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A Review on Treatment Methods for Pesticide Contaminated Water

Sayed Shujahuddin Rasooly[1], Mohsin Anwer[2], Gulafshan Tsnim[3]
[1]*(Department of Civil Engineering, Faculty of Engineering, Takhar University, Afghanistan)*
[2]*(Department of Civil Engineering, Zakir Husain College of Engineering and Technology, Aligarh Muslim University, India)*
[3]*(Department of Civil Engineering, Zakir Husain College of Engineering and Technology, Aligarh Muslim University, India)*

Abstract:
Pesticides have become the most extensively used pernicious chemicals known to human kind with long term health and environmental impacts on our ecosystem and biodiversity. One of the biggest issues in their excessive usage is water contamination which has been increasing at an alarming rate globally. Because of their persistent and easily transportable nature, these chemicals can enter and remain in water bodies for long periods of time. It is quite challenging to detect most of these pesticides and they cannot be treated by the conventional treatment processes. Many factors like media, humic content, light intensity, temperature, nature of active ingredient etc. play an important role in the process of degradation of these pesticides. Therefore, appropriate water treatment methods for the removal of these contaminants depend on their type and efficiency of the chosen process. This article reviews and discusses the various treatment technologies, like membrane filtration, Adsorption, absorption, iron enhanced sand filters (IESF), chlorination, hybrid techniques, advanced oxidation processes (AOPs) and other biological treatment methods, upcoming methods and latest research findings for the removal of such highly recalcitrant chemical from the surface water bodies. Many integrated techniques with conventional biological and physico-chemical treatments like activated sludge and adsorption, etc. that can be easily adopted are also mentioned. Pre or Post treatments often increases the efficiency of conventional approaches by many times.

Key Word: *Pesticide; Treatment methods; Membrane methods; Adsorption; Advanced Oxidation Processes; Biological treatments.*

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I. Introduction

As stated by World Health Organization (WHO), Persistent organic pollutants (POPs) are chemical substances of global concern. They are persistent in nature, are easily transported to far off areas away from original source, can bio-accumulate as well as bio-magnify in the ecosystem and as a result adversely impact human health and environment in general. Some of the most commonly found POPs used are Organochlorine&Organophosphorus pesticides, Industrial chemicals like polychlorinated biphenyls (PCB) as well as unintentionally produced by-products like dioxins. As defined by UN's Food and Agricultural Organization, 'Pesticides comprise of wide range of chemical substances like insecticides, fungicides, fumigants, bactericide, rodenticides, herbicides, etc. that are used for prevention, destruction or control of all kinds of weeds, pathogens, microbes, pests and vectors of human or animal disease. They can create nuisance, destroy properties, cause harm to food, agricultural commodities, wood products and animal or animal feedstuffs, etc. Other than chemical substances, pesticides also comprise of a number of biological agents, antimicrobial agents or disinfectants. All over the world, their frequent detection in both surface water and in groundwater has become a very common occurrencewhere the concentration of these highly toxic pollutants can range from < 0.1 mg/l to even >100 mg/L The increasing and extensive use of these chemicals in agriculture, commercial, industrial and other domestic activities has extreme destructive effects on our ecosystem and biodiversity.Their toxicity, carcinogenicity and mutagenicity make them harmful for life . As mentioned in a research in USA, it was found that more than 95% of sprayed insecticides and herbicides reached a destination other than their target species while being used for agricultural practices Once these persistent and highly toxic chemicals reach water bodies, they can impact the whole ecological food chain either directly or through bio magnification. Their ingestion and exposure causes a series of health issues and life threatening diseases in humans namely, skin diseases, Cancer, Parkinson's disease; asthma neurologic complications, developmental disabilities, hyperactivity disorder, respiratory issues and reproductive impairments (Jariyal*et al.* 2015).

Different treatment methods like biological, chemical, physical, physico-chemical, or a combination of these techniques are being used for Pesticide removal and treatment of the contaminated surface water and groundwater (Marican*et al.* 2018).There are several conventional methods which are widely acceptable for potable water treatment like coagulation–flocculation, activated sludge, adsorption, dual media filtration and sedimentation, etc. but they are not very effective in complete removal of these pesticide residues. Persistent contaminants require incorporationof 1 or more advanced final treatment step**s** for best results and complete treatment. This review provides an overview of most commonly used techniques, upcoming treatment methods and latest research findings for treatment of such contaminated surface water bodies.

II. Origin, Use and Classification of Pesticide

The earliest record of pesticide use dates back to 2000 BC where it was used in agriculture to protect the crops. Elemental sulfur was the first known pesticide and till the beginning of 20^{th} century, pesticide based on toxic heavy metals were predominantly used.With the commencement of 2^{nd} World War in the mid of 20^{th} Century, demand for pesticide grew significantly due to its applications in war and food production. Synthetic pesticides like DDT, 2,4-D and many others which are still in use to this day came into picture during this time. Till 1960s herbicides and pesticides containing triazine, (2, 4-D) and glyphosate had become very common.That is why, this point of time has been called as the "pesticide era". Apart from extensive use in agriculture, pesticides are also widely used in non-agricultural areas such as animal husbandry, public health, disinfection, fisheries and for domestic purposes. Industries manufacturing products like carpet, paint, paper, board, leather, wood preservation also use pesticides for wide range of miscellaneous applications

It is often difficult to pronounce and remember full chemical names of a pesticide. That is why coded names which are generally a shortened version of the full chemical name known as active ingredients are used (abbreviated as 'a.i').Of course, the active ingredient cannot be used on its own, but need additional diluting ingredients or additives namely, Solvents, carriers, synergists, emulsifiers, wetting, colouring& dispersing agents, etc. in order to make this suitable for practical purpose as well as it can be used effectively.

Pesticides also have number of bases for their Classifications and it is important to know them to get an idea of level of toxicity, environmental impact, properties andbehavior of any particular contaminant.

Table 1WHO (2020) Classification of Pesticides

WHO Class	Designation	LD50 for the rat (mg/kg body weight) Oral (mouth)	Dermal (skin)	Examples
Ia	Extremely hazardous	< 5	< 50	Aldicarb,Parathion,Hexachlorobenzene
Ib	Highly hazardous	5–50	50–200	Carbofuran,Calcium arsenate
II	Moderately hazardous	50–2000	200–2000	DDT,Carbosulfan,Chlordane
III	Slightly hazardous	Over 2000	Over 2000	Atrazine,Borax, Glyphosate
U	Unlikely to present acute hazard	5000 or higher		Carbetamide,Mancozeb, Phthalide, Zoxamide

The former WHO Classification scheme used prior to 2009 applied different criteria to liquids and solids but WHO now uses the Acute Toxicity Hazard Categories from the GHS i.e "The Globally Harmonized System of Classification and Labelling of Chemicals" as the starting point for classification as shown in Table 1.As per WHO, "Unless otherwise mentioned, the LD50 value is a statistical approximation of the amount of mg of toxicant per kg of body weight needed to kill 50% of a large population of test animals.. Lower the value of LD50, higher is the toxicity. Based on their chemical origin, Agro-pesticides can be divided into inorganic compounds, synthetic organic chemicals and bio-pesticides. Based on their chemical structure and composition, they are classified into four main categories i.e. organochlorines, organophosphorus, carbamates and pyrethroids. Another common classification is based on the target pest killed by the chemical pesticide as shown in Table 2 below.

Table 2 Classification of Commonly used pesticides and their examples

Type of Pesticide	Target Pests	Example
Insecticide	Insects	Organochlorideslike cyclodienes (which include aldrin, dieldrin, chlordane, heptachlor, and endrin), DDT, BHC, lindane, Chlorobenzilate and methoxychlor. Organophosphates and carbamates like parathion, Chlorpyrifos, diazinon ,carbaryl, carbofuran, oxamyl, aldicarb. Repellants like DEET (N,N-Diethyl-m-toluamide) and Bio insecticides like Bacillus Thuringiensis, BeauveriaBassiana.
Bactericide	Bacteria	Beta-lactam antibiotics and vancomycin,daptomycin, fluoroquinolones, metronidazole, nitrofurantoin, co-trimoxazole and telithromycin. Aminoglycosidic antibiotics
Rodenticide	Rodents, mice and rats	Warfarin, 1080 (sodium fluoroacetate) and red squill
Nematicide	Nematodes	TeloneII, Paladin (dimethyl disulphide or DMDS), Aldicarb(Temik) , chloropicrin, Vapam (metam sodium).
Herbicide	Undesirable plants	Chloroacetanilide herbicides like Alachlor, Metolachlor and Organic phosphorus herbicides like glyphosate Chlorophenoxy acid herbicides like 2,4-D; 2,4,5-T; MCPA; and silvex . Triazine herbicides like atrazine; cynazine ;hexazinone ; metribuzin; and simazine.
Fungicide	Fungis	Captan ,copper sulphate, folpet, mancozeb
Acasicide	Mites, ticks and spiders	DDT, Diazinon, carbaryl, permethrin, flumethrin,formamidines, and avermectins.
Larvicides	Larvae	Microbial larvicides , Bacillus sphaericus and Bacillus thuringiensisisraelensis, temephos, methoprene, oils, and monomolecular films.
Fumigants	Termites, bedbugs	Sulfur dioxide, carbon monoxide, hydrogen cyanide, and methyl bromide

III. Possible Reasons of Pesticide Occurrence in Water

Unsafe methods of disposal leads to the surface run off reaching surface water bodies like streams, rivers and lakes. Not only that, infiltration of these pesticide contaminated water and wastewater through leaching or seepage into the local soil reaches ground water and contaminates it as well. *Like other chemical impurities and pollutants, Pesticides can enter the hydrologic system either from Point or Non-point sources.*

a) *Point sources – Sources associated with specific points of release. For example: Sewage treatment plants, wastewater discharge facilities, Pesticide plants and Industries, accidental spills, illegal dumping etc.*
b) *Non-point sources – Sources which are widely dispersed. For example: Runoff from Agricultural land, Seepage into groundwater, Runoff from urban land use, etc.*

In most hydrologic settings, surface water bodies are much more at risk of pesticide contamination as compared to groundwater sources. Nowadays, water bodies are frequently reported to be contaminated with multi-pesticides and are likely to be present at detectable levels throughout most of the year .*Once pesticides and their residues reach the atmosphere,* surface water bodies*, or ground water, they move through the hydrologic system with air, water, or particles, depending on the chemical and physical properties of the compounds. Common factors influencing the level of contamination in water bodies are mentioned in Table 3 below.*

Table 3 Factors Affecting Pesticide Contamination of Water

Factors	Effect
Characteristics of Pesticide contaminant or residues present in the water:	Unique properties of pesticides, active substances, additives, degradate and contaminants present in them, all play a very important role in determining the extent of pollution in the water body.
Half-life of Pesticides:	Half-life refers to the stability of the pesticide. The more stable the pesticide, the longer it takes to break down and the higher is its persistence.
Solubility of Pesticides in water:	The majority of pesticides are water soluble, allowing them to be applied with water and absorbed by the target. The higher the pesticide's solubility, the greater the chance of leaching.
Rainfall:	High levels of rainfall raise the risk of pesticides contaminating water as surface runoff passes

	through pesticide-sprayed areas and flows directly into water bodies. Unexpected rain on a pesticide-treated area before it binds or degrades may bring the pesticide to surface water sources.
Drainage:	Water from excessive rainfall and irrigation cannot always be held within the soil structure. Therefore, pesticides and residues can be quickly transported to contaminate hydrologic systems through natural drainage, over a large geographical area.
Improper application rate, site or mode:	Poorly handling, illegal dumping, accidental spillage and excess application of these chemical agents above the required level are the most common culprits that lead to frequent detection of pesticides in water bodies. Another example is, intentional use of disinfectants in water treatment plants, which may lead to residues of these chemical agents in water for a long time.
Microbial activity:	Pesticides in the soil are primarily broken down by microorganisms. The Faster the microbial activity, quicker is the degradation. Evaporation and photodecomposition also lead to reduction of pesticide residues in hydrologic settings.
Irrigation Management:	This is necessary to reduce the risk of pesticides infiltrating or leaching into ground water, as well as to prevent pesticides from reaching surface water. Irrigating saturated soils or at a rate that exceeds the rate of soil penetration increases runoff, which can bring pesticides with it.

IV. Treatment methods

The treatment methods currently used for these polluted water can be broadly divided into four categories: 1) Thermal Treatments; 2) Chemical treatments; 3) Physical treatments; 4) Biological treatment. Nowadays, several conventional and modified methods are available for pesticide removal, like: Hydrolysis, Incineration, Advanced oxidation processes(O3/UV, Fenton oxidation, etc.), UV-TiO2 based Photocatalytic degradation , Combined photo-Fenton and biological oxidation, , Membrane filtration methods like Nano-filtration, Ultra Filtration, Reverse osmosis and Electro-dialysis, Ozonation, Coagulation, fluid extraction, solid phase extraction, and Adsorption, Absorption or Sorption (inorganic, organic absorbents and activated carbon), Composting, bio augmentation, phytoremediation and Aerobic degradation. Larramendy and Soloneski (2011) correctly quoted in their book that “At present the most recommended approach for dealing with POPs like pesticides and other harmful industrial chemicals isto incorporate in an integrated processof sequential operations which will ensure acceptable and requisite ultimate removal of all these pollutants as well as their residues”. An important point to note here is that the type of treatment process to be adopted depends on a number of factors, most importantly, the type and concentration of target contaminant/pesticide that we are dealing with. Reason being, as mentioned before, no single method is enough to remove all kinds of complex pesticides that are in use today. Every adopted process is influenced by a number of factors such as pH, temperature, matrix, characteristic of pesticide and investment cost, etc.

Membrane filtration (MF) methods (Nano-filtration (NF), Ultra Filtration (UF), Reverse osmosis (RO) and Electro dialysis (ED), etc.)

As per Karabelas and Plakas (2011), the majority of the pesticide compounds lie in the size range of 1 nm and have molecular weight cut off of (MWCO) > 200 Dalton. This property makes them suitable for removal or treatment through membrane processes. Charcosse (2009) divided the membrane technologies into 2 types for water treatment, i.e. pressure-driven (e.g., RO) and electrically driven (e.g., ED). Compared to NF, RO (lower permeability than NF) is generally more capital intensive and requires much higher investment costs due to the required higher pressures. The other advantages of using NF over RO systems is that it uses lower feed pressure and has lower Fouling rates. NF/RO systems are able to remove specific heavy metals, nitrates, hardness, microbial content (bacteria, viruses, etc.), COD, Total Dissolved salts and large organic molecules etc. very effectively from the water (Asad*et al.* 2020). In past decades, several advanced types of Nano-Filtration membranes (NF), ultralow pressure RO membranes (ULPRO**)** and thin film composite membranes (TFC or TFM),etc. have been developed and used for removal of pesticide traces in water bodies.

Table 4 Types of Membrane Processes

Membrane Process	Typical pore size (nm)	Pressure(bar)	Permeability ($Lm^{-2}h^{-1}bar^{-1}$)
Microfiltartion(MF)	50-1000	0.1 -2.0	> 50
Ultrafiltration(UF)	10-50	1.0 -5.0	10 - 50
Nanofiltration(NF)	< 2	5.0-20	1.4 - 12
Reverse Osmosis(RO)	< 1	10 - 100	0.05 -1.4

Karabelas and Plakas (2012) mentioned in their research some of the important Factors influencing the membrane treatment process such as membrane characteristics, retention properties of membrane, feed water composition, membrane fouling, operating parameters of the filtration system, modelling and prediction of pesticide rejection, etc. It is important to remember that pre-treatment is very important while using these membrane systems for ensuring no fouling and hence, long lasting functioning and less operational and maintenance expenses (Mehta *et al.* 2017). That is why, for optimum results, a conventional membrane treatment system like this one, includes pre-treatment, membrane filtration and a post-treatment too. Membrane based treatments are usually integrated with physical treatments like coagulation, adsorption and biological reactions for efficient removal of POPs. A very good example of the a large scale applicability of these membrane treatment systems are Méry-sur-Oise plant in the northern part of Paris, France where NF technology has been successfully producing drinking water from the river Oise, since 1999.

In a study, rejection of pesticides was evaluated using 4 different type of nano-filtration membranes i.e. NF70, NF45, UTC-20 and UTC-60 in which the NF70 membrane emerged as the best option. This membrane showed a rejection of around 90–95% for all components (i.e. dissolved organic compounds and organic micro pollutants like atrazine, simazine, diuron and isoproturon) with Nitrate and hardness rejection of 76% and 95%, respectively. In another research, an integrated approach of coagulation–adsorption–nano-filtration process to evaluate their efficiency in removal of Isoproturon (IPU) pesticide from contaminated lake and river water. The treatment reduced IPU content up to 3–4 ppb when surface waters were spiked with 1 ppm IPU, confirming that NF (Membrane used-NF 48,200 Dalton MWCO) incorporated with Pre-treatments like coagulation (using Powdered Activated Charcoal) and adsorption is an effective method for separation of these kinds of pesticides from water as well as in improving other water polluting parameters like pathogens, COD, TOC, and hardness Bodzek and Konieczny (2018) research further proved the same theory. Going forward, some researchers combined ultrafiltration and coagulation treatments to obtain pesticide removal efficiency of approximately 84% to 88% based on COD (Acero*et al.* 2012).Recently, combined reverse osmosis filtration and biodegradation has also been studied for the removal of target POPs leading to introduction of another novel hybrid treatment (Hylling*et al.* 2019). In a latest study on impact of solute properties on NF of pesticides, 4 different nanofiltration membranes DK, NF270, NF200, and NF90 were used for the pesticide retention performance in a stirred dead-end filtration system. Similar to some previous studies, here also, NF90 demonstrated the best pesticide retention with over 95 % for atrazine and approximately 80 % for dimethoate (Tan *et al.* 2019).

In a recent work, thin-film composite (TFC) polyamide nanofiltration (NF) membrane were tested for their ability to remove atrazine and diazinon from water. In every experiment, diazinon outperformed atrazine in terms of rejection. The water permeability and diazinon rejection of the 2 percent (w/v) TEA modified membrane increased from 22 l/m2/h and 95.2 percent for the unmodified membrane to around 41.56 l/m2/h and 98.8 percent for the unmodified membrane (Karimi*et al.* 2016). In another one, a experimental study was done to evaluate the removal of atrazine herbicide from water by polyelectrolyte multilayer membranes. The polyamide microfiltration membranes with chitosan/polystyrene sulfonate (CHI/PSS) functional layer showed removal efficiency for atrazine (ATZ). Xu (2005), Sharma and Bhattacharya (2017) and many others have mentioned another membrane based separation technology i.e. Electrodialysis (ED).It is an electric potential-driven treatment process whose basic principle of removal is similar through ion exchange reactions. In a study, it was reported that organochlorine insecticide Endosulfan (ES) showed high adsorption to the ED membranes (Banasiak*et al*. 2011). In another study, a hybrid process by coupling electrodialysis (ED) and nanofiltration (NF90) was proposed to treat highly contaminated and saline Mekong Delta surface. Using NF90, the optimal recovery rate of the NF stage varied from 30 to 50% depending on the salt content in the feed (Nguyen *et al.* 2019). Development of Mobile Membrane Filtration Units is also a worthy mentioning work in this area which was done with the objective of facilitating military out of area missions of the Bundeswehr. The german engineer's studies confirmed the ability of the water purification unit to completely remove all kinds of organic/inorganic contaminants, residues of pharmaceuticals and pathogens, etc. from the surface water.

Physical treatments like Adsorption, Absorption or Sorption using (inorganic, organic absorbents and activated carbon)

As per Al-Ghouti and Da'ana (2020) and numerous other researchers, Adsorption is one of the most well-known and cost effective water purification methods. Adsorbents are mainly classified into natural adsorbents and synthetic adsorbents. The advantage of using natural materials (for example: charcoal, clays, clay minerals, zeolites, and ores) is that they are relatively inexpensive, abundant in supply and have significant potential for enhancement of their adsorption capabilities. On the other hand, Synthetic adsorbents can be prepared from agricultural products and wastes, house hold wastes, Industrial wastes, sewage sludge. Polymeric adsorbents also lie in the same category. Domingues (2005) mentioned the range of waste materials that can be used starting from Fruit wastes, coconut shells, scrap tyres, bark and other tannin-rich products, sawdust, rice husk, petroleum wastes, fertiliser wastes, fly ash, sugar industry wastes, blast furnace slag, chitosan and seafood manufacturing wastes, seaweed and algae, peat moss, clays, red mud, zeolites, sediment and soil, ore minerals, and other waste materials. Modified polymer adsorbents are also used for the removal of organic pollutants from water and wastewater.

In another classification, Adsorbents have been categorized as : Carbonaceous Adsorbents, Agricultural Wastes Adsorbents, Polymeric Adsorbents, Industrial Wastes Adsorbents, Bio adsorbents and Miscellaneous Adsorbents (Ahmad *et al.* 2010).Owing to the expensive regeneration and unstable properties of AC, potential adsorbents such as the polymeric system have been developed to replace AC (Tahar*et al.* 2013).Low-cost alternative adsorbents (LCAs), which comprise of both natural and synthetic materials, are in use for removal of POPs. Another compound is Bio-char with different properties than AC, though both of them are carbon-rich material, Bio-char is a carbon-rich product generated from biomass through pyrolysis (Marican*et al.* 2018). Maximum adsorption capacities, efficiency, ease of modification and cost of bio-sorbents demonstrated that low-cost bio-sorbents obtained from lignocellulose and chitin/chitosan have high potential for removing SOPs such as phenols, PAHs, organic pesticides, organic herbicides from water.

Activated Carbon Filtration

Carbon adsorption is an undisputed, efficient, and reliable method for water and wastewater treatment. As per Gullon and Font (2001), this effective method has the capability to reduce the quantity of certain toxic organics, chlorine, lead, dissolved radon and harmless taste or odour-causing compounds in water. It is frequently used for pesticide removal from surface water bodies as well as for treating pesticide containing wastewater used in the pesticide industries. Zahoor (2013)credits the high surface area of Activated carbon (AC) which makes it an excellent adsorbent that offers great capacity for the trapping (adsorption) of pharmaceuticals, micro-pollutants and hydrophobic pesticides from water .Among these CAC (Colloidal Activated Carbon), GAC (Granular activated carbon), and PAC (Powdered activated carbon) are the more common adsorbents which are frequently applied in conventional laboratories or industrial columns for the treatment of water and wastewater (Jusoh*et al.* 2013). For example, PAC is used as an effective method in to remove residual pesticides in raw water during drinking water treatment. There are a variety of other AC materials, carbon cloth, electrodes, fibers and carbon black. There are numerous factors that affect the adsorption process of activated carbon i.e. structure, surface chemistry (kind and concentration of end groups), the chemical properties of adsorbate (functional groups, ionic nature, polarity, solubility, etc.) and the characteristics of the adsorption solution (pH, temperature, presence of other species, concentration of adsorbate, etc.)(Marczewski*et al.* 2016).For example: Several studies have reported that for activated carbon, maximum adsorption of residual pesticides (like, methoxychlor, atrazine, and methyl parathion) occurs at a low pH (Gupta *et al.* 2011). The table given below lists some research works and kinds of adsorbents used in them to give a basic idea about their applications in the field of water and wastewater treatment.

A study combined coagulation as well as integrated adsorption-coagulation system for removing multi-pesticides where the integrated system reported 50-60 percent removal more removal than the former method. In this case, Nano-clays were used as the adsorbent and alum + polyaluminium chloride (PAC) were used as the coagulants (Ahammed*et al.* 2015). Chaara*et al.* 2010 proved the effectiveness of high specific area activated carbon-cloth adsorbent (ACC) for adsorption of pesticides ametryn, diuron, dinose and aldicarb from aqueous solution. ACC showed maximum capacity of elimination for diuron. In another work, high adsorption ability of Mg/Al layered double hydroxides (LDHs) and their calcined products for pesticides contaminants like,2,4-dinitrophenol (DNP) and 2-methyl-4,6-dinitrophenol (DNOC) was demonstrated. In a latest study, a researcher synthesized and then evaluated the effectiveness of an iron catalyst supported on activated carbon for atrazine removal aqueous solutions. The resulting efficiency of the system was over 70% (Morales-Pérez *et al.* 2016). Shankar *et al.* (2020) developed a modified chitosan material bio-adsorbent for eliminating pentachlorophenol (PCP) from water. The modification improved the uptake capacity of Chitosan by a significant 75-95%. In an early study, Biochar capacity to sorb pesticides was studied and high capacity of sorption for atrazine and simazine was reported (Zheng*et al.* 2010). In another study, it was observed that within 1-3 days, poplar (BP) and conifer (BC) biochars completely removed Phenanthrene and pentachlorophenol from contaminated water (Rao *et al.* 2017).

A research work tested cotton and filter paper based adsorbents in the form of Magnetic and graphitic carbon nanostructures. Here, Filter paper based adsorbent showed better capacity of adsorption for pesticide (Maryam *et al.* 2012). Hussein and Fahmi (2016) in their study proved the high efficacy of activated carbon prepared from dried date pits for removal of Chlorophenol from water. In a latest study, a group of researchers demonstrated the use of Macadamia nutshell activated carbon (MAC) and grafted Macadamia nutshell activated carbon (GMAC) for chlorinated phenols, showing a maximum uptake of 75-85% (Machedi*et al.* 2019). Another study showcased the excellent adsorption capacity of chemically and thermally treated watermelon peels (TWMP) for the removal of methyl parathion (MP) pesticide from water (Memon*et al.* 2008). A study also explored the significant adsorption capacity of Activated carbon prepared from banana stalk (BSAC) for the removal of pesticides (Salman J *et al.* 2011). The next year, a group of researchers studied Activated carbon adsorbents made from lignocellulosic wastes of vegetable origin (coffee grounds (CG), melon seeds (MS) and orange peels (OP)) for removal of Nitrophenols. The achieved maximum adsorption ranged between 70-90% (Djilani*et al.* 2012).

Iron-enhanced sand filter

The major source of the contaminants of emerging concerns (CECs), found usually in the urban rivers, are the wastewater effluents. The significant component of the urban water budget is the urban runoff (stormwater) that may lead to another important pathway of CECs. A research conducted by Fairbairn *et al.* (2018) on urban runoff (stormwater), taken 36 samples from the nine different places of USA's Minneapolis–Saint Paul Metropolitan. This study used three stormwater pipes of large size and three pair of Iron enhanced sand filters (IESFs) and has presented 123 forms of contaminants like veterinary, pharmaceuticals, pesticides, personal care products etc in the water. Results of the study show that the thirty-one of the pollutants were found over 50% of the samples. Each sample contained a mean of 35 CECs (targeted) in the range of 18-54 and mean concentrations, overall, for 25 CECs and 9 CECs were ≥10 ng/L and ≥100 ng/L resp. The 14 CECs were removed out of the 48 most detected CECs including hydrophobic compounds like PAHs, flame retardants etc. and some-polar hydrophilic compounds like caffeine, nicotine etc., by the treatment with IESFs, consist of the conventional filter media with approximate 5% iron filling, for which the efficiencies were between 26%-100%. Many frequently found herbicide and other compounds like 5-methyl-1H-benzotriazole were not removed by IESFs (Fairbairn *et al.* 2018).

Also, a study conducted by Westerhoff*et al.* (2018), to determine the toxicity in the stormwater and to mitigate its effects by applying full scale IESFs. In the study, he took five bioassays of two model organism namely Daphnia magna and fathead minnows, Pimephalespromelas. The water samples were collected from the major conveyances of stormwater and IESF (full scale) during different seasonal events and examined the sample for the wide range of the CECs including chemicals from industries, personal care products, pharmaceuticals, personal care products etc. The study conducted to know the efficacy of the IESFs in the treatment of water from the biological outcomes. In addition, the analysis showed that certain toxins, like certain pesticides, were negatively eliminated from water. This shows the back-transformation in the IESFs of certain derivatives into their toxic formula. Different form of pesticides in water, particularly 2,4-dichlorophenoxyacetic acid and atrazine, are found in the high concentrations in all tested samples. The levels of several pollutants, including the two pesticides studied, did not display a substantial decrease in the IESFs. The large-scale analysis suggests that when it comes to pesticides, IESFs are not a promising method. The chemistry of the water, in comparison to the unimproved and biological outcomes occasionally removed by IESF and late summer samples, shows that many detected metals, nutrients, organic chemicals, etc. were decreased in late summer and with IESFs (Westerhoff*et al.* 2018).

Advanced Oxidation Process (AOPs)

This method of treatment uses the strong oxidising agents to oxidize pollutants present in the water (Wang and Zhuan, R. 2019). Amongst all strongest oxidizing radicals, hydroxyl (OH*) and sulphate radicals are most widely used for removing highly chemically stable pollutants in the water (Tsydenova*et al.* 2015). AOPs are eco- acceptable chemical methods that can degrade wide range of the organic pollutants into harmless products that do not transfer or generate large quantities of sludge from one process to another. In addition, this approach has several benefits like reaction rate is quite fast and as a result retention time becomes less as compared to the conventional techniques used, and hence necessary flow rate does not need the wide area of processing for the device. Nonetheless, different disadvantages, like cost of maintenance and operational cost of the treatment, should also be considered. Also, the chemistry involved for the treatment of the particular pollutants often needs trained workers to develop the system (Marican*et al*. 2018). There are many classifications of the AOPs like ozonation, Fenton, electrochemical oxidations, photochemical degradation etc. (Amir and Mohsin 2020) but relevant AOPs in the treatment of the pesticides are addressed in the following sub section.

Free radicals

Vela *et al* (2019) conducted a study to analyse the efficacy of Sodium Persulfate as an oxidizing agent to remove 17 pesticides (like floupyramflonicamid, cyflufenamid, acrinathrin etc., found in the wastewater generated form washing container and other equipment's like phytosanitary, having initial concentration in the water sample (900 L) as 0.02 to 0.017 mg/l. For the formation of the sulphate radicals, sodium persulfate should be activated by the UV light, which are also the one of the strongest oxidising agents of E0=2.6 V. The UV light of wavelength 245 nm is the ideal activation for persulfate. Nevertheless, sunlight was used instead due to viability and cost saving factors. The 13 percent of the dissolved organic carbon (DOC) was measured and nearly complete degradation (N97%) of the parent molecules was achieved after the treatment of the pesticides. After comparing the results with the grown broccoli (reclaimed and unreclaimed water), there is no substantial difference found. Also, the result justifies that the sodium persulfate is a low-cost and effective method for the degradation of the pesticides in the sample wastewater in the reasonable time (Verma*et al.* 2020).

Golshan*et al.* (2018) studied peroxymonosulfate (PMS), a strong oxidising chemical, that generate both sulfate and hydroxyl radicals in the water. In order to reach the highest degree of oxidation and mineralization, activators have been analyzed. The activation of PMS using photocatalytic activation in the presence of TiO2 anchored on 0.1 g/L copper ferrite (TiO2@CuFe2O4) showed a high efficiency in extracting 2,4-D (20 mg/L) from the water within 60 minutes at a rate of 97.2 percent.2,4-D is a type of herbicide that causes the uncontrolled growth and kills broadleaf weed. Due to the high rate of removal, intermediate by-products should be identified and further degraded using supportive water efficiency treatment techniques. A study conducted by Popova*et al.* (2019) showed that the persulfate system's iron-catalyzed photo-activation can treat 90% of the atrazine from water contaminated with 4 mg/L atrazine pesticides. The atrazine (used in crops like sugar cane and maize) is used to prevent broadleaf weeds.

Ozonation

Ozonation is the mechanism through which ozone is used to eliminate pollutants either by direct or indirect mean. The pollutants can be degraded either by effects of molecules of ozone or by free radicals, resulting from ozone decomposition of the water (Hussian*et al.* 2020). The produced free radicals are highly reactive and less selective in nature as compare to the other chemical oxidising agents. The ozone is produced on treatment site, because of the very small lifespan, and hence raises the treatment cost. Maldonado *et al.* *(*2006) conducted a research on five forms of pesticides in water (alachlor, atrazine, chlorfenvinphos, diuron, and isoproturon), found in Barcelona, Spain, to analyse the impact of ozone by using pilot-scale reactor. The research work is the part of European project related to the integrated biological and chemical treatment for the separation of the no- biodegradable and toxic pollutant from the water. Initially the concentration of these pesticides is taken as 16.6 mg/L, 20.1 mg/L, 16.9 mg/L, 18.1mg/L and 18.1 mg/L for atrazine, alachlor, diuron, isoproturon and chlorfenvinphos respectively. After treatment by ozonation, all the pesticides were removed from water for the time period of 30min (isoproturon) and 270 min (alachor). This has also been found that after 1000 minutes of treatment the total organic carbon level reduced to 26%. The treatment has some demerits also, including complete TOC removal is very difficult, ozonation process is very slow and requires the large amount of ozone during process, also chlorinated organics cannot be removed completely. Therefore, this process is not overall good for removing of these five pesticides but ozonation may be used as a primary treatment to break molecules of the pesticides into biodegradable forms in order to promote the oxidation and photodegradation.

Cruz-Alcalde*et al.* (2017) performed a study, by using the ozonation process, on the degradation of acetamiprid pesticide. The acetamiprid pesticide has been explained well by its reactivity to the OH radical on the basis of the kinetic findings. The HPLC/MS analysis of ozonatedacetamiprid showed that the main transformation products, namely ACMP-N-desmethyl, Ncyano-N-methyacetamidine and N-cyanoacetamidine, etc., all of which were formed by amine alpha carbon oxidation (coupled with hydrolysis). During the ozonation process of acetamiprid removal, there is an increase in toxicity in the medium after the relative reduction in the values. And hence these changes may cause synergetic effects between transformations products and toxic intermediate. While it seems important to follow further the strategies for the decomposition by ozonation, this process is very efficient for the degradation of the ACMP and reduction in the toxicity. Ormad*et al.*, (2008) researched the elimination of 44 distinct pesticides, found in Ebro River Basin, by using ozonation. These pesticides include endrin, dicofol, dieldrin, dimethoate, diuron, isodrin, prometon, alachlor, parathion methyl, aldrin, chlorpyrifos, simazine, tetradifon etc., In the treatment process, peroxidation is done by ozone (chlorine), aluminiumsulphate and activated carbon adsorption is used as the chemical precipitation. The peroxidation has been found as an efficient treatment for removing wide range of the pesticides but not much efficient by using in combination with coagulation. On the other hand, the peroxidation by ozane in combination with activated carbon showed as good result as compare to chorine alone. But this combination have a limit that this cannot remove the DDTs, molinate and desethlatrazine which can be removed efficiently with the combination of chlorine and chemical precipitation. The result of the overall study showed that the 75% diuron and parathion methyl, 70% isoproturon, and 50% of the atrazine was removed by ozonation.

Photochemical degradation

Lee *et al.* (2017) carried out a research to degrade 2,4-dichlorophenoxyacetic acid with the use of Fe2O3(0.5)/TiO2 under Ultraviolet irradiation. The nanocomposites of Fe2O3 and TiO2 is prepared by impregnation which has activity lower than the TiO2 (unmodified). This is because of the lower specific surface area resulting from treatment by heat. The exposure of the photocatalyst to ultraviolet (UV) lights caused the electron (photogenerated) excitation from the valence band to the conduction band of the TiO2. The excitation of the electrons causes the holes in the valence band which then mineralize and oxidize the 2,4-dichlorophenoxyacetic acid into 2,4-dichlorophenol. Due to reduction of the oxygen through the photogenerated holes, superoxide radicals are also formed. The experimental results showed that Fe_2O_3 (0.5)/TiO_2 have the high stability and efficiency for 2,4-dichloropheonol removal. This analysed that the Fe_2O_3 (0.5)/TiO_2 have 18% degradation ability to 2,4-dichlorophenol as compared to the TiO2 unmodified.

A research conducted on the removal of the carbofuran, a toxic insecticide used to protect soya bean, potato and maize, by using TiO2 or ZnO as photo-catalysts, showed as very good removal results. An experiment on influential water, having carbofuran concentrations 50 to 250 mg/L, was performed. This outcome of the research is found that elimination was more successful in TiO2 presence than in the presence of ZnO. In addition, high performance chromatography (HPLC) monitoring of the mineralization process indicated that pesticides deteriorated into smaller fragments within the first hour, and then completely mineralized. The photochemical removal of the pesticides with identical chemical structures could be a very successful method of mineralization (Mahalakshmi*et al.* 2007). AbuKhadra*et al.* (2020) used silica gel based on rice husk and peach leaves green extract (as reducing agents) for synthesizing a novel green nanocomposite which is used for the removal of acephate pesticides as a green nanocomposite photo-catalyst. Results should be superior for the removal of the pesticides to the photocatalytic activities of the green nanocomposites. The 0.25 g of nanocomposite is used to fully degrade pesticides of various concentrations. Furthermore, the degradation processes included the intermediate formulation of compounds prior to their full oxidation to NO3-, SO42- and PO43- after 70 minutes of irradiation.

In addition, for all forms of organic pollutants, photo-degradation is not an acceptable technique, and laboratory research should be performed carefully until any large-scale process is implemented. A 2018 research, for instance, showed that exposure to photo-degradation of dicloran. The conducted study evaluated the effects of the dicloran and products generated by photo-degradation, by using vitro keratinocyte culture and keratinocyte-fibroblast co-culture model. The results showed that dicloran and 1,4-benzoquinone have the greatest toxicity in the culture models when photodegraded for 4 hours. This photo-toxicity by dicloran causes the skin inflammatory diseases in human beings (Xu*et al*. 2018). Another study recently published by I. Carre*et al*. (2020) for the removal of the pesticides by using UV light in combination with chlorination and UV-LEDs. The combination of the UV light and chlorine is becoming popular these years but due to production of the disinfection by-product it is also a cause of major concern for researchers. There is also a need of the pre-treatment in the process to maintain the high UVT and low DOC in the sample. It has also been evaluated that a compromise is needed for the chlorine dosing and concentration as well as pH in order to degrade pesticides more efficiently with of focus onto minimizing the disinfection by products and additionally the combination of the UV and chlorine is very effective and feasible, particularly when the disinfection by product has been adjusted to lower level.

Fenton and hybrid technologies

Advanced oxidation by Fenton technology is considered as one of the effective methods for elimination of organic pollutants from the water and wastewater. Reagents formed by Fenton are the mixture of ferrous iron (typically iron (II) sulphate, FeSO4) with hydrogen peroxide solution. The series of reactions, shown in 1 to 6, demonstrate the redox reactions that occur during treatment with Fenton in the solution (Zhang *et al.* 2019).

$$H_2O_2 + Fe^{2+} \rightarrow HO^* + HO^- + Fe^{3+} \quad (1)$$

$$HO^* + Fe^{2+} \rightarrow HO^- + Fe^{3+} \quad (2)$$

$$HO^* + H_2O_2 \rightarrow H_2O + HOO^* \quad (3)$$

$$HOO^* + H_2O_2 \rightarrow H_2O + HO^* + O_2 \quad (4)$$

$$HO^* + \text{polysaccharide-H} \rightarrow H_2O + \text{polysaccharide}^* \quad (5)$$

$$\text{Polysaccharide}^* + \text{Monomer} \rightarrow \text{Polysaccharide-g-polymer} \quad (6)$$

Barbusinski and Filipek*et al.* (2002) investigated the removal of various pesticides like fentirotgion, DDT, DMDT, alpha and beta-HCH etc., from wastewater of industry using Fenton's method. This method of treatment has shown the efficient results in degrading organophosphate insecticides, called as fenitrothion, of about 98.5 % to 100% and 97.1 % to 100 % for chlorfenvinphos and 90 % for organochlorine pesticides removal from the wastewater. The maximum removal rate was found at the H2O2 concentrations of 2.5 g/dm3 in most of the cases for individual pesticides. And 5.0 g/dm3 also showed a good result for the pesticides analyzed in the experiment. It was evaluated that at concentration ratios of the $Fe2^+$: H2O2 at 1:3 to 1:2 and with pH between 3.0 to 3.5, the best results of removal can be achieved. Saritha*et al.* (2007) worked on the elimination of the 4-chloro-2-nitrophenol (4C-2-NP) by best AOPs from pesticide industry as model contaminant, with an initial 4C-2-NP concentration of 100 mg/l. The final target of the process has been on the complete degradation of the pesticides to prevent the intermediate products having the high toxicity. In this study, the COD reduction was monitored along with the concentration of 4C-2-NP. The used Advanced Oxidation Processes did not show the successful results and even alone using of the UV light and H2O2 were not able to remove COD completely. But when UV light and H2O2 are combined, COD decreased to 50%. Also, TiO2 as a UV catalyst showed the 80 % reduction and photo-Fenton showed 90% reduction in the COD level. The cost analysis showed that for the treatment of per kg of pollutants the cost incurred was 28.7 USD, 785 USD and 58.6 USD for UV/Fenton technique, UV/TiO2 and UV/H2O2 respectively and hence the hybridization of the UV/H2O2 is the most economical method. Zapata *et al.* (2010) invested the efficiency of the hybrid photo-Fenton followed by aerobic biodegradation for the treatment of the water contaminated with pesticides. This hybridization of Photo- Fenton is very efficient, when optimized, for the biodegradation of the bio-recalcitrant compounds present in the wastewater. The study showed that these techniques is very good for the removal of the pesticides tested in the experiment except pyrimethanil. Also, others study showed good removal rate, about 98% of COD and BOD in leachate from landfill by using combined technique of photo-Fenton and biological treatment (Colombo *et al.* 2019). A recent research by Ghanbarlou*et al.* (2020) showed the production of a novel electro-catalyst based on the nitrogen-doped graphene-iron. In the study, most widely used pesticides, namely 2,6-dichlorobenzamide, 2-methy-4-chlorophenoxy acetic acid and mecoprop, of initial concentration of 50 mg/l each, have been targeted for removal from the water. In comparison with other techniques of Fenton, this newly developed techniques showed high removal rate, about 94%, of MCPA and mecoprop. There is also a high removal rate, about 25%, of total organic carbon, showing that the synthesized electrode particle has the excellent electrocatalytic activity and capable to remove up to 93% targeted pesticides from water under favourable conditions.

Biological treatments

The pesticides present in the wastewater are degraded or digested by potential microorganisms and various bio-purification systems are designed for this purpose. The origin of microorganisms, in the bio-mixture (substance made with humic in order increase the retention of pesticides, microorganisms, and soil), can be of exogeneous and endogenous. The pesticides rich soil sample contains microorganisms that have the better endogenous biodegradability. Also, some exogeneous species can be used in place of the endogenous microorganisms because of the limitation of the biomass (Karanasios*et al.* 2012). It has also seen that due to the toxicity of pesticides, it is not easy for microorganism to digest pesticides

(Goodwin *et al*. 2017). The biological aerobic treatment is most common for the removal of the dechlorinated pesticides that oxidizes, break the ether bond and transform the chlorophenol into chlorocatechol. During this process aromatic ring opens and hence made the microorganisms easily digestible, to form water and carbon dioxide, bacterial metabolism by regular.The pesticides removal by biological treatment is not easy and after complete establishment it can be easily maintained. Pre-treatment may be helpful and sometimes becomes necessary requirement for the biological digestion for instance, photochemical process is used as pre-treatment for degradation of certain pesticides (Huang *et al*. 2018).

CatilloMdel*et al.* (2008) worked on the treatment of the fungicides, ligninolytic fungi, a type of the fungi that secrete the ligninolytic enzymes. This treatment is done on the bio-mixture that degrade the pesticides based on lignin. Triazole is one of the persistent and widely find fungicides, having the 100 days life in the soil. When Trametesversicolor added to the bio-mixture, the results are not much good and not showed improvement for the removal of the fungicides. Zhao *et al.* (2017) studied the degradation of the norfloxacin (an antibacterial agent) from the wastewater. The process is carried out by chloroperoxidase and H2O2 is added to trigger the reaction involve in the process. The 82.18% efficiency is achieved in the process just after 25 minutes reaction time that cannot be achieved by any conventional process of treatment. Bercerra*et al.* (2020) adopted aerobic biological process for the treatment chlorpyrifos, an insecticide, from the water as a secondary treatment. The results of the experiment showed a high removal efficiency of the contaminant by using this treatment method.

V. Conclusion and recommendation

Nowadays, several conventional and modified methods are available for pesticide removal like : Hydrolysis, Incineration, Advanced oxidation processes (O3/ UV, Fenton oxidation, etc.), UV-TiO2 based Photocatalyticdegradation , Combined photo-Fenton and biological oxidation , Membrane filteration methods like Nano-filtration, Ultra Filtration, Reverse osmosis and Electrodialysis , Ozonation , Coagulation , fluid extraction , solid phase extraction , and Adsorption, Absorption or Sorption (inorganic, organic absorbents and activated carbon), Composting, bio augmentation, phytoremediation and Aerobic degradation . Even though, several processes and material have been developed to remove pesticides, all of them depend on numerous factors such as pH, kind of matrix, temperature, nature of pesticide, and cost of investment, among others. Among physical processes, membrane filtration methods like Nano/Micro/Ultra filtration and Reverse Osmosis are the most widely accepted and researched technologies with efficiencies varying from 70 to 95 percent in most cases, depending on the type and concentration of contaminant to be removed. Newer researches reported the use of membranes like ultralow pressure RO membranes (ULPRO), thin film composite membranes (TFC or TFM), (TFC) Polyamide nanofiltration (NF) membrane, polyelectrolyte multilayer membranes (with chitosan/polystyrene sulfonate (CHI/PSS)), NF-(70/45/90/200/270) , UTC-(20/60), DK, and Electro Dialysis membranes to achieve the desired removal efficiencies. Many a times, membrane processes are integrated with some kind of pre or post treatment like Coagulation/Adsorption/Biological Treatments to enhance the quality of the permeate and for safe operation and maintainence of these processes on a commercial scale .

Physico–Chemical treatments like Adsorption (using activated carbon (GAC,PAC,CAC,MAC,GMAC)),Carbon cloth/Fibres, Biochar ,synthetic adsorbents (prepared from Agricultural products and wastes, house hold wastes, Industrial wastes, sewage sludge and polymeric adsorbents), natural adsorbents(charcoal, clays, Nano-clays, clay minerals, zeolites, and ores,etc.) , modified polymer adsorbents (like Chitosan biopolymer , cyclodextrin-based polymer (CDPs)), Low-cost alternative adsorbents (LCAs), Bio adsorbents (using fruit seeds or peels, oil palm fronds, coconut-shell/fibres, peat moss, Ground coffee, wood, corn stillage, sal wood, bagasse, date stone, bagasse, etc.) and Absorption or Sorption(low-cost biosorbents obtained from lignocellulose and chitin/chitosan,etc.). Removal of organic contaminants are also enhanced by using novel biodegradable coagulants like chitosan, poly-lactic acid derivatives, etc. Among all others, treatments using cheap and locally available carbons prepared from biomass and other wastes is probably the most well researched and active field of study with new researches and results emerging every year. Chlorination (for few kinds of contaminants) and pilot-scale innovative technologies like Iron enhanced sand filter (IESFs) and Mobile membrane filtration units have also given fairly good results in the local context. Maximum adsorption capacities have been observed in Activated carbon or Chitosan or biochar based based treatments, sometimes followed by coagulation. The efficiency of these methods easily varies between 75 to 90 percent. In the recent years, researches using Biological Treatments like Advance Oxidation Methods (ozone-based treatment, ultraviolet (UV)-based treatment, advanced electrochemical oxidation (eAOP), advanced catalytic oxidation (cAOP) and advanced photo oxidation (pAOP)), Activated sludge (Pressurized, bio-augmented, etc.) , Anaerobic-aerobic biological treatment, moving-bed biofilm reactor combined with Fenton-coagulation pretreatment, Membrane bioreactor (MBR) **,** In-vitro treatment using microbial consortium and bio-mixture augmented with ligninolytic fungi) have been extensively studied. Most of these biological processes are highly efficient in target and COD removal with efficiencies lying between 88 to 98 percent.

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