huerta et al., 2007).

El-Bestawy et al. (2000) investigated the biodegradation of DDT, endrin, and lindane in water using five different species of *Pseudomonas including P. panucimobills, P. aeruginosa, P. mallei, P. pseudomallei,* and *P picketti*. The initial pesticide concentration and incubation time were 0.05-50 ppm and 1-6 days, respectively. At an initial pesticide concentration of 0.05 ppm, *P. panucimobills* degraded only 39% of endrin whereas the complete degradation of lindane and DDT was achieved. The removal efficiencies of endrin, lindane and DDT were 84-100% using the remaining four species of *Pseudomonas*. DDT had the highest removal rate (97-100%) followed by lindane (73.3-100%) by using all five species of *Pseudomonas*, while the endrin removal was 60.5-100% at an initial pesticide concentration of 50 ppm. The degradation by-products of pesticides were not reported.

Matsumoto et al. (2009) reviewed bioremediation of dieldrin and endrin in the soil environment. *Pseudomonas sp., Bacillus sp., and Trichoderma viride* were found to be dieldrin and endrin degraders. Metabolic pathways of both pesticides by these microorganisms are still unclear (Matsumoto et al., 2009). Xiao and Kondo (2013) reported that *Cordyceps militaris* KS-92 degraded dieldrin to dihydrochlordenedicarboxylic acid through oxidation of 6,7dihydroxydihydroaldrin or directly oxidation of dieldrin in potato dextrose medium. In the case of heptachlor, two biodegradation by-products, 1-hydroxy chlordane and heptachlor epoxide, were suggested (Bidleman et al., 1998; Pokethitiyook and Poolpak, 2012).

The microbial degradation of chlorinated pesticides sometimes results in more stable compounds than the parent pesticides (Tewari et al., 2012). For example, degradation of endosulfan by fungi resulted in formation of endosulfan sulfate which is also toxic and more persistent than endosulfan (Weber et al., 2010). Microbial degradation of most of the recalcitrant organic compounds like pesticides is limited by the presence of anionic species in the compound (Rani and Dhania, 2014). The anions such as chloride and sulfate are strongly bonded to the hydrocarbon ring preventing the microbes from attacking the ring structure (Rani and Dhania, 2014). In general, the more extensive the chlorine substitution, the more persistent the pesticide (Tewari et al., 2012).

#### 2.5. Summary

Pesticide contamination in water is a global concern. Agricultural and rural communities are more vulnerable to pesticide contamination and related health effects. In developed and developing countries, these communities do not have centralized water treatment and distribution systems. Therefore, for these communities, there is a need to narrow down water treatment options which can be used and maintained at a household level. Of the removal techniques discussed above, some techniques may not be viable for treatment of OCPs such as solar photolysis because of their recalcitrant nature to sunlight. Although photocatalysis is capable of degrading OCPs in water, the costs of catalyst and energy required for UV lamps would be an issue for the adoption of the technique. Likewise, ozonation and other advanced oxidation processes such as Fenton's reagent have shown their ability to degrade OCPs at bench and laboratory scales; however, the cost associated with Fenton's reagent production and proper handling of O<sub>3</sub> due to its poisonous nature make them unfavorable. AC and membrane processes are capable of removing OCPs in water without degrading them to less toxic/degradable byproducts. Therefore, handling of spent AC and brine would result in economic and environmental issues. Metal nanoparticles such as nZVI have shown its ability to degrade chlorinated pesticides efficiently, however, the associated cost, and rapid oxidation of Fe<sup>0</sup> to Fe<sup>2+</sup> and eventually Fe<sup>3+</sup> results in a short life of the treatment unit. Biodegradation of OCPs requires longer time (days to weeks) and is not feasible for the treatment of OCPs at a household level.

For rural agricultural communities, the treatment method should be less expensive, capable of degrading OCPs into less toxic compounds, and easily manageable.

# 3. IRON TURNING WASTE AS EFFICIENT POINT-OF-USE WATER FILTRATION MEDIA FOR REMOVAL OF ENDRIN AND DIELDRIN

#### **3.1. Introduction**

OCPs became ubiquitous pollutants because of their wide use in agriculture as well as their chemical stability (El Bakouri et al., 2009). OCPs are considered one of the most dangerous products used in crop protection. Among the OCPs, drin group pesticides such as dieldrin, endrin and aldrin are more toxic to wildlife, animals and humans, and persistent in the soil up to several decades (Shukla et al., 2006; Stern, 2014). As a consequence, most of them have been listed as persistent organic pollutants by the United Nations Environment Program (UNEP, 2001). For instance, despite nearly three decades since the removal of dieldrin from the market in United States, it is a commonly found contaminant in New Jersey waste sites and in soils in Connecticut, Texas, and California (Stern, 2014).

In most developing countries, many of these drin-group pesticides are still in use as insecticides in crop fields for termites, wood bores and textile pests because of their effectiveness and low application costs (El Bakouri et al., 2009). These pesticides are transported by diffuse pathways to surface water and groundwater. Surface and groundwater contamination with dieldrin and endrin have been reported in many agricultural communities of Asian countries such as India (Yadav et al., 2015), Pakistan (Azizullah et al., 2011), and China (Bao et al., 2012). Numerous studies have reported contamination of water resources by these pesticides, even at considerable distances from the points of original application (Golfinopoulos et al., 2003; Pazou et al., 2006; Xu et al., 2007; Zhou et al., 2006). The contamination of surface and groundwater by these pesticides impairs the water quality and restricts their use for water supply without proper treatment. According to the USEPA, the drinking water standards for dieldrin and endrin

are 0.2 and 2  $\mu$ g/L, respectively (USEPA, 2004). However, for endrin, the WHO (2006) established as a guideline value that is of health significance in drinking water at 0.6  $\mu$ g/L. Common effects of these pesticides such as nausea, vomiting, headache, convulsions, birth defects, liver issues, and inhibition of neurotransmitter hormone have been reported (Shrivas et al., 2017). Therefore, they need to be removed from water to minimize the human health risk.

Several treatment methods are available to treat dieldrin and endrin in water such as adsorption, membrane filtration, ozonation and photocatalytic degradation (Marican and Duran-Lara, 2018; Plakas and Karabelas, 2012). Adsorption on AC and membrane filtration could only remove them from water without degrading them into less toxic/more degradable compounds leaving behind contaminated brine and activated carbon that need to be managed. Ozonation and photocatalysis can degrade them; however, the complexity and associated costs hinder their use in developing countries especially in rural areas where pesticide contaminated water is more prominent.

Mastumoto et al. (2009) reviewed bioremediation of dieldrin and endrin in the soil environment. *Pseudomonas sp., Bacillus sp., and Trichoderma viride* were found to be dieldrin and endrin degrading microorganisms (Matsumura and Boush, 1967; Matsumura et al., 1971; Patil et al., 1970). Metabolic pathways of both pesticides by these microorganisms are still unclear (Matsumoto et al., 2009). For dieldrin, a major metabolite produced by the abovementioned microorganisms was 6,7-*trans*-dihydroxydihydroaldrin (Matsumura and Boush, 1967; Matsumura and Boush, 1968). Matsumura et al. (1970) reported photodieldrin as the metabolic product of dieldrin by aerobic microorganisms. Endrin aldehyde and ketone derivatives of endrin were reported as metabolites of endrin (Matsumura et al., 1971).

nZVI have also shown their ability to degrade a number of chlorinated compounds at laboratory scales. However, there has been no study on endrin and dieldrin removal using pure metal nanoparticles including nZVI (Rani et al., 2017). Shrivas et al. (2017) recently studied the use of a nanocomposite of graphene oxide and iron oxide magnetic for the removal of endrin and dieldrin in water. However, the concentration of endrin and dieldrin used in their experiment was 5 mg/L for both pesticides which is above their water solubility limits (186 µg/L at 20°C and 230 µg/L at 25°C for dieldrin and endrin, respectively) (WHO, 2003; WHO, 2004). The practical applicability of their results is therefore questionable. Their findings showed that the adsorption capacity of nanocomposite of graphene oxide-magnetic nanoparticles for dieldrin and endrin were 1 mg/g and 99 mg/g, respectively, when the sample volume was 2 mL (Shrivas et al., 2017). Although metal nanoparticles have potential to remove these pesticides in water effectively, their practical application as water treatment media is not possible in the near future due to associated cost and unknown fate and potential toxicity to organisms and environment. Rural agricultural communities, where groundwater is contaminated endrin and dieldrin, do not have access to centralized water systems. Therefore, the communities need an affordable, locally available and easily manageable point-of-use filtration systems at a household level to treat and degrade the pesticides in water.

In this study, a waste from iron industry known as "iron turning waste" was experimented to treat dieldrin and endrin in water. Iron turning waste has the same valence and properties as nZVI except the size. It is available for free or at affordable prices. The objectives of the study were (1) to investigate the optimal operating conditions such as iron dosage, water pH, order of media, water flow rate for the removal of endrin and dieldrin and (2) to identify degradation byproducts of both pesticides and elucidate degradation mechanism and pathways. The study aimed to provide efficient and affordable point-of-use water filtration media for rural communities for treating dieldrin and endrin contaminated water.

# **3.2. Material and Methods**

#### 3.2.1. Materials

Standard solutions of endrin (5,000 μg/mL) and dieldrin in methanol (1,000 μg/mL) were purchased from Sigma-Aldrich (St Louis, MO, USA). Analytical grade methanol, pentane, sodium nitrate, and chloride salts of sodium, magnesium, potassium, and calcium were acquired from Sigma Aldrich (St Louis, MO, USA) and VWR (Radnor, PA, USA). A 100 μm polydimethylsiloxane (PDMS) fiber, and manual fiber support and holder for solid-phase microextraction (SPME) were purchased from Supelco, Sigma-Aldrich. Pre-cleaned glass vials and high performance liquid chromatograph (HPLC) grade water were purchased from VWR (Radnor, PA, USA). Iron turning waste was collected from a local machine shop in Lahore, Pakistan and washed with deionized (DI) water prior to experimentation. Play sand was purchased from a local hardware store (Lowe's, Fargo, ND, USA) and sieved. Sand particles retained on a 600 μm sieve were collected, washed with tap water thoroughly three times and used in the experiments without drying. HPLC grade water or reverse osmosis DI water was used throughout this research.

# 3.2.1.1. Material characterizations

Iron turning waste (0.1 - 0.15 cm in size) and sand were characterized using field emission scanning electron and energy dispersive X-ray spectroscopy (EDS). Samples were attached to cylindrical aluminum mounts using silver paint (SPI Products, West Chester, Pennsylvania, USA). Images were obtained with a JEOL JSM-7600F scanning electron microscope (JEOL USA, Inc., Peabody, Massachusetts). EDS was acquired using an UltraDry silicon drift X-ray detector and NSS-212e NORAN System 7 X-ray Microanalysis System (Thermo Fisher Scientific, Madison, Wisconsin).

### **3.2.2. Sample Preparations**

#### 3.2.2.1. Batch study

Individual stock solutions containing 100 mg/L of both pesticides were prepared by diluting standard solutions in methanol and stored at 4°C. Individual solutions of endrin and dieldrin (20  $\mu$ g/L) were prepared by diluting the stock solution with DI water. For degradation and kinetic experiments, 2.5 and 1 g of iron turning waste were added to different Erlenmeyer flasks containing the pesticide solution (200 mL) and stirred at 400 rpm using an orbital shaker. Samples of 50 mL were collected at time (t) t = 0, 2, 4, 6, 8 and 10 min. Iron turning of 0.5 - 5 g was used to study the effect of its dosage on pesticide removal at a single time point, t = 10 min, after which the pesticide removal remained relatively constant.

Individual stock solutions (1 g/L) of sodium, calcium, magnesium, potassium, and nitrate were prepared in DI water by adding their respective chloride salts, and sodium nitrate. Further dilution was made with DI water to obtain the desired concentrations. To investigate the effects of minerals in groundwater (Na = 250 mg/L, Ca = 150 mg/L, Mg = 60 mg/L, K = 60 mg/L and  $NO_3^- = 40$  mg/L), initial pesticide concentration (1 - 20 µg/L) and pH (4, 7 and 10) on pesticide removal, 2.5 g of iron turning was used in the same manner as the sorbent dosage experiment, and a single sample was collected at 10 min.

To investigate the degradation mechanism, 10-25 g of iron turning was added to an Erlenmeyer flask containing endrin or dieldrin solution (2-5 mg/L, 200 mL) and stirred for 24-96 h. The solution pH for both pesticides was 5.9. Samples of 40-50 mL were taken at t = 24, 48, 72 and 96 h. All collected samples were stored at 4°C, and within 24 h extracted and analyzed for

the pesticides using gas chromatograph (GC)-electron capture detector (ECD) and degradation by-products using GC-mass selective detector (MSD). All batch experiments were conducted in triplicate except the degradation mechanism which was performed in duplicate.

#### 3.2.2.2. Column study

To find the most suitable order and composition of filtration media to treat a mixture of both pesticides in water as they normally coexist in contaminated water, four gravity glass columns (L× I.D × O.D: 81 cm × 40 mm × 45 mm) with different filter media layer configurations were set up and loosely packed with: (1) only sand, (2) only iron turning, (3) sand + iron turning and (4) sand + iron turning + sand. For the first and second filtration columns, 200 g of sand and 125 g of iron turning were used, respectively. The third and fourth filtration columns had 200 g of sand (each layer) and 125 g of iron turning is separate layers. The water flow rate for each column was 8-10 mL/min. Slow water flow rates (1-6 mL/min) were used and recommended for pesticide removal using walnut shell (Memon et al., 2014). Also, the slow flow rate is what allows the physical and chemical processes to occur (Phu, 2016).

To investigate the effect of media dosage, three glass columns were set up with different iron turning dosages (100, 125 and 150 g) while the amount of sand remained constant (200 g for each layer). Preliminary experiments showed that less than 100 g of iron turning could be inadequate to meet drinking water standards and health significance value for dieldrin and endrin. To study the effect of empty bed contact time (EBCT), different water flow rates were applied: 5, 10, and 15 mL/min corresponding to EBCTs of 1.6, 0.8 and 0.5 h, respectively.

To determine the service period of filter media, a breakthrough experiment was conducted using the same glass column as described above and the water flow rate was 5 mL/min. For all column experiments, the influent concentration for both pesticides was  $2 \mu g/L$ ,

which is 10 times higher and equal to drinking water standards set by the USEPA for dieldrin and endrin, respectively (USEPA, 2018). Endrin contamination in groundwater is generally reported to near or less than drinking water standards, however, a new health significance guideline value ( $0.6 \mu g/L$  in drinking water) was issued by WHO (WHO, 2006). For all filtration experiments except the service period of filter media, treated water samples were collected at time (t) = 0, 10, 20, 30, 40, 50 and 60 min for pesticide analysis. The filter media configuration within the columns was sand + iron turning + sand unless mentioned. All the column experiments were performed under gravity flow at room temperature (23-25 °C) and water flow rate was maintained by sustaining a constant water level over the filtration media. The influent and treated water pH values were recorded for all filtration experiments. All filtration experiments were performed in triplicate except the breakthrough experiment which was conducted in duplicate.

# **3.2.3.** Analytical Procedure

For all experiments except the degradation mechanism, endrin and dieldrin were extracted using a liquid-liquid micro extraction method (Munch, 1995). Sodium chloride of 18-20 g was added to a 60 mL glass vial containing 50 mL of collected sample following the addition of 5 mL of pentane. After that, the sample vial was hand shaken vigorously for 30 seconds and stirred at 1,150 rpm for 5 min using a magnetic stirrer. Then the solution was allowed for phase separation by gravity for 5 min and 2 mL of the top layer was pipetted into an autosampler vial for quantitative analysis of pesticides using a GC-ECD. The operating conditions for the GC-ECD were as follows: injection volume of 2  $\mu$ L, He carrier gas constant flow at 1 mL/min, injection temperature at 220°C, splitless injection mode with split valve open at 0.75 min, oven temperature at 100°C for 0 min, then ramping at 100°C/min to 180°C (hold time of 5 min) and at a rate of 5°C/min to 250°C with a 5 min final hold.

To detect the degradation by-products, SPME and liquid-liquid micro extraction techniques were used. For SPME, 4 g of sodium chloride was added to 40 mL of collected samples and PDMS fiber was immersed in the solution and stirred using a magnetic stirrer for 1 h. After that, the PDMS fiber was injected into a GC port. Liquid-liquid micro extraction using pentane as a solvent followed the same procedure as described above. The extracted samples were analyzed by GC-MSD. An Agilent GC (GC-7890B) and HP-5ms capillary column (30 m × 250  $\mu$ m with 0.25  $\mu$ m film thickness) was used.

The operating conditions for the GC-MSD were as follows: injection volume of 4  $\mu$ L, He carrier gas constant flow at 1 mL/min, injection temperature at 30°C, splitless injection mode with split valve open at 3 min, solvent delay for 3 min, oven temperature at 30°C for 0 min, then ramping at 5°C/min to 200°C (hold time of 5 min) and at a rate of 5°C/min to 250°C with a 5 min final hold. The MS was set at scan mode using a scan range from 50 to 550 *m/z* for the analysis of both pesticides and their by-products. A mass spectral search program (NIST, USA) was used for the analysis of the results, by comparing the spectra of the samples and those from the library. All extracted samples using liquid-liquid micro extraction and SPME were analyzed within 24 h of extraction.

For quantitative analysis of both pesticides using GC-ECD, the instrument was subjected to a five-point calibration (0.2 to 20  $\mu$ g/L). Calibration standard solutions were prepared from a stock solution in DI water. The calibration curves for both pesticides (data not shown) fit very well with the data (R<sup>2</sup> = 0.998-0.999). Although the described analytical method can detect both pesticides below 0.05  $\mu$ g/L (Munch, 1995), the detection limit in this study was 0.1  $\mu$ g/L.

Degradation by-products of both pesticides were analyzed (qualitatively) using GG-MSD, and based on peak intensity and area, degradation mechanism was proposed.

For all experiments, pH of water contaminated with both pesticides was measured before and after treatment with iron turning waste, whereas oxidation-reduction potential (ORP) was measured only for the degradation mechanism experiment.

# **3.2.4. Statistical Analysis**

One-way analysis of variance (ANOVA) test was performed using Minitab software (version 18.1, 2017) with the posthoc Tukey Test to compare pesticide removal efficiencies for endrin and dieldrin within each treatment (sorbent dosage, initial pH, initial pesticide concentration, individual and all minerals, order of media and water flow rate). A significance criterion ( $\alpha$ ) is 0.05.

#### **3.3. Results and Discussion**

#### 3.3.1. Surface Morphology and Elemental Compositions of Iron Turning Waste and Sand

The surface morphology of iron turning waste and sand is shown in Figure 2. The surface of iron turning was mainly smooth with some lumps (Figure 2a), which could be due to mechanical abrasion, whereas the EDS analysis (Table 7) reveals that silica and carbon were parts of iron turning. These two elements are typically found in iron ores as impurities. The surface of sand was relatively flat (Figure 2b) and silicon and oxygen were the main elemental compositions of sand along with some impurities such as aluminum and minerals as shown in Table 7.



Figure 2. Surface morphology of (a) iron turning waste and (b) sand.

Floment	Weight (%)			
Element	Iron turning	Sand		
С	4.40	1.62		
0	5.25	42.06		
Si	0.62	31.88		
Fe	89.72	1.21		
Al	-	12.66		
Na	-	6.03		
K	-	0.31		
Ca	-	4.23		

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# 3.3.2. Endrin and Dieldrin Degradation Kinetics

Reactions between the pesticides (endrin and dieldrin) and iron turning were fast, more than 49% and 47% of endrin and dieldrin removal were achieved within 2 min using 2.5 g of iron turning (Figure 3). After 10 min of reaction, more than 92% removal efficiency was attained for both pesticides. The reaction time (2 - 10 min) significantly affected the removal of both pesticides (ANOVA, p = 0.0001, 0.0002). When 1 g of iron turning was used, at t = 10 min the removal efficiency of endrin slightly decreased to 89% while more than 87% dieldrin removal was achieved. Ormad et al. (2008) studied removal of different pesticides including dieldrin and endrin at an initial concentration of 0.5 µg/L in river water. The removal efficiencies of dieldrin and endrin were 90% and 80% by ozonation, and 85% using activated carbon.

Endrin and dieldrin degradation/removal data fit well with the pseudo-first order model ( $R^2 \ge 0.99$ ). The endrin degradation rate constants (k) were 0.29 and 0.25 min<sup>-1</sup> using 2.5 and 1 g of iron turning, respectively. The dieldrin degradation rate constant increased 31% from 0.20 to 0.26 min<sup>-1</sup>, when the amount of iron turning was increased from 1 to 2.5 g. The pH of endrin and dieldrin solution increased after 10 min of reaction from 5.78 and 5.60 to 7.77 and 6.62, respectively. This observation has also been documented, when nZVI was used to treat/degrade different contaminants in water (Freyria et al., 2017; Wilkin and McNeil, 2003). This is due to OH<sup>-</sup> release during the chemical reaction as Fe<sup>0</sup> first hydrolyzes water to produce hydrogen and hydroxide ions. Whereas, iron turning performs reductive dechlorination of both pesticides in the presence of hydrogen ions (H<sup>+</sup>), which is explained in section 3.3.6.



Figure 3. Degradation/removal of endrin and dieldrin from water using iron turning waste.**3.3.3. Effects of Media Dosage and Initial Pesticide Concentration** 

The effect of iron dosage on endrin and dieldrin removal is shown in Figure 4a. The removal efficiencies of endrin and dieldrin increased from 74 and 81% to 93%, with increasing iron dosage from 0.5 to 2.5 g. This is due to increase in the active surface area with increasing amount of sorbent. Since further increase in sorbent dosage (2.5 to 5 g) resulted in no improvement in their removal, other batch experiments were conducted with 2.5 g of iron turning. ANOVA indicates that iron dosage had significant effect (ANOVA, p = 0.001, 0.002) on the removal of both pesticides.

Figure 4b shows the effect of initial pesticide concentration on the removal of both pesticides. The removal efficiencies of endrin and dieldrin were 89-91% and 90-93%, when the initial concentrations of both pesticides were 10-20  $\mu$ g/L. Liu et al. (2007) studied the removal of dieldrin and endrin using cellulose acetate absorbent at an initial concentration of 10  $\mu$ g/L of both pesticides. Less than 50% removal for both pesticides were achieved using 1 g of absorbent

in 60 min. Ru et al. (2007) also found that dieldrin removal increased with the increase of the initial concentration, when triolene-embedded activated carbon was used as adsorbent. However, at low initial pesticide concentration (1  $\mu$ g/L), the removal efficiencies of endrin and dieldrin decreased to 51% and 58%, respectively. A decrease in atrazine removal at lower initial concentrations using nZVI was reported (Bezbaruah et al., 2009). A possible explanation is that it could be due to less interaction between iron turning and pesticides at lower concentrations, which may need more reaction time to achieve better removal. The differences in removal efficiencies of both pesticides were significant (ANOVA, *p* = 0.0001, 0.003) at different initial pesticide concentrations.



Figure 4. Effects of media dosage and initial pesticide concentration on endrin and dieldrin removal.

# 3.3.4. Effects of Minerals and Water pH on Pesticide Removal

Minerals are common in groundwater. Therefore, it is important to evaluate the effect of individual and all typically found minerals in groundwater on the ability of iron turning waste to degrade both pesticides. The studied mineral concentrations are based on typical values found in

rural communities in developing countries (Aleem et al., 2018; Greenman et al., 1967; Mora et al., 2017). The minerals present in groundwater had minimal effect ( $\leq$ 5%) on both endrin and dieldrin removal as shown in Figure 5a and the differences (with and without mineral(s)) were not significant (ANOVA, *p* = 0.995, 0.687). The removal efficiencies of endrin and dieldrin were 90-92% and 87-92%, respectively, regardless of the presence of the mineral(s).

The rate of dehalogenation was found to be extremely dependent on the groundwater chemical characteristics, in particular pH, when metal nanoparticles were used (Eykholt and Davenport, 1998; Ghauch et al., 1999). The effect of initial water pH ranging from 4 to 10 on the removal of both pesticides is illustrated in Figure 5b. It is well known that pH value played a significant role in reducing contaminants by  $Fe^0$  (Han et al., 2015). Under acidic environment (pH = 4), the removal efficiency of endrin increased to 92% as compared to neutral pH (86%). For dieldrin, the removal efficiency was 82-83% at both pH 4 and 7. Previous studies also showed that the ability of zerovalent iron to degrade organic contaminants such as nitrobenzene increased at low pH (3-5) compared to high pH (7-10) (Dong et al., 2010; Yin et al., 2012).

Under acidic environment, zerovalent iron hydrolyzes water and producing large amounts of hydrogen (Wang et al., 2009a). Subsequently, greater disassociation of molecular hydrogen resulted in contaminant degradation rapidly (Wang et al., 2009a). Lower pH hinders ferrous hydroxide and other protective layers accumulation on the surface of ZVI and optimizes the use of its active sites (Dong et al., 2010; Shih and Tai, 2010). When initial pH was increased from 7 to 10, the removal efficiencies of both endrin and dieldrin decreased from 86 and 82% to 81 and 75%, respectively. Previous studies show that the ability of Fe<sup>0</sup> to degrade contaminants decreased at elevated pH (9-10) compared to neutral pH (Fan et al., 2009; Gerbino-Bevins et al., 2012). Under basic conditions, the reactivity of zerovalent iron decreases due to increased

formation and precipitation of iron oxide on its surface (Shih and Tai, 2010). The initial water pH had no significant effect on endrin removal (ANOVA, p = 0.431), but it was significant in the case of dieldrin (ANOVA, p = 0.003).



Figure 5. Effects of minerals and water pH on endrin and dieldrin removal.

# **3.3.5.** Continuous Filtration

It has been documented that precipitation can occur between inorganic elements and minerals in groundwater which might clog and coat iron surface and inhibit the degradation/dehalogenation of chlorinated compounds (Indelicato, 1998). To address this issue, sand, a conventional water filtration medium was used in combination with iron turning waste to treat endrin and dieldrin in water. The sand would also limit iron exposure to oxic environment resulting in longevity and better performance of a filter. Another reason for using sand media was to prevent iron turning waste from escaping the column and minimize the iron content in the product water. The ability of sand media alone to treat pesticides in water was also tested.

#### 3.3.5.1. Effect of order of media

Figure 6a shows that sand filtration alone was not effective for the removal of both pesticides in water. Dieldrin and endrin removal capacity dropped from 62% and 51% to 15% and 23% respectively within 60 min of filtration. EDS analysis (Table 7) shows the presence of organic matter (carbon) and iron in sand as impurities. Although sand was washed prior to its use for filtration experiments, the initial pesticide removal could be either due to reaction with and/or adsorption on organic matter and/or iron content. When only iron turning was used as filtration media, the removal efficiencies of endrin and dieldrin were 83-86% and 87-88% as shown in Figure 6b. Endrin removal slightly increased and remained stable (90%), whereas the removal of dieldrin remained unchanged (88-89%), when sand + iron turning waste was used as filtration media (Figure 6c). Adding another layer of sand in a filtration column (sand + iron turning waste + sand) resulted in no change in both pesticides removal (Figure 6d).

The product/treated water had light yellowish color, when iron turning alone and or sand + iron turning were used as filter media in the column. The light yellowish color of product water

could be due to presence of high iron content. However, this issue was addressed by adding another layer of sand below iron turning layer in the column. To remove both pesticides effectively and limit iron content in the product water, hybrid filtration (sand + iron turning waste + sand) configuration was chosen for further experiments. The order of media had significant effects (ANOVA, p = 0.002, 0.00000003) on the removal of both pesticides.



Figure 6. Effects of order and composition of media on endrin and dieldrin removal: (a) sand, (b) iron turning, (c) sand + iron turning and (d) sand + iron turning + sand.

# 3.3.5.2. Effects of media dosage and EBCT

Figure 7a shows that the removal efficiencies of dieldrin and endrin were 88% and 79-85% using 100 g of iron turning in 60 min of filtration. When 125 g of iron turning was used, the initial removal of endrin improved and stayed stable (88%) as shown in Figure 6b, whereas dieldrin removal slightly increased (89%). However, better removal for both pesticides (95%) was achieved, when the amount of iron turning was increased to 150 g (Figure 7b) but the differences in pesticide removal efficiencies were not significant (ANOVA, p = 0.281, 0.387) using different iron dosage (100 - 150 g). These findings suggest that increasing iron dosage in a filtration column provided longer contact time between pesticides and iron turning, resulting in better removal. Therefore, it is also necessary to study the effect of EBCT through the variation of water flow rate to achieve better pesticide removal.

Figure 7c shows that 94-100% removal was achieved for both pesticides, when the EBCT was 1.6 h. At an EBCT of 0.8 h, the removal efficiencies of dieldrin and endrin were 88-95% in 60 min of filtration as shown in Figure 7d. Further decrease in EBCT (0.5 h) had minimal effect on their removal efficiencies as shown in Figure 7e, and the removal efficiencies of both pesticides were not significantly different (ANOVA, p = 0.885, 0.995) at different EBCT (0.5, 0.8, 1.6 h). To achieve highest possible removal of both pesticides using 150 g of iron turning, it was decided to study the service period of filter media at 1.6 h EBCT.



Figure 7. Effects of media dosage ((a) 100 g and (b) 150 g), and EBCT ((c) 1.6 h, (d) 0.8 h and (e) 0.5 h) on endrin and dieldrin removal.

# 3.3.5.3. Service period of filter media

Figure 8 shows that complete removal (to below the detection limit) of both pesticides in reverse osmosis DI water was achieved for 300 h of continuous filtration. From 300 to 500 h, the removal efficiencies of dieldrin and endrin dropped to 95% and 94%, respectively. In the next 100 h, a sharp decrease (7-8%) in both pesticide removal was observed, the treated water was still meeting the health significance value of endrin set by WHO. However, dieldrin concentration (0.24-0.30  $\mu$ g/L) in treated water was above the drinking water standards. These findings suggest that iron turning needs to be replaced or regenerated after 500 h of filtration to comply the standards for dieldrin. A separate study on iron turning regeneration by a simple biological means is being conducted.

In the presence of minerals in water, after 300 h of filtration, the flow rate of treated water decreased by 40%, which might be due to clogging or precipitation on the surface of filter media. Within 0.25 min of backwashing using tap water, the desired flow rate (5 mL/min) at the outlet was recovered. During the filtration, the pH of treated water increased from 5.8-5.9 to 8.1-8.5. This is due to OH<sup>-</sup> release as  $Fe^{0}$  first hydrolyzes water to produce hydrogen and hydroxide ions. The presence of H<sup>+</sup> facilitates the reductive dechlorination of both pesticides using iron turning (for details, see section 3.3.6). The results indicate that iron turning waste based filter is a sustainable solution to treat dieldrin and endrin in water.





# **3.3.6.** Degradation Mechanism and Pathways

The zero oxidation state of metallic iron (Fe<sup>0</sup>) and dissolved aqueous ferrous ion (Fe<sup>2+</sup>) form a redox couple with a standard reduction potential of -0.440 mV, making Fe<sup>0</sup> a reducing agent (eq. 1). In the presence of a proton donor, Fe<sup>0</sup> can perform reductive dehalogenation of alkyl halides such as endrin and dieldrin (eq. 2). Equation 2 is similar to corrosion of iron where alkyl halide is present as a strong oxidizing agent instead of dissolved oxygen. Under anoxic conditions, water alone can result in oxidation of Fe<sup>0</sup> to Fe<sup>2+</sup> and releasing hydrogen gas (eq. 3) which can also dehalogenate alkyl halides. Under oxic environment, the presence of oxygen resulted in rapid formation of Fe<sup>2+</sup> (eq. 4). Fe<sup>2+</sup> is also capable of dehalogenating alkyl halides (eq. 5).

$$Fe^{2+} + 2e^- \leftrightarrow Fe^0$$
 (1)

 $Fe^0 + RX + H^+ \rightarrow Fe^{2+} + RH + X^-$  (2)

$$Fe^{0} + 2H_{2}O \rightarrow Fe^{2+} + H_{2} + 2OH^{-}$$
 (3)

$$Fe^{0} + \frac{1}{2} O_{2} + H_{2}O \rightarrow Fe^{2+} + 2OH^{-}$$
 (4)

$$Fe^{2+} + RX + H^+ \rightarrow Fe^{3+} + RH + X^-$$
(5)

Figure 9 depicts a conceptual model for reductive degradation of dieldrin and endrin by iron turning waste.  $Fe^0$  first hydrolyzes water to produce hydrogen and hydroxide anions (OH<sup>-</sup>). OH<sup>-</sup> may react with  $Fe^{2+}$  and/or  $Fe^{3+}$  to form iron hydroxide and/or ferric hydroxide precipitates which may form a surface layer on zerovalent iron particles (Dong et al., 2010). Electrons donated by Fe reduce the contaminant and, in the case of hydrodechlorination, hydrogen replaces the liberated chloride ion (Schrick et al., 2002).



Figure 9. Model for reductive dehalogenation of dieldrin and endrin by iron turning waste.

It was observed that rates of degradation and end products of both pesticides depend upon the initial pesticide concentration and amount of iron turning. When the initial concentration and media (iron turning waste) dosage were 5 mg/L and 10-15 g respectively, in the case of endrin small peaks of 2,7:3,6-dimethanonaphth[2,3-b]oxirene,3,4,6,9,9-pentachloro-1a,2,2a,3,6,6a,7,7aoctahydro and 2,6-bis(3,3-dichloroprop-2-enylidene)cyclohexanone were detected. 1,3-dimethyl-5-(1',1',2'-trichloro-3-ethylallyl)benzene was also detected as a degradation by-product, and 2,4di-*tert*-butylphenol was detected as a major final product (Figure 10a). In the case of dieldrin, only 2,4-di-*tert*-butylphenol was detected as a major degradation by-product (Figure 10b). Small peaks of nonanal and decanal were also detected for both pesticides. It has been reported in the literature that trace amounts of chlorinated intermediates/by-products were formed during the dechlorination of organic compounds using nZVI; however, they do not persist (Schrick et al., 2002).

When the initial pesticide concentration was reduced (2 mg/L) and iron dosage was increased (20-25 g), endrin was completely degraded into aldehyde and different alcohols such as nonanal, 1-octanol and 2 ethyl-1-hexanol (Figure 10a). A small peak of phenol was detected instead of 2,4-di-*tert*-butylphenol. The reaction was fast enough that no major peaks of other intermediate/dehalogenation products were detected. For dieldrin, nonanal and 1-decanol were the major by-products. Phenol and 1- and 2-dodecene were also detected as degradation by-products of dieldrin (Figure 10b).

As it can be seen in the list of degradation by-products of both pesticides in Appendix (Table A1), there were traces of intermediate by-products detected, having more carbon atoms than the parent pesticides. For instance, in the case of endrin, 1,3-dimethyl-5-(1',1',2'-trichloro-3-ethylallyl)benzene has one more carbon atom than endrin. Hara (2011) also detected dibutyl

phthalate as a degradation product of dieldrin which has four more carbon atoms than parent compound. A possible explanation for the generation of such intermediates is that chloride present in the unsaturated ring was transferred to the benzene structure after dechlorination and elimination of the excessive carbon present in the ring. Another hydrocarbon ring was then opened, and low molecular weight organic compounds or acids generated was added to it (Hara, 2011).

For endrin and dieldrin, the acute oral median lethal dose (LD50) in rat are 5.6 mg/kg and 37 mg/kg of body weight, whereas 2,318 mg/kg and 11,000 mg/kg for 2,4-di-*tert*-butylphenol and nonanal. This shows that iron turning waste was able to degrade both endrin and dieldrin into much less toxic compounds. The pesticide mineralization degree was not determined in this study because (1) the standard solutions of both pesticides were in methanol and further diluted with water, therefore, it is not possible to measure accurate total organic carbon of endrin and dieldrin and dieldrin before and after treatment and (2) the water solubility limits of the pesticides are lower than typical total organic carbon detection limits.

The pH value of both endrin and dieldrin solutions increased from 5.6-5.8 to 10.5 and 10.8 after 96 h of the degradation mechanism experiments. This is because  $Fe^0$  consumes H<sup>+</sup> ions and reacts with dissolved oxygen and releases OH<sup>-</sup> ions during its chemical reaction with water. Decreases in ORP value of dieldrin and endrin from 180-210 to -596 and -669 mV were observed. Negative ORP values confirm reducing conditions in the systems.





Figure 10. Proposed degradation pathways of pesticides in water using iron turning waste: (a) endrin and (b) dieldrin.
#### 3.4. Summary

The findings of batch and lab-scale column experiments suggest that iron turning waste can be used as sustainable and affordable point-of-use filtration media to treat water contaminated with dieldrin and endrin. Minerals in water and water pH had minimal effect on the performance of iron turning in removing both pesticides. Iron turning completely dechlorinated both pesticides into aldehydes and alcohols which are far less toxic than parent compounds. Identified degradation by-products suggest that dechlorination followed by ring cleavage are involved in the degradation of both pesticides using iron turning. This study provides a solution to small/rural agricultural communities that cannot afford expensive water treatment technologies with a reliable system to address a public health concern due to endrin and dieldrin contaminated water. Moreover, this study demonstrates an effective utilization of industrial waste as a sustainable filtration media in water filters with an easy setup. The proposed filter can remove both pesticides and provide treated water complying with the drinking water standards at a household level for at least three weeks before the media replacement is needed.

## 4. IRON TURNING WASTE MEDIA FOR TREATING ENDOSULFAN AND HEPTACHLOR CONTAMINATED WATER

#### 4.1. Introduction

Pesticide use in agriculture to control the proliferation and ill-effects of pests and boost the crop yield has increased considerably during the last thirty years (Mudhoo et al., 2019). Endosulfan and heptachlor are organochlorine (cyclodiene) pesticides which are still in use on many agricultural crops especially in developing countries and southern hemisphere because of their effectiveness and low application costs (Lucero et al., 2016; Mudhoo et al., 2019). Endosulfan has been documented as a human carcinogen and an endocrine disruptor (Mudhoo et al., 2019), whereas there is inadequate evidence on heptachlor for carcinogenicity in humans, although confirmed in animals (Prado et al., 2009).

Surface and groundwater contaminated with endosulfan and heptachlor have been reported in South Africa (Dalvie et al., 2003) and many Asian countries such as India (Arisekar et al., 2018), Pakistan (Ali et al., 2016; Ismail et al., 2014), and China (Kuranchie-Mensah et al., 2012). Agricultural communities are more vulnerable to associated health risks of these pesticides because of potential contamination of water sources and lack of effective water treatment processes (Yonli et al., 2012). For instance, people living in five different small rural communities of Kerala District, India have been suffering from the side effects of endosulfan even after the permanent ban of its application on the fields in 2006 (Embrandiri et al., 2012). Therefore, endosulfan and heptachlor need to be removed from water to minimize the human health risk.

Adsorption on AC, membrane filtration and photocatalytic techniques were used to remove both pesticides in water (Mudhoo et al., 2019). The initial and energy costs associated

with photocatalysis, AC, and membrane filtration systems restrict their use in rural communities. Moreover, AC and membrane filtration remove contaminants including pesticides from water through separation resulting in contaminated adsorbents and brine that need additional management and cost.

nZVI and iron containing composites have shown their potential to degrade a number of chlorinated contaminants (Lei et al., 2018; Sun et al., 2019). Pillai and Kottekottil (2016) conducted a column study to evaluate the ability of nZVI for the removal of endosulfan in water at a concentration of 105  $\mu$ g/L. Endosulfan concentration in treated water was not reported but it was stated that nZVI can effectively treat endosulfan at a residence time of less than 40 min. Singh and Bose (2016) also studied the ability of micro zerovalent (mZVI) and nZVI to degrade endosulfan in water at concentrations of 200-500  $\mu$ g/L. nZVI was more efficient than mZVI; however, the experiments were conducted at different pH conditions (8.9 for nZVI versus 6.5 for mZVI). Partially dechlorinated by-products were detected but not identified (Singh and Bose, 2016).

Mukherjee et al. (2015) evaluated the performance of zero valent iron (303 nm - 1660 nm in size) to degrade heptachlor in water at a concentration of 550  $\mu$ g/L. Their findings showed that 87-89% reduction of heptachlor was achieved after 48 h. These previous studies did not cover the effects of minerals in water, initial pesticide concentration, water flow rate/empty bed contact time on pesticide removal. Service period of filter media and detailed degradation mechanism of the pesticides were not revealed as well. Moreover, the practical application of nZVI as water filtration media is not possible because of its mobility, potential toxicity, and unaffordability for people living in rural areas and/or poor communities. However, iron filings which are much more affordable than nZVI, have been used to treat arsenic (Cheng et al., 2005; Leupin et al.,

2005; Mehta and Chaudhari, 2015), and nitrate in water (Hao et al., 2005; Laskowski et al., 2016; Liu et al., 2018).

In this study, a waste from iron industry known as "iron turning waste" was experimented to treat endosulfan and heptachlor in water. Iron turning waste has the same valence and properties as nZVI except the size and surface area. The objectives of the study were (1) to conduct batch experiments focusing on the effects of common minerals in groundwater, initial pesticide concentration and water pH on pesticide removal by iron turning waste, and identifying the degradation pathways of both pesticides (2) to investigate the best order of media in a filtration unit and the effect of empty bed contact time on the service period of the media. The study intended to provide simple and affordable point-of-use water filtration media for rural/small communities dealing with endosulfan and heptachlor contaminated water and in turn reduce the associated health risks.

### 4.2. Material and Methods

## 4.2.1. Materials

Standard solutions of endosulfan (100-1,000 mg/L) and heptachlor in methanol (1,000 mg/L) were purchased from Sigma-Aldrich (St Louis, MO, USA) and VWR (Radnor, PA, USA). Analytical grade methanol, pentane, and chloride salts of sodium, magnesium, potassium, calcium, and nitrate were acquired from Sigma Aldrich (St Louis, MO, USA) and VWR (Radnor, PA, USA). A 100 µm PDMS fiber and manual fiber support and holder for SPME were purchased from Supelco, Sigma-Aldrich. Pre-cleaned glass vials and HPLC grade water were purchased from VWR (Radnor, PA, USA). Iron turning waste was collected from a local machine shop in Lahore, Pakistan and washed with DI water and/or methanol. DI water and/or methanol were used to wash iron turning waste to remove any oil residue/organic contaminant (if

present) on its surface. The reasoning of not using tap water for washing iron turning waste was to avoid an interaction between chlorine present in tap water which can corrode the iron surface.

During the preliminary experiments, both DI water and methanol were used to wash iron turning waste prior to pesticide degradation experiment. However, it was found that pesticide removal efficiency remained same, even if DI water was only used to wash the iron turning. Therefore, DI water was only then used to wash iron turning waste prior to all experiments included in this study. The characterization of virgin/fresh iron turning waste was also based on after washing it only with DI water. Play sand was purchased from a local hardware store (Lowe's, Fargo, ND, USA) and sieved. Sand particles retained on a 600 µm sieve were collected, washed with tap water thoroughly three times and used in the experiments without drying. Sand washing was only performed to remove organic matter from it which required relatively large amount of water, therefore, tap water was used instead of DI water. HPLC grade water or reverse osmosis DI water was used throughout this research.

## 4.2.1.1. Material characterizations

Iron turning waste (0.1 - 0.15 cm in size) and sand were characterized using field emission scanning electron and EDS using the same procedure as mentioned in Chapter 3 (section 3.2.1.1). X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were employed to characterize iron turning waste before and after its reactions with both pesticides. XRD analysis was performed using a PANalytical X'Pert Pro diffractometer (United Kingdom). The instrument used copper K $\alpha$  radiation and a copper cathode to produce X-ray with a wavelength of 1.54 Å. The samples were placed in a holder and scanned in a range of 10°- 80° at a step size of 0.02° with time per step of 30 sec. XPS spectra were obtained using a Thermo Scientific K-Alpha XPS. Prior to the scan, all samples underwent soft ion cleaning which

involved argon ion cluster etching at 4,000 eV for 30 seconds. The spectra were obtained by plotting the measured photoelectron intensity as a function of the binding energy.

## **4.2.2. Experimental Procedures**

## *4.2.2.1. Batch study*

Individual stock solutions containing 100 mg/L of both pesticides were prepared by diluting standard solutions in methanol and stored at 4°C. Individual solutions of endosulfan and heptachlor (20  $\mu$ g/L) were prepared by diluting the stock solution with DI water. For degradation and kinetic experiments, 2.5 and 1 g of iron turning waste were added to different Erlenmeyer flasks. Each flask contained the pesticide solution (200 mL) and was shaken at 400 rpm using an orbital shaker at room temperature (24°C). A sample of 50 mL was collected from different flasks corresponding to different time points as follows: 0, 2, 4, 6, 8 and 10 min. Iron turning of 0.25 - 5 g was used to study the effect of its dosage on pesticide removal at a single time point, t = 10 min, after which the pesticide removal remained relatively constant.

Individual stock solutions (1 g/L) of sodium, calcium, magnesium, potassium, and nitrate were prepared in DI water by adding their respective chloride salts, and sodium nitrate. Further dilution was made with DI water to obtain the desired concentrations. To investigate the effects of minerals in groundwater (Na = 250 mg/L, Ca = 150 mg/L, Mg = 60 mg/L, K = 60 mg/L and  $NO_3^- = 40$  mg/L), initial pesticide concentration (1 - 20 µg/L) and pH (4, 7 and 10) on pesticide removal, 2.5 g of iron turning was used in the same manner as sorbent dosage experiment, and a single sample was collected at 10 min.

To investigate the degradation mechanism, 10-25 g of iron turning were added to an Erlenmeyer flask containing endosulfan and heptachlor solution (2-5 mg/L, 200 mL) and stirred for 24-96 h. The solution pH for both pesticides was 5.65-5.8. Samples of 40-50 mL were taken

at t = 24, 48, 72 and 96 h. All collected samples were stored at 4°C, and within 24 h extracted and analyzed for the pesticides using GC-MSD or ECD. All batch experiments were conducted in triplicate except the degradation mechanism which was performed in duplicate.

## *4.2.2.2. Column study*

To find the most suitable order and composition of filtration media to treat a mixture of both pesticides in water as they normally coexist in contaminated water especially in developing countries, four gravity-flow glass columns (L×  $I.D \times O.D$ : 81 cm × 40 mm × 45 mm) with different filter media layer configurations were set up and loosely packed with: (1) only sand, (2) only iron turning, (3) sand + iron turning and (4) sand + iron turning + sand. For the first and second filtration columns, 200 g of sand and 125 g of iron turning were used, respectively. The third and fourth filtration columns had 200 g of sand (each layer) and 125 g of iron turning in separate layers. The water flow rate for each column was 10 mL/min. Slow water flow rates (1-6 mL/min) are suggested for pesticide removal to allow physical and chemical interactions between contaminant and the filter media (Memon et al., 2014; Phu, 2016).

To investigate the effect of media dosage, three glass columns were set up with different iron turning dosages (100, 125 and 150 g) while the amount of sand remained constant (200 g for each layer). The reason of not choosing less than 100 g of iron turning was to meet the drinking water standards for both pesticides and the range of iron dosage was based on preliminary performance data. To study the effect of EBCT, three glass columns with different water flow rates were applied, 5, 10, and 15 mL/min and the corresponding EBCTs were 1.6, 0.8 and 0.5 h, respectively.

To determine the service period of filter media, a breakthrough experiment was conducted using the same glass column as described above and a water flow rate of 5 mL/min.

For all column experiments, the influent concentration for both pesticides was  $2 \mu g/L$ , which is 10 times higher than the USEPA drinking water standards (USEPA, 2018). For all filtration experiments except the service period of filter media, treated water samples were collected at t = 0, 10, 20, 30, 40, 50 and 60 min for pesticide analysis. The filter media configuration within the columns was sand + iron turning + sand unless mentioned. All the column experiments were performed under gravity flow at room temperature (24°C) and water flow rate was maintained by sustaining a constant water level over the filtration media. All filtration experiments were performed in triplicate except the breakthrough experiment which was conducted in duplicate.

## **4.2.3.** Analytical Procedure

For all experiments except the degradation mechanism, both pesticides were extracted using a liquid-liquid micro extraction method (Munch, 1995). To detect the degradation byproducts qualitatively, SPME and liquid-liquid micro extraction techniques were used. GC-ECD and GC-MSD were used for quantitative and qualitative analysis, respectively. The details of analytical procedure are in Chapter 3 (Subsection 3.2.3). The calibration curves for both pesticides (data not shown) fit very well with the data ( $R^2 = 0.998$ -0.999). Although the described analytical method can detect both pesticides below 0.05 µg/L (Munch, 1995), the detection limit in this study was 0.1 µg/L. The recovery and relative standard deviation were 93.67% and 17.44% for endosulfan and 111.34% and 26.09% for heptachlor, respectively.

For all experiments, pH of water contaminated with both pesticides was measured before and after treatment with iron turning waste, whereas ORP was measured only for the degradation mechanism experiment. The iron content in treated water by the iron turning waste filter column was measured using Ferrozine reagent. Twenty five mL of treated water sample was collected and one pillow of Ferrozine reagent (Hach, USA) was added to it. The obtained solution was

hand shaken for 30 seconds and kept idle for another 5 min for completion of reaction. After that, 10 mL of the sample was transferred to a cuvette and measured for iron content spectrophotometrically at a wavelength of 562 nm (DR 5000 Hach UV-Vis spectrophotometer, USA).

#### 4.2.4. Statistical Analysis

One-way ANOVA test was performed using Minitab software (version 18.1, 2017) with the posthoc Tukey Test to compare removal efficiencies for heptachlor and endosulfan within each variable (sorbent dosage, initial pH, initial pesticide concentration, individual and all minerals, order of media and water flow rate/EBCT).

## 4.3. Results and Discussion

## 4.3.1. Surface Morphology and Elemental Compositions of Iron Turning Waste and Sand

The surface morphology of iron turning waste and sand is shown in Figure 11. There were few protuberances on the surface of iron turning (Figure 11a), which could be due to mechanical abrasion. Silica and carbon are naturally present in iron ores as impurities and these two elements were detected by the EDS analysis of iron turning. In the case of sand, the surface was rather smooth (Figure 11b) and silicon and oxygen were the main elements along with some impurities such as carbon, aluminum, iron, and minerals as shown in Table 7 (Chapter 3).



Figure 11. Surface morphology of (a) iron turning waste and (b) sand.

XRD spectra of the virgin and exhausted iron turning are shown in Figure 12. In the case of virgin iron turning, the broad peak at the  $2\theta$  of  $44.9^{\circ}$  indicates the presence of Fe<sup>0</sup> crystalline phase (Sun et al., 2006). There was no broad peak of Fe<sup>0</sup> detected in the case of exhausted iron but the presence of magnetite (Fe<sub>3</sub>O<sub>4</sub>) around 36.0° was observed. Also, during the reaction of iron turning with both pesticides in water (t = 48-96 h), a black color was formed in the solution suggesting the presence of Fe<sub>3</sub>O<sub>4</sub>, and agreeing with XRD results and literature (Abbas et al., 2013; Dai et al., 2016). The peaks around 63° indicate the presence of FeOOH (Dai et al., 2016). FeOOH is formed as result of surface hydroxylation of iron in aqueous solution (Sun et al., 2006).



Figure 12. XRD analysis results of iron turning waste before and after reactions with heptachlor and endosulfan.

Figure 13 shows that XPS analysis of iron turning waste before and after its reaction with both pesticides. In the case of virgin iron turning waste, two main photoelectron peaks at 706.4 eV and 711.0 eV represent the binding energies of Fe<sup>0</sup> and Fe<sup>3+</sup>. These two peaks were also observed during the characterization of fresh nZVI in a previous study (Sun et al., 2006). After reactions with both pesticides, the peak representing Fe<sup>0</sup> was not observed. It is evident that iron is mainly present in the form of Fe<sup>2+</sup> (709.2 eV) and Fe<sup>3+</sup> (711.2 eV) after its reaction with endosulfan. Similar to the case of heptachlor, the analysis of iron turning after reacting with heptachlor shows two photoelectron peaks observed at 709.0 eV and 711.1 eV corresponding to Fe<sup>2+</sup> and Fe<sup>3+</sup>.



Figure 13. XPS analysis results of iron turning waste before and after reactions with heptachlor and endosulfan.

## 4.3.2. Endosulfan and Heptachlor Degradation and Removal Kinetics

Reaction between heptachlor and iron turning was fast compared to endosulfan; more than 90% and 51% of heptachlor and endosulfan removal were achieved within 2 min using 2.5 g of iron turning (Figure 14). After 10 min of reaction, the removal efficiencies for heptachlor and endosulfan were 96% and 85%, respectively. ANOVA indicates that reaction time (2 – 10 min) had significant effect (p = 0.024 for heptachlor, p = 0.00003 for endosulfan) on pesticide removal. When 1 g of iron turning was used, at t = 10 min, the removal efficiency of endosulfan decreased to 80% while heptachlor removal remained the same (96%).



Figure 14. Degradation/removal of heptachlor and endosulfan from water using iron turning waste.

The degradation/removal data for both pesticides fit well with the pseudo-second order model ( $R^2 \ge 0.98-0.99$ ) as shown in Figure 15. The heptachlor degradation rate constants (k) were 0.26 g/µg.min and 0.65 g/µg.min using 1 and 2.5 g of iron turning, respectively. When the amount of iron turning was increased from 1 to 2.5 g, the endosulfan degradation rate constant increased 1.37-fold from 0.30 g/µg.min to 0.71 g/µg.min. The pH of heptachlor and endosulfan solution increased after 10 min of reaction from 6.10 and 6.25 to 6.75 and 6.81, respectively. Lama et al. (2013) reported that the solution pH increased to 9 (initial solution pH was not reported) after 60 h of reaction, when 5 g of high carbon iron filings were used to degrade endosulfan in 20 mL of water. Mukherjee et al. (2015) also reported that the initial pH of heptachlor solution increased from 6.57 to 9.46 within 30 min after 50 g/L of ZVI were applied.  $OH^{-}$  ions, which were released to the solution during the chemical reaction (hydrolysis) between  $Fe^{0}$  and water, are responsible for this change.



Figure 15. Degradation kinetics of pesticides using iron turning waste: (a) heptachlor and (b) endosulfan.

#### **4.3.3.** Effects of Media Dosage and Initial Pesticide Concentration

Figure 16a shows that the removal efficiency of heptachlor increased from 84% to 96%, with increasing iron dosage from 0.25 to 1 g. Further increase in iron dosage (1 to 5 g) offered no removal improvement. On the other hand, the endosulfan removal increased significantly from 50% to 85%, when the amount of iron increased from 0.25 to 2.5 g. This is due to increase in the active surface area with increasing amount of sorbent. Endosulfan removal efficiency only increased to 89%, when 5 g of iron turning was used. Therefore, other batch experiments for both pesticides were conducted with 2.5 g of iron turning. For both pesticides, ANOVA shows that the removal efficiencies were significantly different using different iron dosages (p = 0.042 for endosulfan and p = 0.016 for heptachlor).

Figure 16b shows the effect of initial pesticide concentration on the removal of both pesticides. The removal efficiency of heptachlor increased from 87% to 96%, whereas the endosulfan removal increased minimally (<1%) with increasing initial pesticide concentration (10 to 20  $\mu$ g/L). A similar observation was documented, when activated carbon was used to remove heptachlor in water (Seyhi et al., 2014). Shah et al. (2013) explored the efficacy of ultraviolet based oxidation processes and found that degradation rate of endosulfan increased from 0.02 to 0.05  $\mu$ M/min with increasing initial concentration (0.86 to 3.7  $\mu$ M).

In this study, at low initial pesticide concentration  $(1 \ \mu g/L)$  the removal efficiencies of heptachlor and endosulfan decreased significantly to 56% and 46%, respectively. The differences in removal efficiencies of both pesticides were significant (p = 0.0002 for endosulfan, p =0.00002 for heptachlor) at different initial pesticide concentrations. A possible explanation is that when the initial concentrations of endosulfan and heptachlor were high, the numbers pesticide molecules exposed/available to reactive site of iron turning increased correspondingly, leading to

better removal. At lower initial pesticide concentrations, more reaction time may be required to achieve better removal. Mishra and Patel (2008) found that endosulfan removal decreased from 94% to 84% with the decrease of initial concentration (2 to 0.5 mg/L), when sal wood charcoal was used as an adsorbent. The mechanism of endosulfan removal was not reported.



Figure 16. (a) Effects of media dosage, and (b) initial pesticide concentration on endosulfan and heptachlor removal.

## 4.3.4. Effects of Minerals and Water pH on Pesticide Removal

Minerals in water might precipitate on the iron surface, which could result in lower pesticide removal because of less interaction between iron turning and pesticides. Therefore, it is vital to investigate the effect of individual and all typically found minerals on the removal of both pesticides using iron turning waste. Figure 17a shows that individual and all minerals in water had minimal effect ( $\leq$ 5%) on endosulfan and heptachlor removal except the presence of Ca and K, which decreased the heptachlor removal from 97% to 89% and 86%, respectively. ANOVA also shows that minerals in water had no significant effect on the removal of both pesticides (*p* = 0.537 for endosulfan, 0.593 for heptachlor). It is well known that water pH plays a crucial role during the reductive dehalogenation of organic contaminants, when zerovalent iron is used (Eykholt and Davenport, 1998; Ghauch et al., 1999). Figure 17b shows the effect of initial water pH ranging from 4 to 10 on the removal of both pesticides. In acidic water (pH 4), the removal efficiency of heptachlor increased up to 3% compared to basic environment (pH 10). At pH 4 and 7, the removal efficiencies of heptachlor were comparable (96%). Seyhi et al. (2014) evaluated the adsorption capacity of heptachlor using AC at different water pH. Their findings suggested that the removal efficiencies in acidic (pH 4) and neutral conditions were similar (97-98%); however, the efficiency decreased to 84% under a basic condition (pH 10).

As shown in Figure 17b, iron turning waste removed endosulfan more efficiently (82%) at pH 4 compared to neutral pH (74%). Similar observations were reported in previous studies, when Fe<sup>0</sup> reduced nitrobenzene more efficiently at low pH (3-5) compared to high pH (7-10) (Dong et al., 2010; Yin et al., 2012). Low pH restricts the formation of rust on iron surface resulting in more availability of its active sites to the contaminant (Dong et al., 2010; Shih and Tai, 2010). Under basic conditions, the formation and accumulation of hydroxide layer on iron surface increased and thus resulted in less reactivity of Fe<sup>0</sup> (Shih and Tai, 2010). However, Figure 17b shows that the removal efficiency of endosulfan was higher (95%) in alkaline pH (pH 10) compared to acidic and neutral pH. This is because endosulfan remains stable in acidic water, whereas it undergoes chemical hydrolysis in alkaline water (Peterson and Batley, 1993). Shivaramaiah et al. (2005) incubated endosulfan in river water at pH 8.3, and observed disappearance of endosulfan and formation of endosulfan diol due to alkaline pH. Therefore, the increase in endosulfan removal in this study under alkaline conditions compared to acidic environment was due to the involvement of both chemical hydrolysis and reductive

dehalogenation. The effect of initial water pH on the removal of both pesticides was significant (p = 0.001 for heptachlor and p = 0.0004 for endosulfan).



Figure 17. (a) Effects of minerals, and (b) water pH on endosulfan and heptachlor removal.

It is important to note that the effects of individual and all minerals on the removal of both pesticides were studied at only one pH (pH = 6.10 - 6.25), heptachlor removal efficiency is expected to increase in the presence of mineral(s) at pH lower than the tested pH because conditions inhibit the formation of rust on iron surface resulting in more iron surface for reductive reaction (Dong et al., 2010; Shih and Tai, 2010). Endosulfan removal should improve in the presence of all minerals at pH higher than the tested pH due to the involvement of both reductive dehalogenation and hydrolysis. In other words, pH rather than the presence of mineral(s) is more critical to the removal of heptachlor and endosulfan. Future work to verify this presumption is recommended.

## **4.3.5.** Continuous Filtration

Minerals and inorganic elements in groundwater precipitate and coat iron surface which can inhibit the electron transfer by masking the reactive sites of iron where electron transfer occurs resulting in a decreased reactivity of Fe<sup>0</sup> (Indelicato, 1998). To address this issue, sand, a conventional water filtration medium was used in combination with iron turning waste to treat heptachlor and endosulfan in water effectively. During water filtration, oxic environment can quickly oxidize the iron media. The presence of sand in a filtration column would limit its exposure to oxygen resulting in longevity and better performance of a filter. The escape of iron turning waste and/or high levels of iron content in the product water makes it unpleasant to drink. Adding another layer of sand below the iron media in a filter would prevent this issue. Removal of heptachlor and endosulfan using sand media alone was also investigated.

## 4.3.5.1. Effect of order of media

Sand filtration was not effective for removal of heptachlor in water as shown in Figure 18a. The removal capacity of endosulfan was better (83-85%) than heptachlor (55-57%) during 60 min of filtration. However, the concentrations of both pesticides in the product water were above the drinking water standards. The initial pesticide removal could be due to adsorption on organic matter and/or reaction with metals such as aluminum and iron, which were present in sand as impurities. Mishra and Patel (2008) compared the removal efficiency of endosulfan in

water using sand and different adsorbents. Their findings suggest that the initial removal of endosulfan (90%) in water using sand media was due to more affinity towards sand particles which exhausted quickly.

When only iron turning was used as filtration media, endosulfan removal increased to 90-92%, whereas complete removal (100%) of heptachlor were achieved as shown in Figure 18b, and the product water met drinking water standards for both pesticides. Figure 18c shows that endosulfan removal slightly increased (94%), whereas the removal of heptachlor remained unchanged (100%), when sand + iron turning waste was used as filtration media. Adding another layer of sand below iron turning layer in a filtration column (sand + iron turning waste + sand) resulted in no change in the removal of both pesticides (Figure 18d). However, this configuration (sand + iron turning waste + sand) was chosen for further experiments to limit the escape of iron turning and minimize the iron content in the product water. ANOVA shows that order of media had no significant effect (p = 0.544) on endosulfan removal whereas it was the opposite for heptachlor ( $p = 0.1 \times 10^{-8}$ ).



Figure 18. Effects of order and composition of media on heptachlor and endosulfan removal: (a) sand, (b) iron turning, (c) sand + iron turning and (d) sand + iron turning + sand.

## 4.3.5.2. Effects of media dosage and EBCT

Figure 19a shows that lower endosulfan removal (84%) was achieved using 100 g of iron turning compared to 93% provided by 125 g of iron turning (Figure 18d). Further increase in iron

dosage (150 g), resulted in a slight increase in endosulfan removal (96%) as shown in Figure 19b. ANOVA also indicates that the effect of iron dosage on endosulfan removal was not significant (p = 0.485). Heptachlor removal remained unchanged (100%) regardless of the amount of iron turning used.

The effect of EBCT through the variation of water flow rate on the removal of both pesticides was evaluated. When the EBCT was 1.6 h (Figure 19c), the removal efficiencies of heptachlor and endosulfan were 100% and 93-100% within 60 min of filtration, respectively. At an EBCT of 0.8 h, endosulfan removal was 87-96%, whereas complete heptachlor removal was achieved (Figure 19d). The removal efficiencies of endosulfan and heptachlor were 86-92% and 92-100%, respectively (Figure 19e), when the EBCT was 0.5 h. Endosulfan removal at different EBCT (0.5 h, 0.8 h and 1.6 h) was not significantly different (ANOVA, p = 0.965). ANOVA analysis for heptachlor was not performed because of complete removal (100%) regardless of the iron dosage (100-150 g) and EBCT (0.5 h, 0.8 h and 1.6 h). To achieve highest possible removal of both pesticides using 150 g of iron turning, it was decided to study the service period of filter media at 1.6 h EBCT.



Figure 19. Effects of media dosage ((a) 100 g and (b) 150 g), and EBCT ((c) 1.6 h, (d) 0.8 h and (e) 0.5 h) on heptachlor and endosulfan removal.

## 4.3.5.3. Service period of filter media

Figure 20 shows that complete removal of heptachlor in DI water (100%) was achieved for 600 h of continuous filtration. In the case of endosulfan, the removal efficiency dropped from 100% to 90% after 375 h of filtration but the product water still met the drinking water standards. From 400 to 600 h, endosulfan removal slightly dropped and remained stable (87-89%); however, endosulfan concentration (0.21 - 0.25  $\mu$ g/L) in treated water was above the drinking water standards (0.2  $\mu$ g/L). The findings suggest that iron turning can efficiently remove/degrade heptachlor in water for more than three weeks whereas the filter media (iron turning) needs to be regenerated or replaced after 400 h of filtration to comply the standards for endosulfan. A separate study on iron turning regeneration by a simple biological means is being conducted. It was observed that pH of treated water was higher (8.1-8.5) than influent water (5.8-5.9). This is because Fe<sup>0</sup> hydrolyzes water and produces hydrogen and OH<sup>-</sup> ions. The OH<sup>-</sup> ions produced increased the pH. The iron content in the treated water was 0.057-0.11 mg/L, which is within the allowable limit for drinking water (secondary maximum contaminant level of 0.3 mg/L).



Figure 20. Service period of filtration media for heptachlor and endosulfan removal.

## **4.3.6.** Degradation Mechanism and Pathways

The ability of iron metal to degrade organic compounds has been widely exploited in groundwater remediation applications. Fe<sup>0</sup> and dissolved aqueous ferrous ion (Fe<sup>2+</sup>) form a redox couple with a standard reduction potential of -0.440V, making Fe<sup>0</sup> a reducing agent. Fe<sup>0</sup> can perform reductive dehalogenation of endosulfan and heptachlor in the presence of proton donor. Reduction of organic compounds by Fe<sup>0</sup> is a surface-mediated electron transfer process; the properties of surface coating will affect the reactivity of iron metal (Dong et al., 2010). Under aerobic conditions, dissolved oxygen acts as an oxidant and Fe<sup>0</sup> is rapidly oxidized to Fe<sup>2+</sup>, which can play a role in in enhancing the reduction reaction (Huang and Zhang, 2004). It has been reported that Fe<sup>2+</sup> adsorbed on the surface of iron oxides also performed reductive dehalogenation of trichloroethene (Sivavec and Horney, 1997). While under anoxic conditions, water can oxidize Fe<sup>0</sup> to Fe<sup>2+</sup> and release the hydrogen gas which can also dehalogenate organic compounds.

Figure 21 represents a model for reductive dehalogenation of endosulfan and heptachlor by iron turning waste. In the presence of  $Fe^0$ , water undergoes hydrolysis reaction and generates OH<sup>-</sup> and H<sup>+</sup> ions. Electrons donated by  $Fe^0$  and  $Fe^{2+}$  reduce the pesticides and in the case of hydrodechlorination, hydrogen replaces the liberated chloride ion (Schrick et al., 2002). The reaction between  $Fe^{3+}$ , oxygen and/or OH<sup>-</sup> might form an oxide layer (rust) on iron surface, which inhibits the interaction between pesticide and active sites ( $Fe^0$  and  $Fe^{2+}$ ) of iron.



Figure 21. Conceptual model for reductive dehalogenation of endosulfan and heptachlor by iron turning waste (Fe<sup>0</sup>).

It was observed that degradation rate and end products of both pesticides depend upon the initial pesticide concentration and amount of iron turning. When the initial concentration and media (iron turning waste) dosage were 5 mg/L and 10-15 g respectively, in the case of endosulfan, peaks of endosulfan diol, endosulfan lactone, and 4,5,7-trichloro-2-methyl-2,3-dihydro-1-benzofuran were detected. It is known that iron reacts with water and increases the water pH, and under alkaline conditions (>7.5) endosulfan undergoes hydrolysis reaction (Singh and Bose, 2017), which might play a role in the degradation of endosulfan into endosulfan diol and endosulfan lactone. Therefore, both hydrolysis and reductive dechlorination reactions were involved in the degradation of endosulfan using iron turning waste.

A large peak of 2,4-di-*tert*-butylphenol was detected as a major final degradation product of endosulfan as shown in Figure 22a. Heptachlor was first degraded to chlordane and 1hydroxychlordene, and then 1,2,3,3a,4,6a-hexahydro-2,5,6,7,8-pentachloro-1,4-ethenopentalene, whereas 2,4-di-*tert*-butylphenol was detected as a major final product (Figure 22b). When the iron dosage was increased (20-25 g) and the initial pesticide concentration was reduced (2 mg/L), the reaction between both pesticides and iron was so fast that none of the chlorinated byproducts were detected. However, a small peak of phenol was detected and major end products of endosulfan and heptachlor were different aldehydes such as nonanal, heptanal and octanal (Figure 22).



Figure 22. Proposed degradation pathways of pesticides in water by using iron turning waste: (a) endosulfan and (b) heptachlor.

The acute oral median LD50 of endosulfan and heptachlor in rat are 18-160 mg/kg and 40-220 mg/kg of body weight respectively, whereas the LD50 values for the degradation products are 2,318 mg/kg for 2,4-di-*tert*-butylphenol, 11,000 mg/kg for nonanal and 14 g/kg for heptanal. This shows that degradation products of both heptachlor and endosulfan were much less toxic than the parent compounds.

## 4.3.7. pH, ORP and Mineralization

The pH value of both heptachlor and endosulfan solutions increased from 5.6-5.75 to 10.5 and 10.9 after 96 h of degradation. This is due to OH<sup>-</sup> release as Fe<sup>0</sup> first hydrolyzes water to produce hydrogen and hydroxide anions. The ORP values of heptachlor and endosulfan solutions decreased from 150-180 to -621 and -689 mV after 96 h of reaction with iron turning waste, which indicate that highly reducing conditions generated by iron turning waste. These ORP decreases are in accordance with previous studies (Lama et al., 2013; Mukherjee et al., 2015). The pesticide mineralization degree was not determined in this study because (1) the standard solutions of both pesticides were in methanol and/or in acetone, and further diluted with water, therefore, it is not possible to measure accurate total organic carbon of heptachlor and endosulfan before and after treatment and (2) the water solubility limits of the pesticides are lower than typical total organic carbon detection limits.

#### 4.4. Summary

This study investigated the use of iron turning waste as filter media to remove heptachlor and endosulfan in water. Batch studies showed that it efficiently removed both pesticides in water even when the contamination level was 100 times higher than the USEPA drinking water standards. Endosulfan removal increased in alkaline conditions due to involvement of both hydrolysis and dechlorination reactions, whereas acidic conditions favored heptachlor removal.

Both pesticides undergo reductive dechlorination followed by ring cleavage during their degradation using iron turning waste. Iron turning completely dechlorinated both pesticides into aldehydes which are far less toxic than the parent compounds. This study provides a waste utilization scheme as well as effective water filtration media to minimize public health concerns due to contamination of endosulfan and heptachlor in groundwater. Based on column studies, it is feasible to use iron turning waste in combination with sand as sustainable and affordable point-of-use filtration media to treat water contaminated with endosulfan and heptachlor, especially in rural areas where resources are limited.

# 5. ELUCIDATION OF DDT AND LINDANE DEGRADATION IN WATER USING IRON TURNING WASTE

### **5.1. Introduction**

Pesticide use in agricultural has become a necessity worldwide for increasing crop yields during the last thirty years (Mudhoo et al., 2019). Among commonly used pesticides, OCPs are ubiquitous pollutants because of their wide use in agriculture as well as chemical stability (El Bakouri et al., 2009). In most developing countries, most of the OCPs were banned; however, some of the OCPs are still in use in different parts of the world. For example, DDT which was banned in the past due to potential carcinogenicity, was reintroduced by the WHO to control malaria because of its effectiveness and inexpensive cost (WHO, 2011). For economic reasons, lindane, another OCP is still being used in some developing countries irrespective of severe health effects (Carvalho, 2017). Both pesticides are highly persistent in the environment; the half-life periods for lindane in soil and water are 708 and 2,292 days (Beyer and Matthies, 2001), whereas those for DDT are 2-15 years and 150 years in soil and water, respectively (Augustijn-Beckers et al., 1994; Callahan, 1979; WHO, 1989).

Surface and groundwater contaminated with both pesticides have been reported in different countries such as Greece (Golfinopoulos et al., 2003), India (Jit et al., 2011; Mutiyar et al., 2011), China (Pan et al., 2017), and Pakistan (Eqani et al., 2012; Iram et al., 2009). Lindane and DDT are endocrine disruptors and potential carcinogens compounds (Mnif et al., 2011; Snedeker, 2001), Therefore, the contamination of surface and groundwater by these pesticides impairs the water quality and restricts their use for water supply without proper treatment. According to the USEPA, the drinking water standards for both pesticides are  $0.2 \mu g/L$  (USEPA, 2018).

Several treatment methods are available to treat both pesticides in water such as adsorption on AC, membrane filtration, ozonation, and photocatalytic degradation (Chian et al., 1975; Miguel et al., 2007; Miguel et al., 2012; Pang et al., 2010; Sotelo et al., 2002). Adsorption and membrane filtration remove both pesticides through separation, and the pesticides concentrate on the surface of adsorbent and in the brine, that need additional treatment or create disposal issues. Ozonation and photocatalysis can degrade DDT and lindane; however, high costs and sophisticated operation associated with them restrict their application.

Metal nanoparticles such as nZVI have been used to treat a number of chlorinated contaminants in water at laboratory and full scales (Lei et al., 2018; Sun et al., 2019). Elliott et al. (2009) conducted batch experiments to investigate the efficacy of nZVI and mZVI for treating lindane in water at an initial concentration of 7.5 mg/L. Complete lindane removal was achieved within 24 h using 0.015 and 0.39 g/L of nZVI. However, mZVI only removed 60% of initial lindane concentration after 24 h. 3,4,5,6-Tetrachlorocyclohexene was detected and quantified as a key reaction intermediate of lindane degradation. Wang et al. (2009b) studied the rates of dechlorination of lindane by nZVI under different pH and iron doses. The initial pesticide concentration and solution volume were 24  $\mu$ M and 5 mL. The pseudo first order rate of lindane degradation increased from 0.0021 to 0.0358 min-1 with increasing nZVI dose from 5 to 20 g/L. Lindane degradation rate increased from 0.00039 to 0.0798 min-1 using 10 g/L of nZVI as the solution pH decreased from 8.30 to 4.67. Benzene and chlorobenzene were detected as major and minor degradation products of lindane.

Satapanjaru et al. (2006) compared the performance of various pretreated zerovalent iron (1 mm in size) to treat DDT in water at an initial concentration of 5 mg/L. Different types of zerovalent iron used to treat 150 mL of DDT contaminated water were: commercial iron,

preheated iron by hexane, pretreated iron by heating, and pretreated iron by HCl acid washing. DDT destruction rate using acid washed zerovalent iron was the highest (0.364 day<sup>-1</sup>) and the lowest rate was achieved using preheated zerovalent iron (0.041 day<sup>-1</sup>). The difference in DDT destruction rate could be due to different surface areas of zerovalent iron (1.2 m<sup>2</sup>/g of acid washed iron versus 0.37 m<sup>2</sup>/g of preheated iron) (Satapanajaru et al., 2006). El-Temsah et al. (2016) investigated the degradation of DDT in water using laboratory synthesized and commercial nZVI at an initial pesticide concentration of 10 mg/L. The dose of nZVI used in the pesticide solution (50 mL) was 1 g/L. DDT degradation after 24 h was higher (92%) for synthesized nZVI as compared to the commercial one (78%). It was reported that nZVI used had positive ecotoxic effect on germination of barley and root growth of flax seed, and suggested to consider both positive and negative aspects of nZVI for remediation application of persistent organochlorine pollutants (El-Temsah et al., 2016).

The previous studies on nZVI reviewed above did not address the effects of minerals in water, initial pesticide concentration, water flow rate/empty bed contact time on DDT and lindane removal. Service period of filter media and detailed degradation mechanism of the pesticides were not revealed. Moreover, the practical application of nZVI as water filtration media is not possible because of its mobility, potential toxicity, and unaffordability.

In this study, a waste from iron industry known as "iron turning waste" was experimented for treatment of lindane and DDT in water. Iron turning waste has the same valence and properties as nZVI except the size and surface area. The objectives of this study were (1) to conduct batch experiments focusing on the effects of common minerals in groundwater, initial pesticide concentration and water pH on pesticide removal by iron turning waste, and identify the degradation pathways of both pesticides (2) to investigate the best order of media in a

filtration unit and the effect of EBCT on the service period of the media. The study intended to provide simple and affordable point-of-use water filtration media for the communities dealing with DDT and lindane contaminated water and in turn reduce the associated health risks.

## 5.2. Material and Methods

## 5.2.1. Materials

Standard solutions of lindane (100-1,000 mg/L) and DDT in methanol (5,000 mg/L) were purchased from Sigma-Aldrich (St Louis, MO, USA) and VWR (Radnor, PA, USA). Analytical grade methanol, pentane, and chloride salts of sodium, magnesium, potassium, calcium, and nitrate were acquired from Sigma Aldrich (St Louis, MO, USA) and VWR (Radnor, PA, USA). A 100 µm PDMS fiber, and manual fiber support and holder for SPME were purchased from Supelco, Sigma-Aldrich. Pre-cleaned glass vials and HPLC grade water were purchased from VWR (Radnor, PA, USA). Iron turning waste was collected from a local machine shop in Lahore, Pakistan and washed with DI water. Play sand was purchased from a local hardware store (Lowe's, Fargo, ND, USA) and sieved. Sand particles retained on a 600 µm sieve were collected, washed with tap water thoroughly three times and used in the experiments without drying. Sand washing was only performed to remove organic matter from it which required relatively large amount of water, therefore, tap water was used instead of DI water. HPLC grade water or reverse osmosis DI water was used throughout this research.

## 5.2.1.1. Material characterizations

XRD was employed to characterize iron turning waste (0.1 - 0.15 cm in size) before and after its reactions with both pesticides using the procedure mentioned in Chapter 4 (section 4.2.1.1).

#### **5.2.2. Sample Preparations**

## 5.2.2.1. Batch study

Individual stock solutions of lindane (100 mg/L) and DDT (250 mg/L) were prepared by diluting the standard solutions in methanol and stored at 4°C. Individual solutions of lindane and DDT (20  $\mu$ g/L) were prepared by diluting the stock solution with DI water. For degradation and kinetic experiments, 2.5 and 1 g of iron turning waste were added to different Erlenmeyer flasks. Each flask contained the pesticide solution (200 mL) and was shaken at 400 rpm using an orbital shaker at room temperature (24°C). A sample of 50 mL was collected from different flasks corresponding to different time points as follows: 0, 2, 4, 6, 8 and 10 min. Iron turning of 1 - 5 g was used to study the effect of its dosage on pesticide removal at a single time point, t = 10 min, after which the pesticide removal remained relatively constant.

Individual stock solutions (1 g/L) of sodium, calcium, magnesium, potassium, and nitrate were prepared in DI water by adding their respective chloride salts, and sodium nitrate. Further dilution was made with DI water to obtain the desired concentrations. To investigate the effects of minerals in groundwater (Na = 250 mg/L, Ca = 150 mg/L, Mg = 60 mg/L, K = 60 mg/L and  $NO_3^- = 40$  mg/L), initial pesticide concentration (1 - 20 µg/L) and pH (4, 7 and 10) on pesticide removal, 2.5 g of iron turning was used in the same manner as the sorbent dosage experiment described above, and a single sample was collected at 10 min for pesticide analysis.

To investigate the degradation mechanism, 10-25 g of iron turning were added to a Erlenmeyer flask containing lindane or DDT solution (2-5 mg/L, 200 mL) and stirred for 24-96 h. The solution pH for both pesticides was 5.75-6.5. Samples of 40-50 mL were taken at t = 24, 48, 72 and 96 h. All collected samples were stored at 4°C, and within 24 h extracted and analyzed for the pesticides using gas chromatograph GC-MSD or ECD. All batch experiments

were conducted in triplicate except the degradation mechanism experiment which was performed in duplicate.

### 5.2.2.2. Column study

To find the most suitable order and composition of filtration media to treat a mixture of both pesticides in water as they normally coexist in contaminated water, four gravity-flow glass columns (L× I.D × O.D: 81 cm × 40 mm × 45 mm) with different filter media layer configurations were set up and loosely packed with: (1) only sand, (2) only iron turning, (3) sand + iron turning and (4) sand + iron turning + sand. For the first and second filtration columns, 200 g of sand and 125 g of iron turning were used, respectively. The third and fourth filtration columns had 200 g of sand (each layer) and 125 g of iron turning in separate layers. The water flow rate for each column was 10 mL/min. Slow water flow rates (1-6 mL/min) are suggested for pesticide removal to allow physical and chemical interactions between contaminant and the filter media (Memon et al., 2014; Phu, 2016).

To investigate the effect of media dosage, three glass columns were set up according to configuration # 4 (sand + iron turning + sand) with different iron turning dosages (100, 125 and 150 g) while the amount of sand remained constant (200 g for each layer). The reason of not choosing less than 100 g of iron turning was to meet the drinking water standards for both pesticides and the range of iron dosage was based on preliminary performance data. To study the effect of EBCT, three glass columns with different water flow rates were applied, 5, 10, and 15 mL/min and the corresponding EBCTs were 1.6, 0.8 and 0.5 h, respectively.

To determine the service period of filter media, a breakthrough experiment was conducted using the same glass column as described above and a water flow rate of 5 mL/min. For all column experiments, the influent concentration for both pesticides was  $2 \mu g/L$ , which is

10 times higher than the USEPA drinking water standards (USEPA, 2018). For all filtration experiments except the service period of filter media, treated water samples were collected at t =0, 10, 20, 30, 40, 50 and 60 min for pesticide analysis. The filter media configuration within the columns was sand + iron turning + sand unless mentioned. All the column experiments were performed under gravity flow at room temperature (24°C) and water flow rate was maintained by sustaining a constant water level over the filtration media. All filtration experiments were performed in triplicate except the breakthrough experiment which was conducted in duplicate.

## **5.2.3.** Analytical Procedure

For all experiments except the degradation mechanism, both pesticides were extracted using a liquid-liquid micro extraction method (Munch, 1995). To detect the degradation by-products qualitatively, SPME and liquid-liquid micro extraction techniques were used. GC-ECD and GC-MSD were used for quantitative and qualitative analysis, respectively. The details of analytical procedure are in Chapter 3 (Subsection 3.2.3). The calibration curves for both pesticides (data not shown) fit very well with the data ( $R^2 = 0.97$ -0.99). Although the described analytical method can detect both pesticides below 0.05 µg/L (Munch, 1995), the detection limit in this study was 0.1 µg/L.

For all experiments, pH of water contaminated with both pesticides was measured before and after treatment with iron turning waste, whereas ORP was measured only for the degradation mechanism experiment. The iron content in treated water by the iron turning waste filter column was measured using Ferrozine reagent as mentioned in Chapter 4 (Subsection 4.2.3).

## **5.2.4. Statistical Analysis**

One-way ANOVA test was performed using Minitab software (version 18.1, 2017) with the posthoc Tukey Test to compare removal efficiencies for lindane and DDT within each
variable (sorbent dosage, initial pH, initial pesticide concentration, individual and all minerals, order of media and water flow rate/EBCT). A significance criterion ( $\alpha$ ) was 0.05.

# 5.3. Results and Discussion

# 5.3.1. Iron Turning Waste Characteristics

XRD spectra of the virgin and exhausted iron turning are shown in Figure 23. In the case of virgin iron turning, the broad peak at the  $2\theta$  of  $44.9^{\circ}$  indicates the presence of Fe<sup>0</sup> crystalline phase (Sun et al., 2006). There was no broad peak of Fe<sup>0</sup> detected in the case of exhausted iron but the presence of Fe<sub>3</sub>O<sub>4</sub> around 36.0° was observed. The peaks around 63° indicate the presence of FeOOH (Dai et al., 2016). FeOOH is formed as result of surface hydroxylation of iron in aqueous solution (Sun et al., 2006).



Figure 23. XRD analysis results of iron turning waste before and after reactions with lindane and DDT.

#### 5.3.2. DDT and Lindane Degradation and Removal Kinetics

Iron turning waste removed DDT faster than lindane; 60% and 33% of DDT and lindane removal were achieved within 2 min using 2.5 g of iron turning (Figure 24). After 10 min of reaction, DDT removal increased to 90%, whereas 43% of lindane removal was achieved. ANOVA indicates that reaction time (2-10 min) had no significant effect (p = 0.883 for lindane, p = 0.373 for DDT) on pesticide removal. When 1 g of iron turning waste was used, at t = 10 min, the removal efficiencies of DDT and lindane slightly decreased to 86% and 41%, respectively. Elliott et al. (2009) studied the removal of lindane in aqueous solution at an initial concentration of 7.5 mg/L using different amounts of nZVI. The nZVI dose (0.10 and 0.39 g/L) only affected lindane removal in the initial 10 h of experiment; lindane removal efficiencies provided by the two doses of nZVI (0.10 versus 0.39 g/L) were comparable (more than 95%) after 24 h of reaction.



Figure 24. Degradation/removal of lindane and DDT from water using iron turning waste.

Lindane and DDT degradation/removal data agreed with the pseudo-second order model  $(R^2 \ge 0.93)$  as shown in Figure 25.



Figure 25. Degradation kinetics of pesticides using iron turning waste: (a) lindane and (b) DDT.

Lindane degradation rate constants (k) were 0.62 and 1.32 g/µg.min using 1 and 2.5 g of iron turning, respectively. In the case of DDT, its removal rate increased 142% from 0.26 to 0.63 g/µg.min, when the amount of iron turning was increased from 1 to 2.5 g. After 10 min of reaction, pH of DDT and lindane solution(s) increased from 5.41 and 6.5 to 6.40 and 6.76, respectively. Elliott et al. (2009) reported that the pH of pesticide solution increased from 5.07 to 7.97 after 22-24 h of reaction, when 0.1 g/L of nZVI was used to degrade 0.026 mM of lindane. El-Temsah et al. (2016) also documented that the pH of DDT contaminated water (10 mg/L in 50 mL) increased from 7.0 to 7.8 after 24 h of its reaction with 1 g/L of nZVI. This is due to OH<sup>-</sup> release during the chemical reaction as Fe<sup>0</sup> first hydrolyzes water to produce hydrogen and hydroxide ions.

#### 5.3.3. Effects of Media Dosage and Initial Pesticide Concentration

The removal efficiencies of DDT and lindane increased from 86% and 41% to 91% and 43% respectively, with increasing iron dose from 1 to 2.5 g, respectively (Figure 26a). Further increase in iron dose (to 3.75 and 5 g) resulted in no improvement for DDT removal. In the case of lindane, its removal efficiency increased to 52%, when 5 g of iron turning was used. Dominguez et al. (2016) studied the degradation of lindane in aqueous solution using zerovalent iron microparticles (ZVIM). Their findings suggested that lindane removal increased from 45% to 100%, when the dose of ZVIM was increased from 1 to 10 g/L. As there was a slight improvement (<10%) only for lindane removal using 5 g of iron turning. For both pesticides, ANOVA shows that the removal efficiencies were not significantly different using different iron dosages (p = 0.258 for lindane and p = 0.618 for DDT).

Figure 26b shows that DDT removal increased significantly from 37% to 79%, with increasing initial pesticide concentration from 1 to 10  $\mu$ g/L, respectively. Further increase in initial pesticide concentration (20  $\mu$ g/L) offered more improvement in DDT removal (91%).



Figure 26. (a) Effects of media dosage, and (b) initial pesticide concentration on lindane and DDT removal.

For sparingly soluble compounds, their removal increases as the concentration of contaminant increases in solution (Park et al., 2005). DDT degradation with Fe<sup>0</sup> is a surface mediate reaction that requires close contact between iron surface and DDT (Satapanajaru et al., 2006). Therefore, the number of DDT molecules available to iron surface increased correspondingly with increasing initial pesticide concentration, resulted in better removal. The differences in removal efficiencies of DDT were significant (p = 0.0004) at different initial pesticide concentrations. On the other hand, lindane removal decreased from 60% to 43%, when the initial concentration increased from 1 to 20 µg/L. Dominguez et al. (2016) reported that same lindane removal was achieved independent of its initial concentration (0.5, 3 and 6 mg/L) after more than 95 h of reaction with ZVIM. ANOVA indicates that the effect of initial pesticide

concentration on lindane removal was not significant (p = 0.506). A possible explanation for less lindane removal at higher initial pesticide concentration could be due to less active sites of iron turning waste available for lindane molecules during 10 min of reaction.

# 5.3.4. Effects of Minerals and Water pH on Pesticide Removal

Minerals in water might precipitate on the iron surface and limit interaction between pesticide molecules and iron turning. Therefore, it is important to investigate the effect of individual and all typically found minerals in water on pesticide removal. Figure 27a shows that individual minerals either favored or had minimal effect on DDT removal. However, the removal efficiencies of DDT were 86% in the presence of all minerals versus 91% without minerals. The removal efficiencies of lindane were higher (45-68%) in the presence of calcium, potassium, and sodium than without minerals (43%). The presence of nitrate and magnesium lowered its removal to 30% and 35%, respectively. Lindane removal decreased to 38% in the presence of all minerals. This could be due to nitrate present in combined minerals which also undergoes reductive reaction with iron surface (Liu and Wang, 2019). ANOVA shows that minerals in water had significant effect on the removal of both pesticides (p = 0.0002 for lindane, 0.022 for DDT).

Figure 27b shows the effect of initial water pH on the removal of both pesticides. The removal efficiency of lindane increased from 34% to 51%, when the initial pH decreased from 10 to 4. Lindane removal was 37% under neutral conditions. Wang et al. (2009b) studied the effect of solution pH on lindane removal using nZVI; the removal rate constant (0.0798 min<sup>-1</sup>) under acidic conditions (pH 4.67) were higher than basic conditions (0.00039 min<sup>-1</sup> at pH 8.3). Similar to lindane, the removal efficiency of DDT was better (96%) in acidic environment as compared to basic conditions (89%) as shown in Figure 27b. At pH 4 and 7, the removal

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efficiencies of DDT were comparable (95-96%). Satapanajaru et al. (2006) reported that DDT degradation rate increased more than 20% by lowering the solution pH from 9 to 3.





During dechlorination of organic contaminants using Fe<sup>0</sup>, proton and electron transfer play a vital role (Wang et al., 2009b). Acidic conditions favor high activities of both proton and electron transfer and thus accelerate the dechlorination reaction (Wang et al., 2009b). In aqueous environment, Fe<sup>0</sup> is transformed to iron containing oxides and hydroxides which form a passive layer on iron surface. Low water pH restricts and/or removes the passive layer (iron oxides) from iron core resulting in more availability of its active sites to the contaminant (Dong et al., 2010; Shih and Tai, 2010), and hence increases the contaminant removal (Satapanajaru et al., 2006). Under basic conditions, the formation and accumulation of hydroxide layer on iron surface increased and thus resulted in less reactivity of Fe<sup>0</sup> (Shih and Tai, 2010). The effect of initial water pH on the removal of both pesticides was significant (p = 0.047 for lindane and p =0.009 for DDT).

# **5.3.5.** Continuous Filtration

During water filtration, oxic environment can quickly oxidize iron and hence reduce the performance of filter media. The presence of sand in a filtration column would limit its exposure to oxygen resulting in longevity and better performance of a filter. The escape of iron turning waste and/or high levels of iron content in the product water makes it unpleasant to drink due to taste and color. To address these issues, sand, a conventional water filtration medium was used in combination with iron turning waste.

# 5.3.5.1. Effect of order of media

Sand filtration was not effective for removal of lindane in water as shown in Figure 28a. The removal efficiencies of lindane dropped from 32% to 0.20% within 60 min of filtration. During the first thirty min of sand filtration, DDT was completely removed, after that, its removal efficiency dropped to 73% within the next 30 min of filtration.

The initial pesticide removal could be due to adsorption on organic matter and/or reaction with metals such as aluminum and iron, which were present in sand as impurities (as discussed in Chapter 3). Mishra and Patel (2008) compared the removal efficiency of endosulfan in water using sand and different adsorbents. Their findings suggest that the initial removal of endosulfan (90%) in water using sand media was due to more affinity towards sand particles which exhausted quickly. When only iron turning was used as filtration media, the removal efficiencies of lindane and DDT were 85% and 59%, and remained stable during 60 min of filtration (Figure 28b). Figure 28c shows that DDT removal increased (79%), whereas lindane removal decreased from 79% from 54%, when sand + iron turning waste was used as filtration media. A possible explanation of low lindane removal is that organic matter in sand might leach and masked active sites of iron surface resulting in poor interaction between lindane molecules and iron. Adding another layer of sand below iron turning layer in a filtration column (sand + iron turning waste + sand) resulted in minimal improvement of both pesticides removal (Figure 28d).



Figure 28. Effects of order and composition of media on lindane and DDT removal: (a) sand, (b) iron turning, (c) sand + iron turning and (d) sand + iron turning + sand.

The sand + iron turning waste + sand configuration was chosen for further experiments to minimize the iron content in the product water. ANOVA shows that order of media had significant effect (p = 0.0002) on lindane removal whereas it was the opposite for DDT (p = 0.561).

# 5.3.5.2. Effects of media dosage and EBCT

Figure 29a shows that lower lindane removal (48-64%) was achieved using 100 g of iron turning compared to 58-79% provided by 125 g of iron turning (Figure 28d). DDT removal remained unchanged (79%) regardless of iron turning dose (100 g versus 125 g). Further increase in iron dosage (150 g) offered better removal for DDT (90-100%) during 60 min of filtration (Figure 29b). However, there was a minimal increase for lindane removal using 150 g of iron turning. ANOVA indicates that the effect of iron dosage on the removal of both pesticides was not significant (p = 0.216 for DDT, and p = 0.725 for lindane). Therefore, the removal of both pesticides as a function of EBCT (by varying the water flow rate) was also investigated.

When the EBCT was 1.6 h (Figure 29c), the removal efficiencies of lindane and DDT, were 93% and 100%, respectively and remained stable during 60 min of filtration. Lindane removal decreased from 75% to 61% within 60 min of filtration, when the EBCT was 0.8 h (Figure 29d). The removal efficiencies of DDT were 90-100% at an EBCT of 0.8 h. Further decrease in EBCT (0.5 h), resulted in lower removal of both pesticides. The removal efficiencies of DDT and lindane were 73-90% and 58-74%, respectively as shown in Figure 29e. ANOVA analysis shows that the effect of EBCT was significant (p = 0.027) for lindane removal whereas it was the opposite for DDT (p = 0.065). Better pesticide removal was achieved at 1.6 h EBCT compared to 0.5 and 0.8 h; therefore, for further investigations on the service period of filter media, 1.6 h EBCT was applied.



Figure 29. Effects of media dosage ((a) 100 g and (b) 150 g), and EBCT ((c) 1.6 h, (d) 0.8 h and (e) 0.5 h) on lindane and DDT removal.

# 5.3.5.3. Service period of filter media

Figure 30 shows that complete removal of DDT in DI water (100%) was achieved for 600 h of continuous filtration. In the case of lindane, the removal efficiency dropped from 100% to 90% after 500 h of filtration but the product water still met the drinking water standard of 0.2  $\mu$ g/L. The findings suggest that iron turning can efficiently remove/degrade both pesticides in water for at least 25 days of continuous filtration. It was observed that pH of treated water was higher (8.1-8.5) than influent water (5.8-5.9). This is because Fe<sup>0</sup> hydrolyzes water and produces hydrogen and OH<sup>-</sup> ions. The OH<sup>-</sup> ions produced increased the pH. The iron content in the treated water was 0.057-0.11 mg/L, which is within the allowable limit for drinking water (secondary maximum contaminant level of 0.3 mg/L).



Figure 30. Service period of filtration media for lindane and DDT removal.

# **5.3.6.** Degradation Mechanism and Pathways

 $Fe^{0}$  can perform reductive dehalogenation of lindane and DDT in the presence of proton donor. Reduction of organic compounds by  $Fe^{0}$  is a surface-mediated electron transfer process; the properties of surface will affect the reactivity of iron metal (Dong et al., 2010). Under aerobic conditions, dissolved oxygen in water acts as an oxidant and  $Fe^{0}$  is rapidly oxidized to  $Fe^{2+}$ , which can play a role in enhancing the reduction reaction (Huang and Zhang, 2004). Under anoxic conditions,  $Fe^{0}$  reacts with water and produces  $Fe^{2+}$  and releases hydrogen gas which can contribute to the dehalogenation of chlorinated organic compounds (Adeleye et al., 2013).

Figure 31 shows degradation mechanism of both pesticides based on detected dechlorinated by-products. Lindane was dechlorinated to 1,3,4,5,6-pentachloro-1-cyclohexane, 3,4,5,6-tetrachloro-1-cyclohexene, and chlorobenzene within 26 h. Afterwards, it was degraded to benzene in 41 h. 1-hexanol, 2-ethyl was detected as a result of ring cleavage. Chlorobenzene and benzene were also identified as two final degradation products of lindane using nZVI (Wang et al., 2009b). Lindane likely underwent dichloroelimination to form tetrachlorocyclohexene, followed by dichloroelimination to dichlorocyclohexadiene, which could be further degraded to benzene via dichloroelimination (Wang et al., 2009b).

Reaction between DDT and iron turning was fast, and 2,4-di-*tert*-butyl phenol was detected as a major degradation product after 26 h, whereas small peaks of different chlorinated compounds were detected such as dicofol, DDD, 1-chloro-2,2-bis(p-chlorophenyl)ethane, 1- chloro-4-[1-(4-chlorophenyl)ethyl]benzene, and 4,4'-dichloro- $\alpha$ -methylbenzhydrol. DDD was also reported as a product of DDT degradation by zerovalent iron (Sayles et al., 1997).



Figure 31. Proposed degradation pathways of pesticides in water using iron turning waste: (a) lindane and (b) DDT.

The oral LD50 of lindane and DDT in rat are 88-270 mg/kg and 113-800 mg/kg of body weight respectively, whereas the LD50 values for the degradation products are 930 mg/kg for benzene and 2053 mg/kg for 2-ethyl-1-hexanol, and 2,318 mg/kg for 2,4-di-*tert*-butylphenol. This shows that degradation products of both lindane and DDT were much less toxic than the parent compounds.

#### 5.3.7. pH and ORP Measurement

The pH value of both lindane and DDT solutions increased from 5.5-5.7 to 10.6 and 10.8 after 96 h of degradation. This is due to OH<sup>-</sup> release as Fe<sup>0</sup> first hydrolyzes water to produce hydrogen and hydroxide anions. The ORP values of lindane and DDT solutions decreased from 160-190 to -664 and -693 mV, respectively after 96 h of reaction with iron turning waste, indicating highly reducing conditions generated by iron turning waste. These ORP decreases are in accordance with previous studies (Elliott et al., 2009; Sayles et al., 1997).

#### 5.4. Summary

This study investigated the use of iron turning waste as filter media to remove/degrade lindane and DDT in water. Batch studies showed that the removal efficiencies of DDT were higher than lindane. Both lindane and DDT degradation followed pseudo-second order kinetics, and their degradation rates were  $0.75 \text{ g/}\mu\text{g.min}$  and  $0.42 \text{ g/}\mu\text{g.min}$ , respectively based on 2.5 g of iron turning. Low water pH favored the removal of both pesticides compared to neutral and basic conditions. Nitrate in water significantly lowered lindane removal. Degradation products of both pesticides were less toxic than parent compound(s). Iron turning waste filter in combination with sand media efficiently removed both pesticides for at least 25 days of continuous filtration, and the treated water met USEPA drinking water standards. This study provides a cost-effective treatment scheme for lindane and DDT contaminated water.

# 6. IRON TURNING WASTE MEDIA FOR TREATING CHLORINATED PESTICIDES IN WATER AND ITS MICROBIAL REGENERATION WITH S. ONEIDENSIS 6.1. Introduction

Pesticides use in agriculture to boost the crop production has increased substantially during last three decades (Mudhoo et al., 2019). OCPs have been used worldwide due to their low cost and broad-spectrum toxicity compared to other pesticides such as organophosphates. Although most of the OCPs are banned in developed countries, they are still being used in developing countries (Jayaraj et al., 2016). Among the OCPs in regular usage, lindane, endosulfan, aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, and hexachlorobenzene are known to be persistent (Chang, 2018). Their inability to easily break down in the environment has resulted in surface and groundwater contaminations especially in developing countries.

Surface and groundwater contaminations with OCPs have recently been reported in Asian countries and their contamination levels were higher than U.S. drinking water standards (0.2  $\mu$ g/L for most of the OCPs) (Iram et al., 2009; Mutiyar et al., 2011; Sankararamakrishnan et al., 2005; Zhou et al., 2008). For instance, surface water and groundwater of Dibrugarh and Nagaon districts of Northeast India were contaminated with lindane and DDT. The levels of lindane and DDT were more than 4  $\mu$ g/L (Mutiyar et al., 2011; Sankararamakrishnan et al., 2005). In China, the total concentration of different OCPs in Qiantang River water was 0.007–0.62  $\mu$ g/L (Zhou et al., 2008). Long-term low-dose exposure to OCPs is linked to human health effects such as immune-suppression, hormone disruption, diminished intelligence, reproductive abnormalities, and cancer (Gupta, 2004). Due to such health effects, water supply contaminated with OCPs needs proper treatment.

Several physiochemical treatment technologies such as activated carbon and membrane filtration are available to treat OCPs in water (Mudhoo et al., 2019). These technologies remove OCPs from water through separation without degrading them to less toxic compounds resulting in contaminated adsorbents and brine that need additional management and cost. nZVI has shown promising results for treatment/degradation of different organic water contaminants including OCPs (Lei et al., 2018; Pillai and Kottekottil, 2016; Sun et al., 2019). Singh and Bose (2016) studied the ability of mZVI and nZVI to degrade endosulfan in water at concentrations of 200-500  $\mu$ g/L. The surface area normalized degradation rate constant for endosulfan was 6.33 × 10<sup>-4</sup> L/h/m<sup>2</sup> and 2.58 × 10<sup>-2</sup> L/h/m<sup>2</sup> using mZVI and nZVI, respectively. Elliott et al. (2009) also found that nZVI was more efficient than mZVI for treating lindane in water at an initial concentration of 7.5 mg/L. nZVI completely removed lindane whereas only 60% lindane removal was achieved using mZVI in 24 h.

Commercial and laboratory synthesized nZVI have been used to degrade DDT in water at an initial concentration of 10 mg/L (El-Temsah et al., 2016). One g/L of laboratory synthesized nZVI degraded 92% of DDT while the efficiency of commercial nZVI was 78% after 24 h of reaction time. Mukherjee et al. (2015) conducted a batch study to degrade heptachlor in water at an initial concentration of 550  $\mu$ g/L using pure and polyacrylic acid modified mZVI. Heptachlor removal was 87% and 89% for pure and modified mZVI after 48 h of reaction.

The degradation rates of halogenated organic contaminants provided by nZVI decrease with time (Devlin et al., 1998). This is because  $Fe^0$  in nZVI is readily oxidizable to  $Fe^{2+}$  and  $Fe^{3+}$ ions during reductive dehalogenation in water (Wang et al., 2016). The formation and accumulation of oxidized layer ( $Fe^{3+}$ ) on nZVI affect the reduction by inhibiting the contact between contaminant and zerovalent iron surface (Johnson et al., 1996; Scherer et al., 1999). Several metal reducing bacteria use metals as terminal electron acceptors are capable of reducing the valence of the metals (Lovley, 1997; Dong et al., 2019). Among them, *Shewanella* has attracted a great attention for its ability to reduce several metals including  $Fe^{3+}$  to  $Fe^{2+}$  (Gerlach et al., 2000; Nealson and Scott, 2006). *Shewanella alga* BrY regenerated iron was investigated for its ability to reduce chlorinated contaminants such as trichloroethene and carbon tetrachloride (Gerlach et al., 2000; Shin et al., 2007). *S. alga* BrY regenerated iron increased the transformation of carbon tetrachloride to chloroform (Gerlach et al., 2000) whereas  $Fe^{2+}$  produced by *S. alga BrY* covered the reactive surfaces of zerovalent iron filings and inhibited the reduction of trichloroethene by zerovalent iron filings (Shin et al., 2007; Honetschlägerová., 2018). Trichloroethene is widely used in different industries; therefore, the above mentioned studies focused on groundwater remediation of trichloroethene rather than point-of-use application (Gerlach et al., 2000; Shin et al., 2007).

Recent advancements in the taxonomy and clinical microbiology show that most human infections caused by *Shewanella* genus is linked to *S. algae* (Janda and Abbott, 2014). *S. algae* causing gastroenteritis with bloody diarrhea (Dey et al., 2015; Nath et al., 2011), acute enteritis (Fernández-Fernández et al., 2018) and skin and soft tissue infections in humans (Srinivas et al., 2015) were reported. Srinivas et al. (2015) suggested that *S. algae* should be considered as an emerging pathogen of skin and soft tissues infections. Therefore, bioreduction of iron using *S. alga* is not suitable when intended for point-of-use water treatment application.

*Shewanella oneidensis* (non-pathogenic bacteria) has shown its ability to reduce iron on Fe(III) coated porous glass beads (20 mg) in minimal media (Lies et al., 2005). Iron reduction of 86.5% within the cortex of iron-beads was achieved within 3 days of anaerobic incubation (Lies et al., 2005). Most of the work on *S. oneidensis* so far focused on the microbial aspects for iron

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reduction in natural environments (Bennett et al., 2015; Bose et al., 2009; Cheng et al., 2013; Xiao et al., 2017). There has not been a single study that focuses on the bioregeneration (reduction) of iron using *S. oneidensis* for point-of-use water treatment application.

Although nZVI and mZVI have shown their potential to degrade individual OCPs in water with a focus on in-situ remediation, information on the ability of nZVI/mZVI to treat mixture of OCPs (typically detected in surface and groundwater) at different water pH and initial pesticide concentrations, and in the presence of minerals is extremely limited for point-of-use application. The above reviewed literature suggested that Fe<sup>0</sup> is mainly responsible for reductive dehalogenation of halogenated contaminants such as OCP in water and as a result is readily oxidized to Fe<sup>2+</sup> and Fe<sup>3+</sup> (Pillai and Kottekottil, 2016; Singh and Bose 2016; Elliott et al., 2009; El-Temsah et al., 2016; Mukherjee et al., 2015) resulting in shorter life of treatment media. Moreover, there has been no scientific report which indicates whether Fe<sup>2+</sup> alone contributes during dehalogenation of parent OCPs.

The intention of this study was to investigate the application of iron turning waste which has the same valence as nZVI but more affordable as point-of-use media to treat mixture of OCPs at different water pH, initial pesticide concentrations, and in the presence of minerals. For the first time, *S. oneidensis* was used to microbially regenerate  $Fe^{2+}$  from exhausted iron turning waste (Fe<sup>3+</sup>) for the treatment of OCPs. In addition, the degradation of parent OCPs using virgin iron turning, exhausted iron, and microbially regenerated iron was examined to provide insight information whether *S. oneidensis* regenerated Fe<sup>2+</sup> alone can degrade mixture of parent OCPs, if so, to what extent.

# 6.2. Materials and Methods

# 6.2.1. Materials

Standard solutions of six pesticides including lindane, heptachlor, endosulfan, endrin, dieldrin, and DDT (100-5000 mg/L) in methanol were purchased from Sigma-Aldrich (St Louis, MO, USA) and VWR (Radnor, PA, USA). Analytical grade methanol, pentane, and chloride salts of sodium, magnesium, potassium, calcium, nitrate, and sodium lactate were acquired from Sigma Aldrich (St Louis, MO, USA) and VWR (Radnor, PA, USA). Pre-cleaned glass vials and HPLC grade water were purchased from VWR (Radnor, PA, USA). Iron turning waste was collected from a local machine shop (Lahore, Pakistan) and shipped to North Dakota State University (Fargo, ND, USA) for experimentation. DI water was used to wash iron turning waste to remove any residual oil/organics (if present) on its surface. *S. oneidensis* MR-1 (ATCC 700550), gasPak EZ container and sachets, and tryptic soy broth were purchased from ATCC, USA and VWR (Radnor, PA, USA). HPLC grade water or reverse osmosis DI water was used throughout this research. Ferrozine and hydroxylamine hydrochloride were acquired from Sigma Aldrich (St Louis, MO, USA).

# 6.2.2. Characterization of Iron Turning Waste

Iron turning waste (0.1 - 0.15 cm in size) was characterized using field emission scanning electron microscopy. XRD and XPS analyses were employed to examine the oxidation state of iron turning waste before and after its reaction with OCPs. The details of sample preparations and analyses are in Chapters 3 and 4.

# **6.2.3. Experimental Procedures**

# 6.2.3.1. Degradation of mixture of OCPs using virgin iron turning

A stock solution of mixture of six pesticides (10 mg/L of each pesticide) was prepared by diluting standard solutions and stored at 4°C. A working solution of mixture of pesticides was prepared by diluting the stock solution with DI water. The concentration of each pesticide in the working solution was 20  $\mu$ g/L. For degradation and kinetic experiments, 3 and 1.5 g of iron turning waste were added to different Erlenmeyer flasks. Each flask contained the pesticide solution (200 mL) and was shaken at 400 rpm using an orbital shaker at room temperature (24-25 °C). A sample of 50 mL was collected from different flasks corresponding to different time points: 0, 2, 4, 6, 8 and 10 min. Iron turning of 0.5 – 7.5 g was used to study the effect of its dosage on pesticide removal at a single time point, t = 10 min, after which the pesticide removal remained relatively constant.

To investigate the effect of minerals in groundwater on pesticide removal, individual stock solutions (1 g/L) of sodium, calcium, magnesium, potassium, and nitrate were prepared in DI water by adding their respective chloride salts, and sodium nitrate. Individual mineral stock solutions were then added to Erlemenary flask containing pesticide solution ( $20 \mu g/L$ , 200 mL) to obtain desired mineral concentration (Na = 250 mg/L, Ca = 150 mg/L, Mg = 60 mg/L, K = 60 mg/L and NO<sub>3</sub>- = 40 mg/L) in the solution. Three grams of iron turning were added to the solution and shaken at 400 rpm and a single sample was collected at time point, t = 10 min for pesticide analysis.

To investigate the effects of initial pesticide concentration  $(1 - 20 \mu g/L)$  and pH (4, 7 and 10) on OCPs removal, 3 g of iron turning was used in the same manner as the sorbent dosage

experiment described above, and a single sample was collected at 10 min for pesticide analysis. All batch experiments were conducted in triplicate.

#### 6.2.3.2. Bioregeneration of iron turning

Freeze dried S. oneidensis MR-1 pellet was rehydrated in 1 mL tryptic soy broth and stored in 0.25 mL of glycerol solution (16%) at -80°C. Fifty µL of the glycerol solution containing S. oneidensis was then added in 10 mL of tryptic soy broth and the mixture was incubated aerobically at 30°C without shaking as recommended by the culture supplier (ATCC, USA). The incubation was for 24 h corresponding to the mid-late log phase ( $OD_{600} = 0.8$ ). After that, the culture was used for bioregeneration. For bioregeneration of iron, there were three experimental steps: (1) complete oxidation of virgin iron turning waste (to obtain exhausted iron), (2) bioregeneration of exhausted iron turning waste (to reduce  $Fe^{3+}$  using S. oneidensis and lactate as a carbon source), and (3) bioregeneration of exhausted iron using different carbon sources and possible inhibition of bioregeneration of iron by OCPs. For the first step, 2-3 g of iron turning waste was added to a 200 mL solution containing a mixture of OCPs (2 mg/L for each pesticide) and stirred for 18 h at 400 rpm. Ten mL of liquid sample containing suspended iron (0.25 g) was collected after 18 h to confirm the oxidation of  $Fe^0$  to  $Fe^{3+}$ . The ferrozine method with and without addition of hydroxylamine was used to determine Fe<sup>2+</sup> and combined Fe<sup>2+</sup> and Fe<sup>3+</sup>, respectively, in the liquid portion of the sample. For the solid portion of the sample, XRD and XPS were applied to find the oxidation state of suspended iron.

For the second step, the sample collected from step 1, was added to the prepared culture solution (~10 mL) and incubated at 130 rpm and 30°C in a gasPak container for 72 h. To achieve anaerobic environment, 7-8 gasPak sachets were placed in the gasPak container. Sodium lactate (10 mM) was used as a source of carbon for the bacterial culture (Garlech et al., 2000). This step

was conducted to measure the  $Fe^{3+}$  and  $Fe^{2+}$  concentrations before and after the incubation to confirm the ability of *S. oneidensis* to bioregenerate  $Fe^{2+}$ .

In the last step, 0.25 g of the collected exhausted iron turning was incubated with the bacterial culture in tryptic soy broth in two different carbon sources. The incubation conditions were the same as mentioned above (the second step) whereas different carbon sources were: (1) (1) lactate (10 mM), and (2) only growth media (tryptic soy broth containing dextrose (2 g/L)). For possible inhibition of bioregeneration of iron using *S. oneidensis* in the presence of OCPs, 0.25 g of collected exhausted iron turning (obtained from step 2) was incubated with the bacterial culture in the same manner as mentioned above (lactate as a carbon source (10 mM)) with 2  $\mu$ g/L of each pesticide.

Based on the performance of bioregenerated iron (obtained in Step 3) towards OCPs removal, the best carbon source was chosen for *S. oneidensis* to bioregenerate exhausted iron for at least three cycles. For this experiment, 0.25 g of exhausted iron turning was incubated with *S. oneidensis* in different centrifuge tubes using the best carbon source in the same manner as described above (Step 3) except the incubation time increased to 96 h. It was suggested that the increased incubation time resulted in more reduction of Fe(III) using *S. oneidensis* (Lies et al., 2005). After 96 h of incubation with *S. oneidensis*, 0.25 g of iron turning (after bioregeneration) was collected from each centrifuge tube to obtain a total of 0.5 g of iron turning. The ability of microbially regenerated iron (0.5 g) to degrade/remove mixture of OCPs in water during 10 min of reaction was investigated (details are in the next section). After 10 min of reaction with OCPs in water, iron turning was collected and added to another pesticide solution as mentioned in step 1 to obtain exhausted iron again for its second time bioregeneration using *S. oneidensis*. This cycle was repeated to investigate whether bioregenerated iron had the ability to degrade/remove

mixture of OCPs in water after three cycles of regeneration. For degradation time profile of OCPs in water using microbially regenerated iron, 0.25 g of iron turning (after bioregeneration) was collected from each centrifuge after 96 h of incubation with *S. oneidensis* as mentioned above to obtain a total of 1 g of iron turning (details are in the next subsection).

# 6.2.3.3. Effect of iron regeneration frequency on OCPs removal and comparison of degradation profile of OCPs using different types of iron

The microbially regenerated iron (0.25 - 0.5 g) was used to degrade a mixture of OCPs (100 mL, 20 µg/L for each pesticide) batch wise as described in section 6.2.3.1, and a single sample was collected at 10 min for pesticide analysis. To compare the ability of microbially regenerated iron for OCPs degradation/removal, virgin iron turning (0.25 - 0.5 g) was also used to degrade the mixture of OCPs (100 mL, 20 µg/L for each pesticide) in the same manner as described above. Moreover, degradation/removal time profile of the mixture of OCPs was investigated using microbially regenerated, virgin, and exhausted iron turning. For that, 1 g of iron (virgin, exhausted, and regenerated) was added to Erlemenary flask containing pesticide solution (250 mL, 20 µg/L for each pesticide) and stirred at 400 rpm for 10 min, and samples were collected at different times (t = 0, 2, 4, 6, 8 and 10 min) for pesticide analysis.

#### **6.2.4.** Analytical Procedure

For all experiments, pesticides were extracted from the samples using either a liquidliquid micro extraction or SPME method, and analyzed using a GC-ECD. The details of analytical procedures are in previous chapters (3-5). pH of water contaminated with pesticides was measured before and after treatment with iron turning waste. Dissolved Fe<sup>2+</sup> and total iron (Fe<sup>2+</sup> plus Fe<sup>3+</sup>) were measured using the ferrozine and hydroxylamine hydrochloride methods (Lovley and Phillips, 1987; Stookey, 1970). For dissolved Fe<sup>2+</sup>, one pillow of ferrozine reagent

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solution was added to 10 mL of the collected solution and hand mixed for few seconds. The obtained solution was kept for 5 min for the completion of reaction before measuring the  $Fe^{2+}$  spectrophotometrically. For total iron ( $Fe^{2+}$  plus  $Fe^{3+}$ ), 5 mL of 0.25 M hydroxylamine hydrochloride in 0.25 M HCl was added to 10 mL of the collected solution and gently mixed for 30 s for the reduction of  $Fe^{3+}$  to  $Fe^{2+}$ . One pillow of ferrozine reagent was then added to the obtained solution as discussed above for the determination of  $Fe^{2+}$ . The amount of  $Fe^{3+}$  was calculated as the difference between the  $Fe^{2+}$  measured in the hydroxylamine and ferrozine methods.

#### 6.2.5. Statistical Analysis

One-way ANOVA test with the posthoc Tukey Test was performed using Minitab software (version 18.1, 2017) to compare removal efficiencies for OCPs within each variable (sorbent dosage, initial pH, initial pesticide concentration, individual and all minerals, and microbially regenerated iron). A significance criterion ( $\alpha$ ) was 0.05.

#### **6.3. Results and Discussion**

#### 6.3.1. Characteristics of Iron Turning Waste

The surface of iron turning was smooth with some lumps (Figure 32a), which could be due to mechanical abrasion. XRD analysis of iron turning waste shows a broad peak at the  $2\theta$  of  $44.9^{\circ}$ (Figure 32b) indicating the presence of Fe<sup>0</sup> crystalline phase (Sun et al., 2006), whereas Fe<sub>3</sub>O<sub>4</sub> and FeOOH around 36.0° and 64.0° were observed in the case of exhausted iron (after 18 h of reaction with OCPs). A small peak of Fe<sub>2</sub>O<sub>3</sub> was also detected around 32.0° during the analysis of exhausted iron. For virgin iron turning, XPS spectra of Fe2p regions indicates two binding energies 706.4 and 711.0 eV which represent Fe<sup>0</sup> and Fe<sup>3+</sup> (Figure 33a). Binding energies of iron turning waste changed to  $Fe^{3+}$  (711.58 eV) and  $Fe_2O_3$  (718.78 eV) indicating the oxidation of  $Fe^0$  to  $Fe^{3+}$  after 18 h of reaction with OCPs (Figure 33b).



Figure 32. (a) Surface morphology, and (b) XRD result of virgin and exhausted iron turning waste.



Figure 33. XPS spectra of Fe2p regions of iron turning waste (a) before and (b) after its reaction with OCPs.

#### 6.3.2. Degradation of Chlorinated Pesticides by Virgin Iron Turning

Reaction between lindane and iron turning was substantially slower compared to other pesticides as shown in Figure 34. After 10 min of reaction, by using 1.5 and 3 g of iron turning, 32 and 35.7% of lindane, 89.5 and 92.3% of heptachlor, 84 and 91% of endosulfan, 79.3 and 89.6% of dieldrin, 69.2 and 84.5% of endrin, and 87.8 and 90% of DDT were removed. ANOVA indicates that reaction time had significant effect on OCPs removal (p < 0.05). The pH of pesticide solution barely increased within 10 min of reaction with 1.5 and 3 g of iron turning.



Figure 34. Degradation/removal of mixture of pesticides from water using iron turning waste (a) 3 g of iron and (b) 1.5 g of iron.

#### 6.3.3. Effects of Media Dosage and Initial OCP Concentration

The effect of iron dosage on pesticide removal is shown in Figure 35a. The removal efficiencies of endosulfan, dieldrin, and endrin increased from 80%, 73%, and 61% to 91%, 90%, and 85%, with increasing iron dose from 0.5 g to 3 g. Iron dose (0.5 g to 3 g) had minimal effect on lindane and DDT removal. Further increase in iron dose (3 g to 7.5 g) resulted in limited increases ( $\leq$ 5%) of heptachlor, endosulfan, and dieldrin removal, whereas 8-10% better

removal was observed for DDT, endrin, and lindane. The differences in removal efficiencies of OCPs were significant (p < 0.05) for all the studied iron doses (0.5 to 7.5 g). Since the removal efficiencies of pesticides only increased by 5-10%, when 3-7.5 g of iron turning was used, further batch experiments for the removal of pesticides were conducted with 3 g of iron turning.

Figure 35b shows the effect of initial pesticide concentration on the removal of pesticides. The removal efficiencies of endosulfan and DDT increased from 82% and 77% to 91% and 90%, with increasing initial pesticide concentration (10 to 20 µg/L). In the case of heptachlor, endrin, and dieldrin, minimal increase ( $\leq$ 5%) was observed. Ru et al. (2007) also found that dieldrin removal increased with the increase of the initial concentration, when triolene-embedded activated carbon was used as adsorbent. However, in this study, lindane removal decreased from 45% to 35%, when the initial concentration increased from 10 to 20 µg/L. It could be due to its higher water solubility and stable chemical structure as compared to other OCPs.

The removal efficiencies of all pesticides decreased except lindane, when the initial concentration of pesticide solution was 1  $\mu$ g/L. DDT removal decreased substantially to 32%, whereas the removal efficiencies of endosulfan and heptachlor were 63-64%. The removal efficiencies of dieldrin and endrin decreased to 75-77% at an initial concentration of 1  $\mu$ g/L. A decrease in atrazine removal by nZVI at lower initial concentrations was also reported (Bezbaruah et al., 2009). It could be due to less interaction between iron turning and pesticides at lower concentrations, which may need more reaction time to achieve better removal.

On the contrary, Zhang et al. (2011) reported that atrazine removal by nZVI increased at lower initial concentrations. nZVI (2 g/L) removed 56.6% atrazine at an initial concentration of 4 mg/L; while the removal was 26.6% at an initial concentration of 28 mg/L (Zhang et al., 2011).

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Similarly, in this study, lindane removal increased from 36% to 56%, when the initial concentration of pesticide solution decreased from 20  $\mu$ g/L to 1  $\mu$ g/L.





**(b)** 



Figure 35. (a) Effects of media dosage, and (b) initial pesticide concentration on OCPs removal (iron dose: 3 g).

Lower removal of lindane at higher initial concentrations by iron turning could be due to its stable chemical structure and higher water solubility compared to other studied OCPs (as mentioned in section 2.2). Therefore, iron turning may require more time and/or higher iron dose may be needed to achieve better lindane removal at higher initial concentrations. Future work is required to verify this presumption. ANOVA shows that initial pesticide concentration had significant (p = < 0.05) effect on their removal.

#### 6.3.4. Effects of Minerals and Water pH on OCP Removal

Minerals in water might precipitate on the iron surface resulting in lower pesticide removal because of less interaction between iron turning surface and pesticides. Therefore, it is important to investigate the pesticide treatment performances of iron turning waste in the presence of minerals in water. Figure 36a shows that the presence of minerals favored the removal of DDT. The removal efficiencies of DDT in the presence of individual and all minerals in water were 93-100%, versus 90% without the minerals. Similarly, calcium, nitrate, and sodium increased the removal of lindane (43-63%) whereas the removal in the presence of potassium was comparable (35%) to without the mineral. The solubility of weak polar organic compounds decreased in water in the presence of inorganic salts known as salting-out effect (Berkowitz et al., 2008). Dong et al. (2014) reported that the addition of ions such as K, NO<sub>3</sub><sup>-</sup>, Mg, K, and Na in aqueous solution increased humic acid removal using magnetic chitosan nanoparticles due to salting-out effect. Therefore, better pesticide removal in the presence of minerals could be due to salting-out effect providing better interaction between iron and pesticides in water.

Individual and all minerals in water had minimal effect ( $\leq$ 5%) on heptachlor, endosulfan, dieldrin, and endrin removal. The effect of minerals as a whole on OCPs removal was significant

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except for dieldrin and endrin (p = 0.225 for dieldrin, p = 0.076 for endrin). The salting-out effect might not be prominent at the studied concentrations of minerals in the pesticide solution because the removal efficiencies of heptachlor, endosulfan, endrin, and dieldrin were even high ( $\geq 84\%$ ) without minerals.

It is well known that water pH plays a crucial role during the reductive dehalogenation of organic contaminants, when zerovalent iron is used (Eykholt and Davenport, 1998; Ghauch et al., 1999). Figure 36b shows the effect of initial water pH ranging from 4 to 10 on the removal of mixture of chlorinated pesticides. In acidic water (pH 4), the removal efficiency of lindane is better (34%) than in neutral and basic waters (31% and 29%). At pH 4, DDT and dieldrin removal increased by 16% and 8% compared to basic environment (pH 10). Similar observations were reported in previous studies, when Fe<sup>0</sup> reduced nitrobenzene more efficiently at low pH (3-5) compared to high pH (7-10) (Dong et al., 2010; Yin et al., 2012). Low pH restricts the formation of rust on iron surface resulting in more availability of its active sites to the contaminant (Dong et al., 2010; Shih and Tai, 2010). A possible release of Fe<sup>2+</sup> under weak acidic conditions could result in enhanced reactivity of iron in aqueous environment (Huang and Zhang, 2004). Lower removal of pesticides at high pH (10) compared to neutral and acidic conditions was due to the formation of passive layer (iron hydroxide) on iron turning surface inhibiting/limiting the contact between active sites of iron and pesticide (Abbas et al., 2019).

The effect of initial water pH on endrin and heptachlor removal was minimal (<5%). However, the removal efficiency of endosulfan was higher (95%) under basic conditions than neutral and acidic conditions (88 and 91%). This is because endosulfan undergoes chemical hydrolysis in alkaline water (Peterson and Batley, 1993). Shrivaramaiah et al. (2005) reported that endosulfan was transformed to endosulfan diol in water at pH 8.3. Therefore, the increase in

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endosulfan removal under alkaline conditions compared to acidic environment was due to the involvement of both chemical hydrolysis and reductive dehalogenation. ANOVA indicates that water pH had significant effect only on endosulfan removal (p = 0.005).





Figure 36. (a) Effects of minerals, and (b) water pH on OCPs removal (iron dose: 3 g).

# 6.3.5. Microbial Regeneration of Iron Turning

There was no Fe<sup>2+</sup> detected in liquid samples obtained after 18 h of reaction of iron with the mixture of pesticides suggesting complete oxidation of virgin iron turning to  $Fe^{3+}$  (also evident by XRD analysis and XPS spectra of Fe2p regions, Figure 33b). The total iron concentration (Fe<sup>3+</sup> plus Fe<sup>2+</sup>) was  $0.51\pm 5$  mg/L, also after 18 h of reaction of iron with the mixture of pesticides. In the presence of sodium lactate as carbon source, S. oneidensis reduced  $80\pm5\%$  of Fe<sup>3+</sup> to Fe<sup>2+</sup> in 72 h agreeing a previous study (Lies et al., 2005). It was reported that 86.5% of Fe<sup>3+</sup> deposited within nanoporous glass beads was reduced within three days in anaerobic environment using S. oneidensis MR-1 (Lies et al., 2005). Garlech et al. (2000) suggested that iron reducing bacteria restore the reactivity of corroded iron by producing surfacebound reactive Fe(II) sites through microbial reduction of Fe(III) precipitates or by reductive dissolution of Fe(III) corrosion products. For direct contact between S. oneidensis and iron, electrons are transferred directly from outer membrane-localized c-type cytochromes MtrC and OmcA to insoluble, extracellular Fe(III) oxides (Cooper et al., 2016). Previous studies suggested that purified MTrC and OmcA display Fe(III) oxide reduction activity and have a direct role in solid Fe(III) reduction (Fredrickson and Zachara, 2008; Lower et al., 2007; Xiong et al., 2006).

When lactate was used as a carbon source for bioregeneration of exhausted iron, the removal efficiencies of heptachlor and DDT were 76% and 82% whereas 67-71% removal was achieved for endosulfan, dieldrin and endrin as shown in Figure 37. The removal efficiencies of heptachlor and DDT were 83% and 87%; while 72-88% removal was achieved for endosulfan, dieldrin and endrin by 0.25 g of fresh iron turning. In the case of lindane, only 15% removal was achieved. Yang et al. (2017) investigated the reactivation of aged millimetric ZVI (1-3 mm) by *Shewanella putrefaciens* in the presence of sodium lactate as energy source (20 mmole/L) for

trichloroetylene removal. The concentration of trichloroethylene decreased from 30 mg/L to approximately 13 mg/L by aged millimetric ZVI + S. *putrefaciens*; while trichloroethylene concentration decreased to 20 mg/L by aged millimetric ZVI alone after 21 days of incubation. Better removal using millimetric ZVI + S. *putrefaciens* might be due to generation of reactive Fe(II) from microbial Fe(III) oxide reduction (Yang et al., 2017).

When only the growth media (tryptic soy broth) was used as a carbon source for the bioregeneration, the removal efficiencies of DDT and heptachlor were comparable to when sodium lactate was used as a carbon source. However, endosulfan, dieldrin, and endrin removal decreased from 67-71% to 52%, 56%, and 60% respectively. It could be due to less generation of Fe<sup>2+</sup> from Fe<sup>3+</sup> in 72 h, when tryptic soy broth was used as a carbon source for *S. oneidensis*. The effect of less microbially regenerated Fe<sup>2+</sup> on the removal efficiencies of endosulfan, dieldrin, and endrin was more prominent than those of DDT and heptachlor possibly due to more sensitivity of endosulfan, dieldrin, and endrin towards Fe<sup>2+</sup> amount. There was minimal difference (<10%) in heptachlor, endosulfan, DDT, dieldrin, and endrin removal with or without the presence of OCPs during the bioregeneration of iron using sodium lactate as a carbon source for *S. oneidensis*. Lindane removal decreased from 77% to 59% in the presence of OCPs during bioregeneration of iron but was still higher than when only growth media by itself was used as a carbon source (48%). This indicates that the presence of OCPs did not inhibit bioregeneration of iron using *S. oneidensis* substantially.



Chlorinated pesticides

Figure 37. Comparison of performances of fresh and bio-regenerated iron turning for treatment of OCPs in water. FeR2: regenerated iron when lactate was used as a carbon source, FeR3: regenerated iron when no additional carbon source was added (only tryptic soy broth media), FeR4: regenerated iron when OCPs were added and lactate was used as a carbon source (iron dose: 0.25 g).

# 6.3.6. Effect of Bioregeneration Frequency of Iron Turning on OCPs Removal

Figure 38 shows the capacity of microbially regenerated iron turning waste for OCPs removal in water. ANOVA indicates that there was no signifcant difference (p > 0.05 for all six pesticides) in OCPs removal using iron turning waste (0.5 g) even after three cycles of microbial regeneration. The removal efficiencies of heptachlor (89%), endosulfan (83-84%), DDT (88-91%), endrin (69-79%), and dieldrin (76-79%) were comparable between microbially regenerated and virgin iron turning. However, lindane removal increased from 32% to 87% using microbially regenerated iron turning. Better lindane removal using microbially regenerated iron (Fe<sup>2+</sup>) could be due to faster and more efficient reaction between lindane and Fe<sup>2+</sup> compared to Fe<sup>0</sup> (virgin iron). Lindane is more soluble in water than other studied OCPs and Fe<sup>2+</sup> is a water soluble species. Future work is required to verify this presumption.


Figure 38. Performance comparison of three times bioregenerated iron turning waste versus fresh iron turning waste for OCPs removal (iron dose: 0.5 g).

# 6.3.7. OCPs Degradation/Removal Profile with Time for Virgin, Exhausted, and

### **Microbially Regenerated Iron**

Reactions between two OCPs (heptachlor and DDT) and virgin iron turning were fast and completed within 2 min (Figure 39a). After 10 min of reaction, by using 1 g of iron turning, 99.8% of heptachlor, 98% of DDT, 94% of dieldrin, 90% of endosulfan, 87% of endrin, and 42% of lindane were removed. In the case of exhausted iron, lindane, endrin and endosulfan removal decreased from 20-30% to 0-16% using 1 g of iron in 10 min as shown in Figure 39b. It could be due to initial sorption of these pesticides on passive layer/corrosion products such as Fe<sub>3</sub>O<sub>4</sub> and FeOOH which might later be released/desorbed due to weak sorption. Gerlach et al. (2000) investigated the degradation/removal of carbon tetrachloride at an initial concentration of 100  $\mu$ M using the passivated iron. It was reported that the concentration of carbon tetrachloride only decreased from 100  $\mu$ M to approximately 75  $\mu$ M after 80-100 h, and there was minimal (<5%)

transformation of carbon tetrachloride to chloroform (degradation by-product of carbon tetrachloride) using the passivated iron (Gerlach et al., 2000). Heptachlor and DDT removal using exhausted iron was 67-80% in 10 min which could be due to more precipitation and/or sorption on the passive layer of exhuasted iron (FeOOH and Fe<sub>3</sub>O<sub>4</sub>) as their log Kow values are higher than those of the other studied OCPs (Table 1). Iron oxides/corrosion products of iron including Fe<sub>3</sub>O<sub>4</sub> and FeOOH are known for their adsoptive and co-precipitation properties of organic contaminants (Noubactep, 2009).

Figure 39c shows that reaction between OCPs and microbially regenerated iron (1 g) with *S.oneidensis* cells was fast. From 0-10 min, the removal efficiencies of DDT, endosulfan, lindane, and endrin were 88-91%, 70-80%, 71-81%, and 41-52%, respecitvely. Heptachlor and dieldrin removal increased graudally from 81 to 91% and 68 to 79% in 10 min. A similar observation was reported in a previous study when *S. alga* BrY was used to regenerate ferrous iron from the passive iron; carbon tetrachloride removal increased gradually from 35 to 100% (initial concentration of 100  $\mu$ M) from 20 to 95 h (Gerlach et al., 2000). Removal kinetics of OCPs could not be determined due to fast reaction between OCPs and iron turning (virgin and microbially regenerated iron).



Figure 39. OCPs removal time profile for different types of iron turning waste: (a) virgin iron, (b) exhausted iron, and (c) microbially regenerated iron (iron dose: 1 g).

# 6.4. Summary

This study demonstrates the effectiveness and feasibility of iron turning waste as a pointof-use filtration media for treating a mixture of six OCPs in water. In batch experiments, the removal efficiencies of OCPs increased significantly with increasing the iron dose from 0.5 g to 3 g. Minerals in water had positive effect on pesticide removal possibly due to salting-out effect. Acidic water pH increased the removal efficiencies of all pesticides except for endosulfan. *S. oneidensis* successfully regenerated  $Fe^{2+}$  in the presence of sodium lactate. Microbially regenerated  $Fe^{2+}$  showed its ability to degrade OCPs in water. OCPs removal efficiencies using virgin and microbially regenerated iron turning were comparable. The utilization of nonpathogenic bacteria for the regeneration of exhausted iron type media can potentially be used an environmental friendly and less expensive approach to treat different halogenated organics in water for extended period of time.

#### 7. CONCLUSIONS AND FUTURE WORK RECOMMENDATIONS

# 7.1. Conclusions

OCPs contamination in surface and groundwater is major concern. Metal nanoparticles such as nZVI have gained attention as a method to degrade halogenated organic contaminants including OCPs in water with a primary focus of in-situ treatment/remediation. However, the application of nZVI as point-of-use filtration media is not possible because of high cost, mobility and potential toxic effects to human and environment. Moreover, rapid oxidation of nZVI to Fe<sup>3+</sup> in the presence of oxygen limits the life of filtration media and requires frequent replacement of nZVI.

In this dissertation, the application and effectiveness of iron turning waste, which is affordable and has the same valence and properties as nZVI, to treat individual and mixture of OCPs in water in both batch and continuous systems were demonstrated. The ability of iron turning waste to degrade OCPs to less toxic compounds was examined and degradation pathways of OCPs were proposed. Moreover, the capacity of microbially regenerated Fe<sup>2+</sup> to degrade OCPs was demonstrated.

For objective 1, the degradation kinetics of individual and mixture of OCPs was determined using iron turning waste. Batch experiments (individual pesticides) showed that iron turning waste removed more than 93% and 92% of endrin and dieldrin, 96% and 85% of endosulfan, and 50% and 85% of lindane and DDT in 10 min using 2.5 iron turning in 200 mL of pesticide solution ( $20 \mu g/L$ ). Endrin and dieldrin removal followed pseudo-first order kinetics and their removal rates were 0.29 and 0.26 min<sup>-1</sup>. For heptachlor, endosulfan, lindane, and DDT, the removal data fitted better with pseudo second order model and the removal rate constants were 0.65, 0.71, 1.32, and 0.63 g/µg.min, respectively.

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For objective 2, the effects of water pH, initial pesticide concentration and minerals in water on removal of individual and mixture of OCPs by iron turning waste were investigated. The research findings showed that acidic water pH favored the removal of all studied OCPs (both individually and in mixture) except endosulfan because low acidic pH limits the formation of passive oxide layer on iron surface resulting in better interaction between contaminant and iron surface. Endosulfan removal increased in alkaline environment because of the involvement of both hydrolysis and dechlorination. The removal of OCPs (both individually and in mixture) increased with initial pesticide concentration except for lindane. This could be due to stable chemical structure and higher water solubility of lindane compared to other OCPs studied. Minerals in water favored the removal of OCPs because of salting-out effect.

The findings of objective 3 showed that both  $Fe^0$  and  $Fe^{2+}$  were involved in reductive dechlorination of OCPs in water. The ORP values decreased significantly after the reaction between OCPs and iron turning waste confirming the reducing environment. During the degradation of OCPs using iron turning waste, OCPs first underwent dechlorination followed by ring cleavage. Benzene, 2,4 di-*tert*-butylphenol, nonanal, and 2-ethyl-1-hexanol were detected as major degradation products of OCPs. Based on the LD<sub>50</sub> values of OCPs and their degradation by-products, iron turning waste degraded OCPs into less toxic compounds.

Iron turning waste based filter treated OCPs better with sand layer(s) included (objective 4). The sand layer limited exposure of iron turning to oxygen and kept the iron content in treated water within permissible limits (0.3 mg/L). At an EBCT of 1.6 h (objective 4), iron turning waste filter completely removed heptachlor, lindane and DDT whereas the removal efficiencies of endrin, dieldrin, and endosulfan were initially 100% (until 300 h); however, it dropped to 94-95% for endrin and dieldrin, and 88% for endosulfan at 500 h of filtration.

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The findings of the last objective (objective 5) demonstrated that *S. oneidensis* successfully reduced  $Fe^{3+}$  to  $Fe^{2+}$  in anerobic environment. Microbially regenerated  $Fe^{2+}$  proved its ability to remove/degrade all six OCPs in water. OCPs removal efficiencies using microbially regenerated iron turning waste were comparable to virgin iron turning. Lindane, endosulfan, dieldrin removal increased 4-fold using *S. oneidensis* regenerated iron compared to exhausted iron. These findings lay the foundation for the application of *S. oneidensis* in iron based filter to increase the longevity of filter media during the treatment of other organic contaminants in water.

# 7.2. Future Work Recommendations

It is necessary to investigate the ability of iron turning waste for treating OCPs in the presence of natural organic matter which is common in natural waters. Also, bicarbonate, which is common in natural water, can affect the reactivity of zerovalent iron. Therefore, its effect on the removal of OCPs by iron turning waste should be investigated. Results from this dissertation research showed that the degradation of OCPs using iron turning waste first underwent dechlorination followed by the ring cleavage. However, it is important to measure chloride content of the OCPs solution through their degradation to confirm the dechlorination mechanism. During the microbial regeneration of iron, ORP should be measured as this would verify reducing conditions, which are necessary for iron reduction. The retention and effectiveness of *S. oneidensis* for the regeneration of iron in a column setting, which is more practical, should be determined. The growth, survival, and activity of *S. oneidensis* in the column under practical conditions such as natural mixed culture environment should be explored because other microorganisms present may compete with *S. oneidensis* for resources including carbon source.

### REFERENCES

- Abbas M, Rao BP, Naga S, Takahashi M, Kim C. Synthesis of high magnetization hydrophilic magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles in single reaction—surfactantless polyol process. Ceramics International 2013; 39: 7605-7611.
- Abbas T, Wadhawan T, Khan A, McEvoy J, Khan E. Iron turning waste media for treating
   Endosulfan and Heptachlor contaminated water. Science of The Total Environment 2019;
   685: 124-133.
- Abron LA, Osburn JO. A transport mechanism in hollow nylon fiber reverse osmosis membranes for the removal of ddt and aldrin from water. Water Research 1973; 7: 461-477.
- Adeleye AS, Keller AA, Miller RJ, Lenihan HS. Persistence of commercial nanoscaled zerovalent iron (nZVI) and by-products. Journal of Nanoparticle Research 2013;15:1418.
- Agarwal A, Prajapati R, Singh OP, Raza S, Thakur L. Pesticide residue in water—a challenging task in India. Environmental Monitoring and Assessment 2015; 187: 54.
- Ahad K, Hayat Y, Ahmad I, Soomro M. Capillary chromatographic determination of pesticides residues in groundwater of Multan Division. Nucleus 2001; 38: 145-9.
- Ahad K, Mohammad A, Khan H, Ahmad I, Hayat Y. Monitoring results for organochlorine pesticides in soil and water from selected obsolete pesticide stores in Pakistan.
   Environmental Monitoring and Assessment 2010; 166: 191-199.
- Ahmad T, Rafatullah M, Ghazali A, Sulaiman O, Hashim R, Ahmad A. Removal of pesticides from water and wastewater by different adsorbents: a review. Journal of Environmental Science and Health, Part C 2010; 28: 231-271.
- Aktar MW, Sengupta D, Chowdhury A. Impact of pesticides use in agriculture: their benefits and hazards. Interdisciplinary Toxicology 2009; 2: 1-12.

- Aleem M, Shun C, Li C, Aslam A, Yang W, Nawaz M, Ahmed W, Buttar N. Evaluation of groundwater quality in the vicinity of Khurrianwala industrial zone, Pakistan. Water 2018; 10: 1321.
- Ali U, Bajwa A, Iqbal Chaudhry MJ, Mahmood A, Syed JH, Li J, Zhang G, Jones KC, Malik RN. Significance of black carbon in the sediment–water partitioning of organochlorine pesticides (OCPs) in the Indus River, Pakistan. Ecotoxicology and Environmental Safety 2016; 126: 177-185.
- Ali U, Syed JH, Malik RN, Katsoyiannis A, Li J, Zhang G, Jones KC. Organochlorine pesticides
  (OCPs) in South Asian region: A review. Science of The Total Environment 2014; 476-477: 705-717.
- Ameta R, Solanki MS, Benjamin S, Ameta SC. Chapter 6 Photocatalysis. In: Ameta SC, Ameta R, editors. Advanced Oxidation Processes for Waste Water Treatment. Academic Press, 2018, pp. 135-175.
- Ananpattarachai J, Kajitvichyanukul P. Photocatalytic degradation of p, p'-DDT under UV and visible light using interstitial N-doped TiO<sub>2</sub>. Journal of Environmental Science and Health, Part B 2015; 50: 247-260.
- Arienzo M, Masuccio AA, Ferrara L. Evaluation of sediment contamination by heavy metals, organochlorinated pesticides, and polycyclic aromatic hydrocarbons in the berre coastal lagoon (Southeast France). Archives of Environmental Contamination and Toxicology 2013; 65: 396-406.
- Arisekar U, Shakila RJ, Jeyasekaran G, Shalin R, Kumar P, Malani AH, Rani V. Accumulation of organochlorine pesticide residues in fish, water, and sediments in the Thamirabarani

river system of southern peninsular India. Environmental Nanotechnology, Monitoring & Management 2019; 11.

- Asi M, Hussain A, Muhmood S. Solid phase extraction of pesticide residues in water samples:
   DDT and its metabolites. International Journal of Environmental Research 2008; 2: 43-48.
- ATSDR. Toxicological profile for endosulfan. US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, GA, 2000.
- Augustijn-Beckers P, Hornsby A, Wauchope R. The SCS/ARS/CES pesticide properties database for environmental decision-making. II. Additional compounds. Reviews of Environmental Contamination and Toxicology. Springer 1994:1-82.
- Azizullah A, Khattak MNK, Richter P, Häder D-P. Water pollution in Pakistan and its impact on public health—a review. Environment International 2011; 37: 479-497.
- Bajaj A, Mayilraj S, Mudiam MKR, Patel DK, Manickam N. Isolation and functional analysis of a glycolipid producing Rhodococcus sp. strain IITR03 with potential for degradation of 1, 1, 1-trichloro-2, 2-bis (4-chlorophenyl) ethane (DDT). Bioresource Technology 2014; 167: 398-406.
- Bao L-J, Maruya KA, Snyder SA, Zeng EY. China's water pollution by persistent organic pollutants. Environmental Pollution 2012; 163: 100-108.
- Barbusiński K, Filipek K. Use of Fenton's reagent for removal of pesticides from industrial wastewater. Polish Journal of Environmental Studies 2001; 10: 207-212.
- Barragan-Huerta BE, Costa-Pérez C, Peralta-Cruz J, Barrera-Cortés J, Esparza-García F, Rodríguez-Vázquez R. Biodegradation of organochlorine pesticides by bacteria grown in

microniches of the porous structure of green bean coffee. International Biodeterioration & Biodegradation 2007; 59: 239-244.

- Berkowitz B, Dror I, Yaron B. Contaminant geochemistry: interactions and transport: The subsurface environment, Springer, Heidelberg 2008: 136.
- Begum A, Agnihotri P, Mahindrakar AB, Gautam SK. Degradation of endosulfan and lindane using Fenton's reagent. Applied Water Science 2017; 7: 207-215.
- Bennett BD, Brutinel ED, Gralnick JA. A ferrous iron exporter mediates iron resistance in Shewanella oneidensis MR-1. Applied and Environmental Microbiology 2015; 81: 7938-7944.
- Beyer A, Matthies M. Long-range transport potential of semivolatile organic chemicals in coupled air-water systems. Environmental Science and Pollution Research 2001; 8: 173-179.
- Bezbaruah AN, Thompson JM, Chisholm BJ. Remediation of alachlor and atrazine contaminated water with zero-valent iron nanoparticles. Journal of Environmental Science and Health, Part B 2009; 44: 518-524.
- Bhalerao TS, Puranik PR. Biodegradation of organochlorine pesticide, endosulfan, by a fungal soil isolate, Aspergillus niger. International Biodeterioration & Biodegradation 2007; 59: 315-321.
- Bidleman T, Jantunen L, Wiberg K, Harner T, Brice K, Su K, Falconer RL, Leone AD, Aigner EJ, Parkhurst WJ. Soil as a source of atmospheric heptachlor epoxide. Environmental Science & Technology 1998; 32: 1546-1548.

- Bose S, Hochella Jr MF, Gorby YA, Kennedy DW, McCready DE, Madden AS, Lower BH. Bioreduction of hematite nanoparticles by the dissimilatory iron reducing bacterium Shewanella oneidensis MR-1. Geochimica et Cosmochimica Acta 2009; 73: 962-976.
- Boul H. DDT residues in the environment-a review with a New Zealand perspective. New Zealand Journal of Agricultural Research 1995; 38: 257-277.
- Boussahel R, Irinislimane H, Harik D, Moussaoui KM. Adsorption, kinetics, and equilibrium studies on removal of 4, 4-DDT from aqueous solutions using low-cost adsorbents.
   Chemical Engineering Communications 2009; 196: 1547-1558.
- Callahan MA. Water-related environmental fate of 129 priority pollutants. Vol 1: Office of Water Planning and Standards, Office of Water and Waste Management, US Environmental Protection Agency 1979.
- Cara IG, Jitareanu G. Application of Low-Cost Adsorbents for Pesticide Removal. Bulletin of the University of Agricultural Sciences & Veterinary Medicine Cluj-Napoca. Veterinary Medicine 2015; 72.
- Carvalho FP. Pesticides, environment, and food safety. Food and Energy Security 2017; 6: 48-60.
- Cerejeira MJ, Viana P, Batista S, Pereira T, Silva E, Valério MJ, Silva A, Ferreira M, Silva-Fernandes AM. Pesticides in Portuguese surface and ground waters. Water Research 2003; 37: 1055-1063.
- Chang GR. Persistent organochlorine pesticides in aquatic environments and fishes in Taiwan and their risk assessment. Environmental Science and Pollution Research 2018; 25: 7699-7708.

- Cheng Y-Y, Li B-B, Li D-B, Chen J-J, Li W-W, Tong Z-H, Wu C, Yu H-Q. Promotion of iron oxide reduction and extracellular electron transfer in Shewanella oneidensis by DMSO. PloS One 2013; 8: e78466.
- Cheng Z, Van Geen A, Louis R, Nikolaidis N, Bailey R. Removal of methylated arsenic in groundwater with iron filings. Environmental Science & Technology 2005; 39: 7662-7666.
- Chian ES, Bruce WN, Fang HH. Removal of pesticides by reverse osmosis. Environmental Science & Technology 1975; 9: 52-59.
- Cooper RE, Goff JL, Reed BC, Sekar R, DiChristina TJ. Breathing iron: molecular mechanism of microbial iron reduction by Shewanella oneidensis. Manual of Environmental Microbiology, Fourth Edition. American Society of Microbiology, 2016.
- Dai N-W, Zhang J-X, Chen Q-M, Zhang X, Cao F-H, Zhang J-Q. Influence of direct current electric field on the formation, composition and microstructure of corrosion products formed on the steel in simulated marine atmospheric environment. Acta Metallurgica Sinica (English letters) 2016; 29: 373-381.
- Dalvie MA, Cairncross E, Solomon A, London L. Contamination of rural surface and ground water by endosulfan in farming areas of the Western Cape, South Africa. Environmental Health 2003; 2: 1.
- Devlin JF, Klausen J, Schwarzenbach RP. Kinetics of nitroaromatic reduction on granular iron in recirculating batch experiments. Environmental Science & Technology 1998; 32: 1941-1947.
- Dey S, Bhattacharya D, Roy S, Nadgir S, Patil A, Kholkute S. Shewanella algae in acute gastroenteritis. Indian Journal of Medical Microbiology 2015; 33: 172-175.

- Dominguez CM, Parchão J, Rodriguez S, Lorenzo D, Romero A, Santos A. Kinetics of lindane dechlorination by zerovalent iron microparticles: effect of different salts and stability study. Industrial & Engineering Chemistry Research 2016; 55: 12776-12785.
- Dong J, Zhao Y, Zhao R, Zhou R. Effects of pH and particle size on kinetics of nitrobenzene reduction by zero-valent iron. Journal of Environmental Sciences 2010; 22: 1741-1747.
- Dong C, Chen W, Liu C, Liu Y, Liu H. Synthesis of magnetic chitosan nanoparticle and its adsorption property for humic acid from aqueous solution. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2014; 446: 179-89.
- Dong H, Li L, Lu Y, Cheng Y, Wang Y, Ning Q, Wang B, Zhang L, Zeng G. Integration of nanoscale zero-valent iron and functional anaerobic bacteria for groundwater remediation: a review. Environment International 2019; 124: 265-77.
- Duranceau SJ, Taylor JS, Mulford LA. SOC removal in a membrane softening process. Journal-American Water Works Association 1992; 84: 68-78.
- El-Bestawy E, Mansy A, Mansee A, El-Koweidy A. Biodegradation of selected chlorinated pesticides contaminating lake Maruiut ecosystem. Pakistan Journal of Biological Sciences 2000; 3: 1673-1680.
- El-Temsah YS, Sevcu A, Bobcikova K, Cernik M, Joner EJ. DDT degradation efficiency and ecotoxicological effects of two types of nano-sized zero-valent iron (nZVI) in water and soil. Chemosphere 2016; 144: 2221-2228.
- El Bakouri H, Morillo J, Usero J, Ouassini A. Potential use of organic waste substances as an ecological technique to reduce pesticide ground water contamination. Journal of Hydrology 2008; 353: 335-342.

- El Bakouri H, Usero J, Morillo J, Rojas R, Ouassini A. Drin pesticides removal from aqueous solutions using acid-treated date stones. Bioresource Technology 2009; 100: 2676-2684.
- Elliott DW, Lien H-L, Zhang W-X. Degradation of lindane by zero-valent iron nanoparticles. Journal of Environmental Engineering 2009; 135: 317-324.
- Embrandiri A, Singh RP, Ibrahim HM, Khan AB. An epidemiological study on the health effects of endosulfan spraying on cashew plantations in Kasaragod District, Kerala, India. Asian Journal of Epidemiology 2012; 5: 22-31.
- EPA. Source water protection practices bulletin: Managing small-scale application of pesticides to prevent contamination of drinking water, Washington, DC, 2001.
- Eqani SA-M-A-S, Malik RN, Alamdar A, Faheem H. Status of organochlorine contaminants in the different environmental compartments of Pakistan: a review on occurrence and levels. Bulletin of Environmental Contamination and Toxicology 2012; 88: 303-310.
- Eykholt GR, Davenport DT. Dechlorination of the chloroacetanilide herbicides alachlor and metolachlor by iron metal. Environmental Science & Technology 1998; 32: 1482-1487.
- Fan J, Guo Y, Wang J, Fan M. Rapid decolorization of azo dye methyl orange in aqueous solution by nanoscale zerovalent iron particles. Journal of Hazardous Materials 2009; 166: 904-910.
- Fang W, Jiang X, Bian Y-r, Yao F-x, Gao H-j, Yu G-f, Munch JC, Schroll R. Organochlorine pesticides in soils under different land usage in the Taihu Lake region, China. Journal of Environmental Sciences 2007; 19: 584-590.
- Faniband M, Lindh CH, Jönsson BA. Human biological monitoring of suspected endocrinedisrupting compounds. Asian Journal of Andrology 2014; 16: 5-16.

- Feng K, Yu BY, Ge DM, Wong MH, Wang XC, Cao ZH. Organo-chlorine pesticide (DDT and HCH) residues in the Taihu Lake Region and its movement in soil–water system: I. Field survey of DDT and HCH residues in ecosystem of the region. Chemosphere 2003; 50: 683-687.
- Fernández-Fernández E, Martín-Rodríguez AJ, Hernández M, Navarro-Marí JM, Römling U, Gutiérrez-Fernández J. First clinical isolation report of Shewanella algae from the stools of a patient with acute enteritis in Spain. Revista Española de Quimioterapia 2018; 31: 160-163.
- Foo KY, Hameed BH. Detoxification of pesticide waste via activated carbon adsorption process. Journal of Hazardous Materials 2010; 175: 1-11.
- Fredrickson JK, Zachara JM. Electron transfer at the microbe–mineral interface: a grand challenge in biogeochemistry. Geobiology 2008; 6: 245-253.
- Freyria F, Esposito S, Armandi M, Deorsola F, Garrone E, Bonelli B. Role of pH in the aqueous phase reactivity of zerovalent iron nanoparticles with acid orange 7, a model molecule of azo dyes. Journal of Nanomaterials 2017; 2017.
- Gerbino-Bevins B, Tuan CY, Mattison M. Evaluation of Ice-Melting Capacities of Deicing Chemicals. Journal of Testing and Evaluation 2012; 40: 952-960.
- Gerlach R, Cunningham AB, Caccavo F. Dissimilatory iron-reducing bacteria can influence the reduction of carbon tetrachloride by iron metal. Environmental Science & Technology 2000; 34: 2461-2464.
- Ghauch A, Rima J, Amine C, Martin-Bouyer M. Rapid treatment of water contamined with atrazine and parathion with zero-valent iron. Chemosphere 1999; 39: 1309-1315.

- Ghosh S, Das SK, Guha AK, Sanyal AK. Adsorption behavior of lindane on rhizopus oryzae biomass: physico-chemical studies. Journal of Hazardous Materials 2009; 172: 485-490.
- Gilliom RJ. Pesticides in U.S. Streams and Groundwater. Environmental Science & Technology 2007; 41: 3408-3414.
- Golfinopoulos SK, Nikolaou AD, Kostopoulou MN, Xilourgidis NK, Vagi MC, Lekkas DT.
  Organochlorine pesticides in the surface waters of Northern Greece. Chemosphere 2003;
  50: 507-516.
- Gonçalves CM, Esteves da Silva JCG, Alpendurada MF. Evaluation of the pesticide contamination of groundwater sampled over two years from a vulnerable zone in Portugal. Journal of Agricultural and Food Chemistry 2007; 55: 6227-6235.
- Greenman DW, Swarzenski WV, Bennett GD. Ground-water hydrology of the Punjab, West Pakistan, with emphasis on problems caused by canal irrigation: US Government Printing Office, 1967.
- Gupta P. Pesticide exposure-Indian scene. Toxicology 2004; 198: 83-90.
- Gupta V. Removal of lindane and malathion from wastewater using bagasse fly ash—a sugar industry waste. Water Research 2002; 36: 2483-2490.
- Gupta VK, Ali I. Removal of endosulfan and methoxychlor from water on carbon slurry. Environmental Science & Technology 2008; 42: 766-770.
- Gupta VK, Jain C, Ali I, Chandra S, Agarwal S. Removal of lindane and malathion from wastewater using bagasse fly ash—a sugar industry waste. Water Research 2002; 36: 2483-2490.

- Han L, Xue S, Zhao S, Yan J, Qian L, Chen M. Biochar supported nanoscale iron particles for the efficient removal of methyl orange dye in aqueous solutions. PloS One 2015; 10: e0132067.
- Hao Z-W, Xu X-H, Wang D-H. Reductive denitrification of nitrate by scrap iron filings. Journal of Zhejiang University Science 2005; 6B: 182-186.
- Hara J. The effect of oxygen on chemical dechlorination of dieldrin using iron sulphides. Chemosphere 2011; 82: 1308-1313.
- Honetschlägerová L, Škarohlíd R, Martinec M, Šír M, Luciano V. Interactions of nanoscale zero valent iron and iron reducing bacteria in remediation of trichloroethene International Biodeterioration & Biodegradation. 2018; 127: 241-6.
- Huang YH, Zhang TC. Effects of low pH on nitrate reduction by iron powder. Water Research 2004; 38: 2631-2642.
- Hussain S, Arshad M, Saleem M, Zahir ZA. Screening of soil fungi for in vitro degradation of endosulfan. World Journal of Microbiology and Biotechnology 2007; 23: 939-945.
- Ikehata K, Gamal El-Din M. Aqueous pesticide degradation by ozonation and ozone-based advanced oxidation processes: a review (Part I). Ozone: Science and Engineering 2005; 27: 83-114.
- Indelicato BM. Comparision of zero-valent iron and activated carbon for treating chlorinated contaminants in groundwater. Massachusetts Institute of Technology 1998.
- IPSC. Endrin, international programme on chemical safety (environmental health criteria 130). World Health Organization, Geneva 1992.
- Iram S, Ahmad I, Ahad K, Muhammad A, Anjum S. Analysis of pesticides residues of Rawal and Simly lakes. Pakistan Journal of Botany 2009; 41: 1981-1987.

- Ismail M, Sayed M, Khan HM, Cooper WJ. Analysis of pesticides in water samples and removal of monocrotophos by gamma irradiation. Journal of Analytical and Bioanalytical Techniques 2014; 5: 1-10.
- Janda JM, Abbott SL. The genus Shewanella: from the briny depths below to human pathogen. Critical Reviews in Microbiology 2014; 40: 293-312.
- Jayaraj R, Megha P, Sreedev P. Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. Interdisciplinary Toxicology 2016; 9: 90-100.
- Jit S, Dadhwal M, Kumari H, Jindal S, Kaur J, Lata P, Niharika N, Lal D, Garg N, Gupta SK, Sharma P. Evaluation of hexachlorocyclohexane contamination from the last lindane production plant operating in India. Environmental Science and Pollution Research 2011; 18: 586-597.
- Johnson TL, Scherer MM, Tratnyek PG. Kinetics of halogenated organic compound degradation by iron metal. Environmental Science & Technology 1996; 30: 2634-2640.
- Joo SH, Zhao D. Destruction of lindane and atrazine using stabilized iron nanoparticles under aerobic and anaerobic conditions: effects of catalyst and stabilizer. Chemosphere 2008; 70: 418-425.
- Kafilzadeh F, Ebrahimnezhad M, Tahery Y. Isolation and identification of endosulfan-degrading bacteria and evaluation of their bioremediation in Kor River, Iran. Osong Public Health and Research Perspectives 2015; 6: 39-46.
- Katagi T. Direct photolysis mechanism of pesticides in water. Journal of Pesticide Science 2018; 43: 57-72.

- Keenan CR, Sedlak DL. Ligand-enhanced reactive oxidant generation by nanoparticulate zerovalent iron and oxygen. Environmental Science & Technology 2008; 42: 6936-6941.
- Khan N, Muller J, Khan SH, Amjad S, Nizamani S, Bhanger MI. Organochlorine pesticides (OCPs) contaminants in sediments from Karachi Harbour, Pakistan. Journal of the Chemical Society of Pakistan 2010; 32: 542-549.
- Kole R, Bagchi M. Pesticide residues in the aquatic environment and their possible ecological hazards. Jounral of Inland Fish Society India 1995; 27: 79-89.
- Kouras A, Zouboulis A, Samara C, Kouimtzis T. Removal of pesticides from aqueous solutions by combined physicochemical processes—the behaviour of lindane. Environmental Pollution 1998; 103: 193-202.
- Kuranchie-Mensah H, Atiemo SM, Palm LMN-D, Blankson-Arthur S, Tutu AO, Fosu P. Determination of organochlorine pesticide residue in sediment and water from the Densu river basin, Ghana. Chemosphere 2012; 86: 286-292.
- Kwon G-S, Sohn H-Y, Shin K-S, Kim E, Seo B-I. Biodegradation of the organochlorine insecticide, endosulfan, and the toxic metabolite, endosulfan sulfate, by Klebsiella oxytoca KE-8. Applied Microbiology and Biotechnology 2005; 67: 845-850.
- Lama Y, Sinha A, Singh G. Treatment of endosulfan by high carbon iron filings (HCIF). International Journal of Environmental Engineering and Management 2013; 4: 177-184.
- Laskowski T, Sroka M, Olejnik A, Biernacki W, Nawrocki J. Cast iron filings-based model for observation of nitrate reduction in corroded system. Desalination and Water Treatment 2016; 57: 19418-19430.

- Ledirac N, Antherieu S, d'Uby AD, Caron J-C, Rahmani R. Effects of organochlorine insecticides on MAP kinase pathways in human HaCaT keratinocytes: key role of reactive oxygen species. Toxicological Sciences 2005; 86: 444-452.
- Lei C, Sun Y, Khan E, Chen SS, Tsang DC, Graham NJ, Ok YS, Yang X, Lin D, Feng Y, Li, XD. Removal of chlorinated organic solvents from hydraulic fracturing wastewater by bare and entrapped nanoscale zero-valent iron. Chemosphere 2018; 196: 9-17.
- Leupin OX, Hug SJ, Badruzzaman A. Arsenic removal from Bangladesh tube well water with filter columns containing zerovalent iron filings and sand. Environmental Science & Technology 2005; 39: 8032-8037.
- Li F, Li X, Zhou S, Zhuang L, Cao F, Huang D, Xu W, Liu TX, Feng CH. Enhanced reductive dechlorination of DDT in an anaerobic system of dissimilatory iron-reducing bacteria and iron oxide. Environmental Pollution 2010; 158: 1733-1740.
- Li J, Zhang G, Qi S, Li X, Peng X. Concentrations, enantiomeric compositions, and sources of HCH, DDT and chlordane in soils from the Pearl River Delta, South China. Science of the Total Environment 2006; 372: 215-224.
- Li W, Dai Y, Xue B, Li Y, Peng X, Zhang J, Yan Y. Biodegradation and detoxification of endosulfan in aqueous medium and soil by Achromobacter xylosoxidans strain CS5. Journal of Hazardous Materials 2009; 167: 209-216.
- Lies DP, Hernandez ME, Kappler A, Mielke RE, Gralnick JA, Newman DK. Shewanella oneidensis MR-1 uses overlapping pathways for iron reduction at a distance and by direct contact under conditions relevant for biofilms. Applied and Environmental Microbiology. 2005; 71: 4414-4426.

- Lin C, Lin K-S. Photocatalytic oxidation of toxic organohalides with TiO<sub>2</sub>/UV: the effects of humic substances and organic mixtures. Chemosphere 2007; 66: 1872-1877.
- Lin P, Zhang Y, Zhang X, Chen C, Xie Y, Suffet IH. The influence of chlorinated aromatics' structure on their adsorption characteristics on activated carbon to tackle chemical spills in drinking water source. Frontiers of Environmental Science & Engineering 2015; 9: 138-146.
- Liu H, Chen Z, Guan Y, Xu S. Role and application of iron in water treatment for nitrogen removal: a review. Chemosphere 2018; 204: 51-62.
- Liu H, Qu J, Dai R, Ru J, Wang Z. A biomimetic absorbent for removal of trace level persistent organic pollutants from water. Environmental Pollution 2007; 147: 337-342.
- Liu Y, Wang J. Reduction of nitrate by zero valent iron (ZVI)-based materials: a review. Science of the Total Environment 2019; 671: 388-403.
- Lovley DR. Microbial Fe (III) reduction in subsurface environments. FEMS Microbiology Reviews 1997; 20: 305-313.
- Lovley DR, Phillips EJ. Rapid assay for microbially reducible ferric iron in aquatic sediments. Applied and Environmental Microbiology. 1987; 53: 1536-1540.
- Lower BH, Shi L, Yongsunthon R, Droubay TC, McCready DE, Lower SK. Specific bonds between an iron oxide surface and outer membrane cytochromes MtrC and OmcA from Shewanella oneidensis MR-1. Journal of Bacteriology 2007; 189: 4944-4952.
- Lu LC, Wang CI, Sye WF. Applications of chitosan beads and porous crab shell powder for the removal of 17 organochlorine pesticides (OCPs) in water solution. Carbohydrate Polymers 2011; 83: 1984-1989.

- Lucero PA, Ferrari MM, Orden AA, Cañas I, Nassetta M, Kurina-Sanz M. Treatment of endosulfan contaminated water with in vitro plant cell cultures. Journal of Hazardous Materials 2016; 305: 149-155.
- Madsen HT. Membrane filtration in water treatment–removal of micropollutants. Chemistry of Advanced Environmental Purification Processes of Water. Elsevier, 2014: 199-248.
- Malaiyandi M, Blais P, Sastri V. Separation of Lindane from Its Aqueous Solutions by Reverse Osmosis System. Separation Science and Technology 1980; 15: 1483-1488.
- Marican A, Duran-Lara EF. A review on pesticide removal through different processes. Environmental Science and Pollution Research 2018: 1-14.
- Matsumoto E, Kawanaka Y, Yun S-J, Oyaizu H. Bioremediation of the organochlorine pesticides, dieldrin and endrin, and their occurrence in the environment. Applied Microbiology and Biotechnology 2009; 84: 205-216.
- Matsumura F, Boush G. Dieldrin: degradation by soil microorganisms. Science 1967; 156: 959-961.
- Matsumura F, Boush MG. Degradation of insecticides by a soil fungus, Trichoderma viride. Journal of Economic Entomology 1968; 61: 610-612.
- Matsumura F, Khanvilkar VG, Patil KC, Boush GM. Metabolism of endrin by certain soil microorganisms. Journal of Agricultural and Food Chemistry 1971; 19: 27-31.
- Matsumura F, Patil K, Boush G. Formation of "photodieldrin" by microorganisms. Science 1970; 170: 1206-1207.
- McGarrigle M, Lucey J, Cinnéide MÓ, Castle J. Water quality in Ireland 2007-2009. Environmental Protection Agency, Ireland 2010.

- Mehta VS, Chaudhari SK. Arsenic removal from simulated groundwater using household filter columns containing iron filings and sand. Journal of Water Process Engineering 2015; 6: 151-157.
- Memon GZ, Moghal M, Memon JR, Memon NN, Bhanger M. Adsorption of selected pesticides from aqueous solutions using cost effective walnut shells. IOSR Journal of Engineering 2014; 4: 43-56.
- Miguel N, Ormad MP, Lanao M, Ibarz C, Ovelleiro JL. Effectiveness of advanced oxidation processes with O<sub>3</sub> and O<sub>3</sub>+H<sub>2</sub>O<sub>2</sub> in pesticides degradation. IOA Conference and Exhibition, Valencia, Spain, October 29-31, 2007.
- Miguel N, Ormad MP, Mosteo R, Ovelleiro JL. Photocatalytic degradation of pesticides in natural water: effect of hydrogen peroxide. International Journal of Photoenergy 2012; 2012.
- Miller L, Narang R. Induced photolysis of DDT. Science 1970; 169: 368-370.
- Mishra K, Sharma RC. Contamination of aquatic system by chlorinated pesticides and their spatial distribution over North-East India. Toxicology and Environmental Health Sciences 2011; 3: 144.
- Mishra P, Patel R. Removal of endosulfan by sal wood charcoal. Journal of Hazardous Materials 2008; 152: 730-736.
- Mnif W, Hassine AIH, Bouaziz A, Bartegi A, Thomas O, Roig B. Effect of endocrine disruptor pesticides: a review. International Journal of Environmental Research and Public Health 2011; 8: 2265-2303.
- Moma J, Baloyi J. Modified titanium dioxide for photocatalytic applications. Photocatalysts-Applications and Attributes. IntechOpen 2018.

- Moon H-B, Kim H-S, Choi M, Yu J, Choi H-G. Human health risk of polychlorinated biphenyls and organochlorine pesticides resulting from seafood consumption in South Korea, 2005-2007. Food and Chemical Toxicology 2009; 47: 1819-1825.
- Mora A, Mahlknecht J, Rosales-Lagarde L, Hernández-Antonio A. Assessment of major ions and trace elements in groundwater supplied to the Monterrey metropolitan area, Nuevo León, Mexico. Environmental Monitoring and Assessment 2017; 189: 394.
- Mudhoo A, Bhatnagar A, Rantalankila M, Srivastava V, Sillanpää M. Endosulfan removal through bioremediation, photocatalytic degradation, adsorption and membrane separation processes: a review. Chemical Engineering Journal 2019; 360: 912-928.
- Mukherjee I, Gopal M. Degradation of beta-endosulfan by Aspergillus Niger. Toxicological & Environmental Chemistry 1994; 46: 217-221.
- Mukherjee I, Mittal A. Bioremediation of endosulfan using Aspergillus terreus and Cladosporium oxysporum. Bulletin of Environmental Contamination and Toxicology 2005; 75: 1034-1040.
- Mukherjee R, Sinha A, Lama Y, Kumar V. Utilization of zero valent iron (ZVI) particles produced from steel industry waste for in-situ remediation of ground water contaminated with organo-chlorine pesticide heptachlor. International Journal of Environmental Research 2015; 9: 19-26.
- Munch DJ, and Hautman, D. P. Method 551.1: Determination of chlorination disinfection
  byproducts, chlorinated solvents, and halogenated pesticides/herbicides in drinking water
  by liquid-liquid extraction and gas chromatography with electron-capture detection.
  Methods for the Determination of organic compounds in drinking water. 1995.

- Mutiyar P, Mittal A, Pekdeger A. Status of organochlorine pesticides in the drinking water wellfield located in the Delhi region of the flood plains of river Yamuna. Drinking Water Engineering and Science 2011; 4: 51-60.
- Nath R, Saikia L, Choudhury G, Das P. Isolation of Shewanella algae from rectal swabs of patients with bloody diarrhoea. Indian Journal of Medical Microbiology 2011; 29: 422-425.
- Nealson KH, Scott J. Ecophysiology of the genus Shewanella. The Prokaryotes 2006: 1133-1151.
- Neyens E, Baeyens J. A review of classic Fenton's peroxidation as an advanced oxidation technique. Journal of Hazardous Materials 2003; 98: 33-50.
- Nicolopoulou-Stamati P, Maipas S, Kotampasi C, Stamatis P, Hens L. Chemical pesticides and human health: The urgent need for a new concept in agriculture. Frontiers in Public Health 2016; 4: 148.
- Ninkovic MB, Petrovic RD, Lauševic MD. Removal of organochlorine pesticides from water using virgin and regenerated granular activated carbon. Journal of the Serbian Chemical Society 2010; 75.
- Noubactep C. A critical review on the process of contaminant removal in Fe<sup>0</sup>-H<sub>2</sub>O systems. Environmental Technology. 2008; 29: 909-20.
- Ofomaja AE. Kinetic study and sorption mechanism of methylene blue and methyl violet onto mansonia (Mansonia altissima) wood sawdust. Chemical Engineering Journal 2008; 143: 85-95.

- Ohashi N, Tsuchiya Y, Sasano H, Hamada A. Screening on reactivity of organic pesticides with ozone in water and their products. Japanese Journal of Toxicology and Environmental Health 1993; 39: 522-533.
- Ormad MP, Miguel N, Claver A, Matesanz JM, Ovelleiro JL. Pesticides removal in the process of drinking water production. Chemosphere 2008; 71: 97-106.
- Paknikar KM, Nagpal V, Pethkar AV, Rajwade JM. Degradation of lindane from aqueous solutions using iron sulfide nanoparticles stabilized by biopolymers. Science and Technology of Advanced Materials 2005; 6: 370-374.
- Pan H-W, Lei H-J, He X-S, Xi B-D, Han Y-P, Xu Q-G. Levels and distributions of organochlorine pesticides in the soil–groundwater system of vegetable planting area in Tianjin City, Northern China. Environmental Geochemistry and Health 2017; 39: 417-429.
- Pan X, Lin D, Zheng Y, Zhang Q, Yin Y, Cai L, Fang H, Yu Y. Biodegradation of DDT by Stenotrophomonas sp. DDT-1: characterization and genome functional analysis. Scientific Reports 2016; 6: 21332.
- Pang W, Gao N, Xia S. Removal of DDT in drinking water using nanofiltration process. Desalination 2010; 250: 553-556.
- Park J, Comfort SD, Shea PJ, Kim JS. Increasing Fe<sup>0</sup>-mediated HMX destruction in highly contaminated soil with didecyldimethylammonium bromide surfactant. Environmental Science & Technology 2005; 39: 9683-9688.
- Parra S, Elena Stanca S, Guasaquillo I, Ravindranathan Thampi K. Photocatalytic degradation of atrazine using suspended and supported TiO<sub>2</sub>. Applied Catalysis B: Environmental 2004; 51: 107-116.

- Patil K, Matsumura F, Boush G. Degradation of endrin, aldrin, and DDT by soil microorganisms. Applied Microbiology 1970; 19: 879-881.
- Pazou EYA, Boko M, Van Gestel CA, Ahissou H, Lalèyè P, Akpona S, van Hattum B, Swart K, van Straalen NM. Organochlorine and organophosphorous pesticide residues in the Ouémé River catchment in the Republic of Bénin. Environment International 2006; 32: 616-623.
- Peterson SM, Batley GE. The fate of endosulfan in aquatic ecosystems. Environmental Pollution 1993; 82: 143-152.
- Phu N. Evaluating pilot scale slow sand filtration columns to effectively remove emerging contaminants in recycled water. Doctoral Dissertation, UC Riverside, 2016.
- Pillai HP, Kottekottil J. Nano-phytotechnological remediation of endosulfan using zero valent iron nanoparticles. Journal of Environmental Protection 2016; 7: 734.
- Plakas KV, Karabelas AJ. Removal of pesticides from water by NF and RO membranes—a review. Desalination 2012; 287: 255-265.
- Podowski AA, Banerjee BC, Feroz M, Dudek MA, Willey RL, Khan MAQ. Photolysis of heptachlor and cis-chlordane and toxicity of their photoisomers to animals. Archives of Environmental Contamination and Toxicology 1979; 8: 509-518.
- Pokethitiyook P, Poolpak T. Heptachlor and its metabolite: accumulation and degradation in sediment. Pesticides-Recent Trends in Pesticide Residue Assay. IntechOpen 2012.
- Poznyak TI, Chairez Oria I, Poznyak AS. Biodegradation. In: Ozonation and Biodegradation in Environmental Engineering. Elsevier 2019: 353-388.

- Prado G, Bhalli JA, Marcos R. Genotoxicity of heptachlor and heptachlor epoxide in human TK6 lymphoblastoid cells. Mutation Research/Genetic Toxicology and Environmental Mutagenesis 2009; 673: 87-91.
- Qiu X, Zhu T, Li J, Pan H, Li Q, Miao G, Gong J. Organochlorine pesticides in the air around the Taihu Lake, China. Environmental Science & Technology 2004; 38: 1368-1374.
- Ranade VV, Bhandari VM. Industrial wastewater treatment, recycling and reuse: Butterworth-Heinemann, Elsevier 2014.
- Rani K, Dhania G. Bioremediation and biodegradation of pesticide from contaminated soil and water-a noval approach. International Journal of Current Microbiology and Applied Sciences 2014; 3: 23-33.
- Rani M, Shanker U, Jassal V. Recent strategies for removal and degradation of persistent & toxic organochlorine pesticides using nanoparticles: a review. Journal of Environmental Management 2017; 190: 208-222.
- Ratola N, Botelho C, Alves A. The use of pine bark as a natural adsorbent for persistent organic pollutants–study of lindane and heptachlor adsorption. Journal of Chemical Technology & Biotechnology 2003; 78: 347-351.
- Reynolds G, Graham N, Perry R, Rice R. Aqueous ozonation of pesticides: a review. Ozone: Science & Engineering 1989; 11: 339-382.
- Ribeiro AR, Nunes OC, Pereira MF, Silva AM. An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU. Environment International 2015; 75: 33-51.
- Roche P, Prados M. Removal of pesticides by use of ozone or hydrogen peroxide/ozone. Ozone: Science & Engineering 1995; 17: 657-672.

- Rodante F, Marrosu G, Catalani G. Thermal analysis and kinetic study of decomposition processes of some pesticides. Journal of Thermal Analysis and Calorimetry 1992; 38: 2669-2682.
- Rodríguez AGP, López MIR, Casillas ÁD, León JAA, Banik SD. Impact of pesticides in karst groundwater. Review of recent trends in Yucatan, Mexico. Groundwater for Sustainable Development 2018; 7: 20-29.
- Ru J, Liu H, Qu J, Wang A, Dai R. Removal of dieldrin from aqueous solution by a novel triolein-embedded composite adsorbent. Journal of Hazardous Materials 2007; 141: 61-69.
- Sankararamakrishnan N, Kumar Sharma A, Sanghi R. Organochlorine and organophosphorous pesticide residues in ground water and surface waters of Kanpur, Uttar Pradesh, India. Environment International 2005; 31: 113-120.
- Satapanajaru T, Anurakpongsatorn P, Pengthamkeerati P. Remediation of DDT-contaminated water and soil by using pretreated iron byproducts from the automotive industry. Journal of Environmental Science and Health, Part B 2006; 41: 1291-1303.
- Sayles GD, You G, Wang M, Kupferle MJ. DDT, DDD, and DDE dechlorination by zero-valent iron. Environmental Science & Technology 1997; 31: 3448-3454.
- Scherer MM, Balko BA, Tratnyek PG. The role of oxides in reduction reactions at the metalwater interface. ACS Symposium Series 1999; 715: 301-322.
- Schrick B, Blough JL, Jones AD, Mallouk TE. Hydrodechlorination of trichloroethylene to hydrocarbons using bimetallic nickel– iron nanoparticles. Chemistry of Materials 2002; 14: 5140-5147.

- Schwarzenbach G, Imboden and Dieter. Direct Photolysis. Environmental Organic Chemistry. John Wiley & Sons, Inc., 2005.
- Senthilnathan J, Philip L. Removal of mixed pesticides from drinking water system by photodegradation using suspended and immobilized TiO<sub>2</sub>. Journal of Environmental Science and Health Part B 2009; 44: 262-270.
- Seyhi B, Drogui P, Gortares-Moroyoqui P, Estrada-Alvarado MI, Alvarez LH. Adsorption of an organochlorine pesticide using activated carbon produced from an agro-waste material.
   Journal of Chemical Technology & Biotechnology 2014; 89: 1811-1816.
- Shah NS, He X, Khan HM, Khan JA, O'Shea KE, Boccelli DL, Dionysiou DD. Efficient removal of endosulfan from aqueous solution by UV-C/peroxides: a comparative study. Journal of Hazardous Materials 2013; 263: 584-592.
- Shakerkhatibi M, Mosaferi M, Jafarabadi MA, Lotfi E, Belvasi M. Pesticides residue in drinking groundwater resources of rural areas in the northwest of Iran. Health Promotion Perspectives 2014; 4: 195-205.
- Shih Y-H, Tai Y-T. Reaction of decabrominated diphenyl ether by zerovalent iron nanoparticles. Chemosphere 2010; 78: 1200-1206.
- Shih YH, Hsu CY, Su YF. Reduction of hexachlorobenzene by nanoscale zero-valent iron: kinetics, pH effect, and degradation mechanism. Separation and Purification Technology 2011; 76: 268-74.
- Shin H-Y, Singhal N, Park J-W. Regeneration of iron for trichloroethylene reduction by Shewanella alga BrY. Chemosphere 2007; 68: 1129-1134.
- Shivaramaiah H, Sanchez-Bayo F, Al-Rifai J, Kennedy I. The fate of endosulfan in water. Journal of Environmental Science and Health Part B 2005; 40: 711-720.

- Shrivas K, Ghosale A, Nirmalkar N, Srivastava A, Singh SK, Shinde SS. Removal of endrin and dieldrin isomeric pesticides through stereoselective adsorption behavior on the graphene oxide-magnetic nanoparticles. Environmental Science and Pollution Research 2017; 24: 24980-24988.
- Srinivas J, Pillai M, Vinod V, Dinesh RK. Skin and soft tissue infections due to Shewanella algae–an emerging pathogen. Journal of Clinical and Diagnostic Research 2015; 9: DC16-DC20.
- Shukla G, Kumar A, Bhanti M, Joseph PE, Taneja A. Organochlorine pesticide contamination of ground water in the city of Hyderabad. Environment International 2006; 32: 244-247.
- Singh SP, Bose P. Degradation kinetics of Endosulfan isomers by micron-and nano-sized zero valent iron particles (MZVI and NZVI). Journal of Chemical Technology & Biotechnology 2016; 91: 2313-2321.
- Singh SP, Bose P. Reductive dechlorination of endosulfan isomers and its metabolites by zerovalent metals: reaction mechanism and degradation products. RSC Advances 2017; 7: 27668-27677.
- Sivavec T, Horney D. Reduction of chlorinated solvents by Fe (II) minerals. In Abstracts of Papers of the American Chemical Society. 1997; 213: 30-ENVR.
- Smith E, Smith J, Naidu R, Juhasz A. Desorption of DDT from a contaminated soil using cosolvent and surfactant washing in batch experiments. Water, Air, and Soil Pollution 2004; 151: 71-86.
- Snedeker SM. Pesticides and breast cancer risk: a review of DDT, DDE, and dieldrin. Environmental Health Perspectives 2001; 109: 35-47.

- Sotelo JL, Ovejero G, Delgado JA, Martínez I. Comparison of adsorption equilibrium and kinetics of four chlorinated organics from water onto GAC. Water Research 2002; 36: 599-608.
- Speight JG. Environmental organic chemistry for engineers: Butterworth-Heinemann, Elsevier 2016.
- Stern AH. Hazard identification of the potential for dieldrin carcinogenicity to humans. Environmental Research 2014; 131: 188-214.
- Stookey LL. Ferrozine-a new spectrophotometric reagent for iron. Analytical Chemistry 1970; 42: 779-781.
- Sun Y-P, Li X-Q, Cao J, Zhang W-X, Wang HP. Characterization of zero-valent iron nanoparticles. Advances in Colloid and Interface Science 2006; 120: 47-56.
- Sun Y, Iris K, Tsang DC, Cao X, Lin D, Wang L, Graham NJ, Alessi DS, Komárek M, Ok YS, Feng Y. Multifunctional iron-biochar composites for the removal of potentially toxic elements, inherent cations, and hetero-chloride from hydraulic fracturing wastewater. Environment International 2019; 124: 521-532.
- Tang X, Zhang Q, Liu Z, Pan K, Dong Y, Li Y. Removal of Cu (II) by loofah fibers as a natural and low-cost adsorbent from aqueous solutions. Journal of Molecular Liquids 2014; 199: 401-407.
- Tewari L, Saini J, Arti. Bioremediation of pesticides by microorganisms: general aspects and recent advances. In book: Bioremediation of Pollutants, I.K. International Publishing House Pvt. Ltd 2012.
- Tian H, Li J, Mu Z, Li L, Hao Z. Effect of pH on DDT degradation in aqueous solution using bimetallic Ni/Fe nanoparticles. Separation and Purification Technology 2009; 66: 84-89.

- Tomlin C. The Pesticide manual incorporating the agrochemical handbook. British Crop Protection, Surrey, England 1994.
- UNEP. Final act of the conference of plenipotentiaries on the Stockholm Convention on Persistent Organic Pollutants (POPs), United Nations Environment Program, Geneva, Switzerland 2001.
- USEPA. Drinking Water Standards and Health Advisories: United States Environmental Protection Agency, Office of Water, 2004.

USEPA. National Primary Drinking Water Regulations 2018.

- Varela O. Oxidative reactions and degradations of sugars and polysaccharides. Advances in Carbohydrate Chemistry and Biochemistry 2003; 58: 307-369.
- Vega M, Romano D, Uotila E. Lindane (Persistent Organic Pollutant) in the EU. Directorate General for Internal Policies. Policy Department C: Citizens' Rights and Constitutional Affairs. Petitions (PETI). PE 571.398, 2016.
- Vela N, Pérez Lucas G, Fenoll J, Navarro S. Recent overview on the abatement of pesticide residues in water by photocatalytic treatment using TiO<sub>2</sub>. Application of Titanium Dioxide 2017.
- Waldman M, Shevah Y. Biodegradation and leaching of pollutants: Monitoring aspects (Technical Report). Pure and Applied Chemistry 1993; 65: 1595-1603.
- Wang S, Chen S, Wang Y, Low A, Lu Q, Qiu R. Integration of organohalide-respiring bacteria and nanoscale zero-valent iron (Bio-nZVI-RD): a perfect marriage for the remediation of organohalide pollutants? Biotechnology Advances 2016; 34: 1384-1395.
- Wang X, Chen C, Chang Y, Liu H. Dechlorination of chlorinated methanes by Pd/Fe bimetallic nanoparticles. Journal of Hazardous Materials 2009a; 161: 815-823.

- Wang Z, Peng Pa, Huang W. Dechlorination of γ-hexachlorocyclohexane by zero-valent metallic iron. Journal of Hazardous Materials 2009b; 166: 992-997.
- Weber J, Halsall CJ, Muir D, Teixeira C, Small J, Solomon K, Hermanson M, Hung H,Bidleman T. Endosulfan, a global pesticide: a review of its fate in the environment andoccurrence in the Arctic. Science of the Total Environment 2010; 408: 2966-2984.
- WHO. DDT and its derivatives. Environmental aspects. Environmental Health Criteria. 83, 1989.
- WHO. Aldrin and dieldrin in drinking-water, background document for development of WHO guidelines for drinking-water quality 2003.
- WHO. Endrin in drinking-water, background document for development of WHO guidelines for drinking-water quality 2004.
- WHO. Guidelines for drinking-water quality, First Addendum to third edition. Vol 1, 2006.
- WHO. The use of DDT in malaria vector control: WHO position statement. Geneva: World Health Organization 2011.
- Wilkin RT, McNeil MS. Laboratory evaluation of zero-valent iron to treat water impacted by acid mine drainage. Chemosphere 2003; 53: 715-725.
- Wu C, Luo Y, Gui T, Huang Y. Concentrations and potential health hazards of organochlorine pesticides in shallow groundwater of Taihu Lake region, China. Science of the Total Environment 2014; 470-471: 1047-1055.
- Xiao PF, Kondo R. Biodegradation of dieldrin by cordyceps fungi and detection of metabolites. Applied Mechanics and Materials. 2013; 295: 30-34.
- Xiao W, Jones AM, Li X, Collins RN, Waite TD. Effect of Shewanella oneidensis on the kinetics of Fe (II)-catalyzed transformation of ferrihydrite to crystalline iron oxides. Environmental Science & Technology 2017; 52: 114-123.

- Xiong Y, Shi L, Chen B, Mayer MU, Lower BH, Londer Y, Bose S, Hochella MF, Fredrickson JK, Squier TC. High-affinity binding and direct electron transfer to solid metals by the Shewanella oneidensis MR-1 outer membrane c-type cytochrome OmcA. Journal of the American Chemical Society 2006; 128: 13978-13979.
- Xu X, Yang H, Li Q, Yang B, Wang X, Lee FSC. Residues of organochlorine pesticides in near shore waters of LaiZhou Bay and JiaoZhou Bay, Shandong Peninsula, China. Chemosphere 2007; 68: 126-139.
- Yadav IC, Devi NL, Syed JH, Cheng Z, Li J, Zhang G, Jones KC. Current status of persistent organic pesticides residues in air, water, and soil, and their possible effect on neighboring countries: A comprehensive review of India. Science of the Total Environment 2015; 511: 123-137.
- Yang L, Li M, Li W, Jiang Y, Qiang Z. Bench- and pilot-scale studies on the removal of pesticides from water by VUV/UV process. Chemical Engineering Journal 2018; 342: 155-162.
- Yang S-C, Lei M, Chen T-B, Li X-Y, Liang Q, Ma C. Application of zerovalent iron (Fe<sup>0</sup>) to enhance degradation of HCHs and DDX in soil from a former organochlorine pesticides manufacturing plant. Chemosphere 2010; 79: 727-732.
- Yang X, Wang S, Bian Y, Chen F, Yu G, Gu C, Jiang X. Dicofol application resulted in high DDTs residue in cotton fields from northern Jiangsu province, China. Journal of Hazardous Materials 2008; 150: 92-98.
- Yang Z, Wang XL, Li H, Yang J, Zhou LY, Liu YD. Re-activation of aged-ZVI by iron-reducing bacterium Shewanella putrefaciens for enhanced reductive dechlorination of trichloroethylene. Journal of Chemical Technology & Biotechnology 2017; 92: 2642-9.
- Yao CD, Haag WR. Rate constants for direct reactions of ozone with several drinking water contaminants. Water Research 1991; 25: 761-773.
- Yazgan MS, Kinaci C, Toroz I. Ozonation of aqueous solution of alpha endosulfan. Journal of Environmental Science and Health, Part B 2003; 38: 843-853.
- Yedla S, Dikshit AK. Removal of Endosulfan from Water Using Wood Charcoal—Adsorption and Desorption. Journal of Environmental Engineering 2008; 134: 102-109.
- Yin W, Wu J, Li P, Wang X, Zhu N, Wu P, Yang B. Experimental study of zero-valent iron induced nitrobenzene reduction in groundwater: The effects of pH, iron dosage, oxygen and common dissolved anions. Chemical Engineering Journal 2012; 184: 198-204.
- Yonli AH, Batonneau-Gener I, Koulidiati J. Adsorptive removal of α-endosulfan from water by hydrophobic zeolites. An isothermal study. Journal of Hazardous Materials 2012; 203-204: 357-362.

Zhang Y, Li Y, Zheng X. Removal of atrazine by nanoscale zero valent iron supported on organobentonite. Science of the Total Environment 2011;409: 625-30.

- Zhou R, Zhu L, Chen Y. Levels and source of organochlorine pesticides in surface waters of Qiantang River, China. Environmental Monitoring and Assessment 2008; 136: 277-287.
- Zhou R, Zhu L, Yang K, Chen Y. Distribution of organochlorine pesticides in surface water and sediments from Qiantang River, East China. Journal of Hazardous Materials 2006; 137: 68-75.
- Zinovyev SS, Shinkova NA, Perosa A, Tundo P. Liquid phase hydrodechlorination of dieldrin and DDT over Pd/C and Raney-Ni. Applied Catalysis B: Environmental 2005; 55: 39-48.

Dieldrin	Endrin
Phenol	Phenol
2,4-Di-tert-butylphenol	2,4-Di-tert-butylphenol
Heptanal	Octanal
Octanal	Nonanal
Nonanal	1-Hexanol, 2-ethyl
Decanal	1-Octanol
1-Heptanol	1-nonanol
1-Octanol	2-Decanone
1-Decanol	
2-Heptanone	
1-Dodecene	
Dodecanal	
Phenol, 2,6-bis(1,1-dimethylethyl)-4-(1-	
methylpropyl)-	
Butanoic acid, 4-hydroxy-	1,3-Dimethyl-5-(1',1',2'-trichloro-3- ethylallyl)benzene
Naphthalene, 1,3-dimethyl-	2,6-Bis(3,3-dichloroprop-2- envlidene)cvclohexanone
Propanoic acid, 2-methyl-, 2,2-dimethyl-1-(2- hydroxy-1-methylethyl)propyl ester	Endrin ketone, endrin aldehyde
Phenol 2 6-bis(1 1-dimethylethyl)-4-(1-	1-(4-Chlorophenyl)-3-(2.6-
methylpropyl)-	dichlorophenyl)prop-2-en-1-one
Methylnaphthalene	3.5-Di-tert-Butyl-4-hydroxybenzaldehyde
1,4-Dichloro-4-ethylheptane	Phenol, 4.4'-(1-methylethylidene)bis-
4-Ethylbenzoic acid, cyclopentyl ester	2.7:3.6-dimethanonaphth[2.3-
	b]oxirene, 3, 4, 6, 9, 9-pentachloro-
	1a,2,2a,3,6,6a,7,7a-octahydro
2-Heptanone	•
2.5-Cvclohexadiene-1.4-dione, 2.6-bis(1.1-	
dimethylethyl)-	
5,8-Dimethyl-1,2,3,4-tetrahydro-1-naphthol	
Phenol, 2-(1,1-dimethylethyl)-	

## APPENDIX. DEGRADATION BY-PRODUCTS OF DIELDRIN AND ENDRIN