Pesticides and Ozofractionation: An Investigation to Remove Organic and Inorganic Contaminants from Industrial Wastewater

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During the last 50 years, a significant amount of research has been carried out on the treatment of pesticides and industrial wastewater using physico-chemical methods. However, ozofractionation has not been investigated as a means to remove pesticides from wastewater, possibly because it is more typically associated with the treatment of water in aquariums. Therefore, the present study was undertaken to assess the impact of ozofractionation on pesticide-contaminated industrial wastewater. A sample was collected from a storm water holding tank at a pesticide manufacturing site in Australia containing chlorpyrifos, dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethylene (DDE), arsenic and zinc. After preliminary analysis, the sample was subjected to ozofractionation and promising results were observed. Chlorpyrifos, DDT, DDE, arsenic and zinc concentrations were 7.2 µg/L, 108 µg/L, 9.5 µg/L, 0.14 mg/L and 0.44 mg/L before treatment and reduced to < 0.5 µg/L, < 2. 0 µg/L, < 0.5 µg/L, 0.01 mg/L and < 0.005 mg/L respectively after treatment. Before treatment, pesticides and metal concentrations were beyond discharge limits, however ozofractionation brought them within the permissible limits set by environmental agencies and processed wastewater could be discharged to an aquatic ecosystem. These findings indicate that ozofractionation may be a useful method for destroying intractable pesticides and removing heavy metals from industrial wastewater.

Keywords: Pesticides, Chlorpyrifos, Dichlorodiphenyltrichloroethane, Dichlorodiphenyldichloroethylene, Ozofractionation.

INTRODUCTION

Due to their persistent nature and toxicological properties, an extensive corpus of scientific literature concerns itself with the treatment of pesticides in the environment. A pesticide is a chemical compound used to repel or kill pests, which can include insects, animals, weeds, fungi and microorganisms, with most pesticides containing a range of toxic chemicals that are not only effective against target species but may also be unintentionally harmful to people, animals and/or the environment. As a consequence, governmental authorities regulate (and in some cases ban) pesticides to protect public health and the environment, although the widespread use of pesticides and their unconstrained application in some countries remain of concern and historical pesticide practices have left lasting environmental and health legacies, many of which need to be managed for many decades after initial application[1,2]. For these reasons, pesticides must be safely handled, stored, applied and monitored and where possible their long-term residual effects treated[3].

The specific adverse and long-term health effects of pesticides depend largely on the type and amount of pesticide used. Some pesticides, such as organophosphates and carbamates, affect the human nervous system[4] while others distress the skin and eyes[5]; pesticides are also able to affect the hormone and endocrine systems[6]. Perhaps more worrying are findings that some pesticides, such as chlorpyrifos, are carcinogenic[7]. Metabolites or "breakdown products" of pesticides (so-called pesticide "oxons"), produced as a result of degradation of pesticides in water, soil or living organisms such as chlorpyrifos-oxon, are more hazardous than the parent pesticide[8].

Similarly, the "inert" ingredients in a pesticide, which may constitute more than 95 % of the chemical compound, can be more dangerous than the listed "active" ingredient (for example, more than 200 chemicals used as inert ingredients in pesticides are classified as "hazardous" pollutants), the inert ingredients in one pesticide may be the active ingredient in another pesticide (394 inert chemicals were listed as active ingredients in other pesticide products[9]) and chemicals that are considered hazardous in one application may be labelled "inert" when used in pesticides[9,10]. The classification and function of various pesticides are presented in Table-1.

These types of pesticides can be further classified by their chemical composition. For example, organochlorine insecticides have mostly been discontinued due to their acutely toxic health

TABLE-1
GENERAL CLASSIFICATION AND FUNCTION OF VARIOUS PESTICIDES

Pesticide type	Function
Algaecides	To kill or reduce algae in dams, water tanks, swimming pools and spas
Antifouling agents	To kill or discourage organisms that attach to underwater surfaces in seawater, such as boat hulls and marinas, including tributyltin, one of the most toxic substances introduced to the environment by humans
Antimicrobials	To kill microorganisms, such as bacteria and viruses
Attractants	To lure pests, such as insects or rodents, to a trap in which they are killed
Fungicides	To kill fungi, including molds, mildews and rusts
Herbicides	To kill weeds and other unwanted plants that grow; herbicides constitute one of the largest worldwide category of pesticide application
Insecticides	To kill insects and other arthropods, another category of large-scale application, including DDT and chloryrifos
Repellents	To repel a variety of organisms, including ants and birds

and environmental effects and their persistence in the environment[11]; the half-life of organochlorine pesticides is between 2 and 15 years. Carbamate pesticides are organic compounds derived from carbamic acid (NH_2COOH); these include carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl N-methylcarbamate), one of the most toxic pesticides ever manufactured[12]. Carbofuran is used to control insects in crops, but is particularly toxic to birds[13]; for this reason it has been banned in most countries. Carbofuran is also one of the most acutely toxic pesticides to humans; repeated exposure can lead to reproductive disorders[14] and can affect the human nervous system by disrupting enzymic metabolism[15], however these effects are usually reversible.

Organophosphate pesticides (OPs) are insecticides (although some target parasitic infections in cows, pigs and horses) and many are extremely toxic (*e.g.*, organophosphate pesticides were used in World War II as nerve agents[16]). Organophosphate pesticides are also toxic to wildlife and humans and research suggests a link between organophosphate pesticides and neurobehavioral development of fetuses and children[17] and organophosphate pesticides adversely affect the central nervous system[18]. Of relevance to this study is the organophosphate pesticide chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate or $C_9H_{11}Cl_3NO_3PS$). The residues of chlorpyrifos in food and drinking water and the presence of both chlorpyrifos and chlorpyrifos-oxon in the environment, pose a significant risk to human health, particularly infants and children[19]. Studies on the fate of chlorpyrifos in the environment indicate that when used on some crops it poses a broad range of risks. Moreover, there is no evidence to suggest that chlorpyrifos can be removed from drinking water by standard municipal water treatments, including granulated activated carbon and water softening[20]. Pyrethroid pesticides mimic naturally occurring molecules but are synthetically modified to increase their stability and persistence after application[21], making some pyrethroids toxic to the human nervous system[22]. With the declining use of organophosphates, which are more acutely toxic to birds and mammals than pyrethroid insecticides, the application of pyrethroids has increased during the past 10 to 15 years.

Also of relevance to this study is the pesticide dichlorodiphenyltrichloroethane (better known as DDT, $C_{14}H_9Cl_5$), one of the most well-known and controversial insecticides used in the world. Dichlorodiphenyltrichloroethane is a persistent organic pollutant (POP) and being hydrophobic, DDT is well absorbed by soil; depending on climatic conditions. Its half-life in soil can be up to 30 years. Loss and degradation of DDT are mostly due to stormwater runoff (*i.e.*, dissipation), volatilization and natural attenuation through biodegradation. Its breakdown products, dichlorodiphenyldichloroethylene (DDE, $C_{14}H_8Cl_4$) and dichlorodiphenyldichloroethane (DDD, $C_{14}H_{10}Cl_4$), are also persistent and have similar chemical and physical properties to DDT. Moreover, DDT's breakdown products can be transported from warmer regions of the world to the Arctic by a phenomenon known as "global distillation", wherein they bioaccumulate and bio-concentrate in the Arctic food web[23].

Dichlorodiphenyltrichloroethane is toxic to a range of marine animals (in addition to insects), including crayfish, shrimp and some species of fish. As reported over the last 40 years, DDT is reproductively toxic to some birds and is a reason for the decline in a variety of bird species in the U.S. due to eggshell thinning. Moreover, while DDT has also been found to bio-concentrate in beluga whales[24], DDE may be even more potent than DDT. Potential reactions of DDT in humans are genotoxicity and endocrine disruption[25] and it may induce enzymes to produce other genotoxic effects. Dichlorodiphenyltrichloroethane has also been linked to diabetes and liver, pancreatic and breast cancer and is a "probable" carcinogen, according to the World Health Organisation and others[25,26]. Epidemiological studies suggest that DDT and DDE cause leukaemia, lymphoma and testicular cancer and both have been linked to diabetes and pregnancy loss[27,28].

The health and environmental challenges associated with pesticides are generally considered in an agricultural rather than either an urban or industrial context, making systematic investigation of industrial waste uncommon. However, their long-term impact on contaminated soil and run-off in agricultural settings, as well as their bioaccumulation and bioconcentration in industrial and urban settings, are important.

In wastewater, a wide variety of physical, chemical and biological technologies have been deployed to destroy or remove POPs, including pesticides from the environment[29,30], although research has shown that pesticides in general are especially resistant to biodegradation, *i.e.*, to microbial or biological reactions[31]. Similarly, Köck-Schulmeyer's team[32] found that a variety of standard treatments provided at three different wastewater treatment plants to remove 22 different types of pesticides from wastewater had little or no impact on pesticide contamination and in some cases post-treatment

concentrations of pesticides actually went up mysteriously. These researchers also reported that due to extremely low concentrations of pesticides in wastewater, it was often difficult to locate instrumentation and analytical methods sophisticated enough to identify such concentrations, despite them being within the range of toxicity to humans.

However, the majority of treatment modalities investigated do not use oxidizing reagents. For example, Abdel-Gawad et al.[33] investigated the removal of malathion, imidacloprid and chlorpyrifos from wastewater using electrocoagulation. Misra et al.[34] examined treatment of pesticide-contaminated wastewater by coagulation and flocculation. Under the general category of "oxidation", some systems used advanced oxidation processes (AOP) and ozonation[35,36]. More recently, researchers have combined soil washing with various forms of oxidation and biological treatment of the flushing solution[37]. Oxidizing agents used in AOP and ozonation have included ozone (O_3), potassium permanganate ($KMnO_4$), sodium persulfate ($Na_2S_2O_8$), ascorbic acid ($C_6H_8O_6$), Fenton reagents, hydrogen peroxide (H_2O_2) and other sources of chemical energy. Irrespective of whether oxygen species are added directly as O_2 in oxidation or AOP systems or injected as O_3, they are designed to destroy organic compounds, including pesticides, via well-established chemical degradation or reduction reactions.

Most oxidation processes utilize aeration with atmospheric oxygen or pure oxygen injection (such as those related to biological aeration in bioreactors), but some use chemical reactions produced by hydroxyl radicals, such as those generated by potassium permanganate and hydrogen peroxide; these reactions are generally short-lived and produce strong oxidizing species[38,39]. For this reason, reaction vessels must be designed to accommodate short bursts of high temperature and the safety of operators, including the possibility for outgassing, are important considerations in this process.

While ozonation has mostly been used to breakdown organic contaminants in wastewater[40], it has also been applied in conjunction with other chemical additives to treat heavy metals in acid mine drainage[41]. Babu et al.[42] investigated three electrochemical techniques namely, electro-oxidation, electro-coagulation and electro-Fenton reactions, to treat pesticide effluent. The wastewater used in this experiment obtained from a pesticide manufacturing plant contained methyl-parathion (O,O-diethyl-O-4-nitro-phenylthiophosphate), atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine) and triazophos (O,O-diethyl O-1-phenyl-lH-1,2,4-triazol-3-yl phosphorothioate). However, these authors only reported changes in pH, chemical oxygen demand (which was reduced by the treatments) and TDS (which mysteriously increased as a result of the treatments), but incomprehensibly failed to report the effect of these electrochemical techniques on pesticide concentrations. Barbusiñski and Filipek[43] similarly used a Fentons reagent (i.e., H_2O_2) to investigate the removal of pesticides, including DDT and chlorfenvinphos, from industrial wastewater. Most of the pesticides in this experiment were completely degraded with the addition of 2.5 g/L of H_2O_2, however only at a concentration of 5.0 g/L were all pesticides completely removed and results repeatable. The most effective outcome was for fenitrothion (98-100 % reduction) and chlorfenvinphos

(97-100 % reduction), whereas most organochlorine pesticides were removed with an efficiency of 90 %.

A less understood oxidizing process in wastewater treatment is ozofractionation, most commonly associated with disinfecting water in aquariums, swimming pools and spas[44,45]. Like ozonation, ozofractionation injects ozone into the liquid waste stream; however ozofractionation has one key process difference: where standard ozonation "bubbles" O_3 into the waste stream, ozofractionation injects it into a foaming fractionator or chamber. Where simple oxidation and biological aeration techniques inject atmospheric oxygen into a liquid waste stream in order to create an air/water interface which causes contaminants to oxidize and where ozonation bubbles ozone through the liquid stream in order to expose contaminants to oxygen atoms with a larger oxygen/water interface thereby generating greater oxidising (i.e., reducing) reactions, ozofractionation pumps ozone into a foaming fractionator containing wastewater where millions of tiny bubbles of oxygen are generated (these foam-like bubbles have a diameter < 150 μm). The bubbles in an ozofrationator attract and oxidize contaminants in a way that is many times more aggressive than simple aeration, oxidation or ozonation because of the greater agitated oxygen/water surface area generated by the fractionator.

The ozofractionation process is further enhanced by the fact that ozone is more soluble in water than either atmospheric oxygen (which is only 20 % oxygen) or pure oxygen. While it is not within the scope of this paper to describe all known aeration, advanced oxidation processes, ozonation and ozofractionation reactions and processes (indeed many chemical reactions in both ozonation and ozofractionation are largely unknown to the scientific community due to difficulties associated with measuring oxidizing reactions which occur within nanoseconds inside closed-circuit reaction chambers), suffice it here to say that ozofractionation is a candidate for examination in the context of pesticide-contaminated wastewater treatment, particularly as ozone has been used effectively to destroy other complex organic compounds.

To this author's knowledge and as evidenced by the literature, there has been no investigation in the role of ozofractionation for the treatment of pesticide-contaminated wastewater. Even comprehensive surveys of current methods of wastewater treatment make little or no mention of ozofractionation as a viable approach to destroying organic contaminants in wastewater[46]. For this reason, the present study asked the following research question: Does ozofractionation destroy organic pesticide species in, and remove inorganic metals species from, industrial wastewater to a level allowing discharge to the environment?

EXPERIMENTAL

The ozofractionator used in this experiment was composed of the following unit processes: ozone generator (using tube corona discharge to produce ozone from atmospheric oxygen as $3O_2 + energy = 2O_3$ at a rate of about 3-5 percentage ozone by weight[47]) and inlet; wastewater inlet pipe and valve; a venturi pump for circulation of wastewater through the ozofractionator; a lower reaction chamber in which foaming bubbles of ozone were created and mixed with the liquid waste

stream; an upper reaction chamber in which the waste stream and bubbles were separated (O_3 and other residual gas precipitates were discharged from the top of the upper chamber) and a discharge pipe used for wastewater collection. In this experiment, the ozofractionator had a holding capacity of 10 L and a hydraulic retention time (HRT) of approximately 0.5 h; an ozofractionator does not operate under pressure or at elevated temperature. Using Henry's law, it was calculated that at 25 °C, a constant of approximately ± 10.6 mg/L of soluble ozone was reacting with pesticide-contaminated wastewater in the low chamber of the ozofractionator during the experiment (calculation of soluble ozone availability determined from Rice[45]).

According to Rice[45], at a pH of about 8.0 approximately half the ozone introduced into the water column is chemically consumed within 10 min producing hydroxyl free radicals (OH⁻), along with other potential oxidizing species, including hydroxide ions (OH⁻), perhydroxyl free radicals (HO_2^-) and superoxide anions (O_2^-)[45]. Of these, he maintains the hydroxyl free radicals are the most aggressive oxidants, even more aggressive than ozone itself. Thus, Rice refers to ozone providing a "direct" chemical reaction and hydroxyl free radicals providing an "indirect" chemical reaction. When solution pH is strongly acidic, direct reactions predominate; when pH is > 7.0 both direct and indirect reactions are prevalent. Rice also points out that ozone performs both oxidation and disinfection processes in water, but because the half-life of hydroxyl free radicals is no more than a few nanoseconds, hydroxyl free radicals only perform a disinfection function in water.

A 50 L representative sample of pesticide-contaminated wastewater was obtained from a chemical manufacturer in Brisbane, Australia. This wastewater was collected from a 20,000 L stormwater holding tank, which contained contaminated storm water run-off from the production site. The wastewater was pumped into and treated by the ozofractionator and representative untreated and treated samples were retained and sent to a NATA-certified laboratory in Brisbane within 24 h of collection and tested for a variety of analytes.

RESULTS AND DISCUSSION

The properties of untreated wastewater included pH = 8.0, chlorpyrifos = 7.2 µg/L, DDT = 108 µg/L, DDE = 9.5 µg/L, dieldrin < 0.5 µg/L, endrin < 0.5 µg/L, endosulfan sulfate < 0.5 µg/L, arsenic = 0.14 mg/L and zinc = 0.44 mg/L. It should

be noted that As is commonly used in so-called arsenical pesticides, due to its toxic chemical properties[48] and was probably present in this industrial wastewater in its pentavalent state (*i.e.*, as As^{5+}).

To put these pesticide and metal-metalloid concentrations into context, the allowable storm water concentrations for the manufacturer at this site when discharging to an aquatic ecosystem were pH = 6.5-8.5, chlorpyrifos ≤ 0.009 µg/L, DDT ≤ 0.0004 µg/L, dieldrin ≤ 0.01 µg/L, endrin ≤ 0.008 µg/L, endosulfan sulfate ≤ 0.01 µg/L, As ≤ 0.05 mg/L and Zn ≤ 0.015 mg/L[49]. No regulatory discharge limit has been determined for DDE and the detection limit for dieldrin, endrin and endosulfan sulfate was 0.5 µg/L. From this data, it can be seen that all contaminants (excluding pH) were significantly higher than allowable concentrations for wastewater discharge to aquatic ecosystems.

As shown in Table-2, as a result of oxofraction, pH stayed the same, chlorpyrifos was reduced from 7.2 µg/L to < 0.5 µg/L, DDT was reduced from 108 µg/L to < 2.0 µg/L, DDE was reduced from 9.5 µg/L to < 0.5 µg/L, As was reduced from 0.14 mg/L to 0.01 mg/L and Zn was reduced from 0.44 mg/L to < 0.005 mg/L as a result of ozofraction. All post-treatment concentrations for pesticides and Zn were below the limit of detection. The average reduction for organic contaminants was 100 % and the average reduction for inorganic contaminants was 96 %. Dieldrin, endrin and endosulfan sulfate were below the limit of detection both before and after treatment with ozofraction and were below the allowable discharge limit.

After treatment, the wastewater had a pH of 7.8, which was within the acceptable range of 6.5-8.5, thereby allowing the treated wastewater to be discharged to an aquatic ecosystem. Similarly, chlorpyrifos was < 0.5 µg/L (discharge criterion ≤ 0.009 µg/L), DDT was < 2.0 µg/L (discharge criterion ≤ 0.0004 µg/L), arsenic was < 0.01 mg/L (discharge criterion ≤ 0.05 mg/L) and zinc was < 0.005 mg/L (discharge criterion ≤ 0.015 mg/L), thereby meeting the allowable limits for discharge. Therefore, the question of whether or not ozofraction destroys organic pesticide species in and removes inorganic metal species from, industrial wastewater to an acceptable discharge level was answered in the affirmative.

The destruction of pesticide molecules as a result of exposure to oxygen is understandable. For example, the primary degradation pathway by ozonation for chloryrifos

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TABLE-2
RESULT OF OZOFRACTIONATION ON PESTICIDE- AND HEAVY METAL-CONTAMINATED WASTEWATER

Parameter	Wastewater before ozofractionation	Wastewater after ozofractionation	Reduction (%)	Detection limit
pH	8.0	7.8	0	–
Chlorpyrifos (µg/L)	7.2	< 0.5	99.9	0.5
DDT (µg/L)	108	< 2.0	100	2.0
DDE (µg/L)	9.5	< 0.5	100	0.5
Dieldrin (µg/L)	< 0.5	< 0.5	–	0.5
Endrin (µg/L)	< 0.5	< 0.5	–	0.5
Endosulfan sulfate (µg/L)	< 0.5	< 0.5	–	0.5
Total average organic change	–	–	100	–
As (mg/L)	0.14	0.01	93	0.001
Zn (mg/L)	0.44	< 0.005	99	0.005
Total average inorganic change	–	–	96	–

begins with uncoupling of the phosphorus ester bond to form the breakdown product trichloropyridinol (3,5,6-trichloro-2-pyridinol). However, the removal of arsenic and zinc from industrial wastewater using ozofractionation is intriguing. Typically, heavy metals and metalloid concentrations in wastewater are only reduced as a result of immobilization or sequestration through chemical reagent addition or through precipitation or filtration[46] not through chemical degradation. As a general rule, oxidation, aeration and ozonation therefore do not play a major role in removing inorganic species such as arsenic and zinc from wastewater, particularly at ambient temperatures, however after sand filtration the precipitates of Fe and Mn (but not SO_4) can be removed as a result of ozonation[50].

In this case it is more likely that both arsenic and zinc volatilized as a gas at ambient temperature. Mitra *et al.*[51] has observed that some municipal landfills "exhale" neo-generational organotin gases, including alkylated tin compounds dimethyldiethyltin, trimethylethyltin and propyltrimethyltin. Wehmeier and Feldmann[52] found that antimony can be distributed to the atmosphere in a gaseous state from the volatilization of metals in sewage sludge. Therefore, it is reasonable to assume that with the addition of O_3 to this industrial wastewater, both arsenic and zinc atoms bound to O and/or H atoms to form for example, alkylated arsine (AsH_3), and were distributed to the atmosphere. This chemical reduction phenomenon and the potential adverse health effects caused by arsine gas are discussed by Reigart and Roberts[48], particularly as they relate to arsenicals coming into contact with strong reducing agents like ozone. Such phenomena have been observed in the formation of alkylated arsine and other "non-identified" volatile arsenicals in gas and condensate formation[53], although these occurred under pressure. Similarly, research has shown that zinc volatilizes at high temperature[54], but there is little evidence it can volatilize at ambient temperatures.

One of the main objections raised in relation to the use of ozofractionation is its cost. While the argument is made about ozonation in general, by implication the same case can be made against ozofractionation. For example, it has been anecdotally proposed that the cost of generating ozone *via* corona discharge, ultraviolet radiation (UVR), electrolysis or radiochemistry makes the widespread adoption of ozonation to treat industrial wastewater "cost prohibitive" because it takes a significant amount of energy to generate ozone from atmospheric oxygen and the rate of conversion from O_2 to O_3 is low (*i.e.*, anywhere from 0.001 percentage ozone by weight for ultraviolet radiation up to 5 percentage ozone by weight for corona discharge). However, in recent years the cost of both ozone generators and their energy efficiency has improved markedly, and this argument carries less weight than it once did.

There are several areas of future research which this experiment suggests. Firstly, research could focus on better understanding the way ozofractionation volatilizes metals and metalloids; an examination of what the environmental fate of these gases might be could also be worthwhile in the context of human health and environment studies. Safety concerns related to the distribution of metals and metalloids to the atmosphere, despite being at extremely low concentrations, could be addressed. Poisoning from arsenical gas, for example, is unlikely (even for operators at a wastewater treatment plant in a pesticide manufacturing facility, although Reigart and Roberts maintain it has occurred[48]). However, given that arsines are powerful hemolysins (*i.e.*, destructors of red blood cells in the human body) and that as little as 0.5 h exposure to 25 parts per million are considered lethal[48], further analysis of the workplace health and safety of ozofractionation appears to be warranted, particularly in the context of pesticide degradation. Secondly, where possible research could investigate the breakdown pathways of pesticides in industrial wastewater. As discussed above, these reactions occur in nanoseconds within the fractionator's lower reaction chamber and are therefore difficult to measure. However, it may be possible to posit with greater accuracy how long-chain pesticide molecules are destroyed under reducing conditions by ozofractionation. These breakdown pathways are probably the same as the pathways of chemical degradation when using ozonation, but confirmation of these reactions may be justified.

Thirdly, a more thorough investigation into the cost *versus* treatment benefits of ozofractionation at an industrial scale need to be assessed. One of the obvious challenges related to this field of research is the fact that cost of electricity is different in different industrial settings, making reliable and valid conclusions about operating costs difficult. Nevertheless, a more comprehensive assessment of energy costs, ozone generation costs and efficiencies and pesticide destruction costs on a per litre basis needs to be carried out before this method can be considered economically viable for the pesticide manufacturing industry.

Fourthly, this experiment is rather crude in that the ozone concentrations of 3-5 percentage ozone by weight injected into the fractionator are estimates and the hydraulic retention time of contaminants in the fractionator have not been tightly controlled. Further work needs to be carried out to control the relationship between ozone concentrations, wastewater hydraulic retention time, pesticide concentrations and treatment outcomes. Without this knowledge, it will be difficult to draw reliable conclusions about the cost implications of deploying ozofractionation at a cost-efficient, industrial scale.

Finally, a more thorough assessment of the operability and scalability of ozofractionation in treating wastewater industrially should be carried out. For example, in addition to assessing workplace safety and cost efficiencies of ozofractionation, a larger and more rigorous on-site field trial would be worthwhile. Such a field trial focusing on increasing the size of both the ozone generator and ozofractionator, measuring contaminant reductions in wastewater from a real-world pesticide chemical plant and more closely controlling for variables such as variations in the waste stream and peak loads, would be worthwhile.

Conclusion

This study addressed the applicability of ozofractionation to the treatment of pesticide-and heavy metal-contaminated industrial wastewater. The pesticide and metal concentrations in the untreated pesticide manufacturing wastewater were significantly higher than the permissible limits. However, after treatment both pesticide and metal concentrations were within the allowable discharge limits set by the local environmental agency for this site. From these results, it is concluded that

ozofractionation can be used successfully for the remediation of pesticide contaminated wastewater and processed wastewater could be discharged into aquatic systems. This study may also be extendable to other types of industrial wastewater contaminated with organic and inorganic species.

However, cost analyses, applicability at large scale, efficiency and safety are important topics, which should be considered in future research. Moreover, the actual mechanisms for the degradation of pesticides generally and for metal removal specifically must be taken into account before generalizing these results.

ACKNOWLEDGEMENTS

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