Review Article

Pesticide Wastewater Pollution and Treatment Methods: Review

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Abstract

The persistent pesticides occur in the water cause potential adverse effects on the environment and public health. Due to high use of pesticides in the agricultural developed area/ country and public health sector, hence is posing a challenge to remove the pesticides from wastewater. In this paper a review of pesticides in wastewater in India is presented. The current scenario of pesticide wastewater and its various treatment methods are cited. Each method has its own advantages and limitations in terms of removing the pollutants, efficiency and economical effectiveness. Currently, membrane distillation is an effective technique can be used to treat pesticide wastewater.

Keywords: Pesticides, Wastewater, Health effects, Treatment methods, Pollution



Introduction

Water is the source of life, the basis of human survival, and also the principal material base to ensure the economy substantial development of a country. With increasing worldwide population, the gap between the availability and need for water is widening and is reaching such alarming levels that in some part of the world, it's passing a hazard to human survival. A growing demand for water along with the progressing contamination of the conventional water resources creates several technological problems for industry and domestic water supplies. In industrialized countries, widespread shortage of water is caused due to contamination of ground and surface water by industrial effluents, and agricultural chemicals. Wastewater from manufacturing or chemical process industries contributes to water pollution. Industrial wastewater typically contains specific and readily identifiable chemical compounds. It is found that one-third of the total water pollution comes in the form of effluent discharge, solid wastes and other hazardous wastes. Out of this a large portion can be traced to the processing of industrial chemicals and to the food products industry [1-3].

The problem of water pollution has become still worse due to toxic organic components. Organic pollutants include pesticides, fertilizers, hydrocarbons, phenols, proteins, plasticizers and carbohydrates. The main source of pesticides is the pesticides production plants and agricultural area.

Scenario of pesticide use in India

The pesticide production in India started with the production of Benzene Hexa Chloride (BHC) near Calcutta in 1952 [4]. Now, India is the second largest producer of pesticides in Asia after China and rank 12th in the world [5,6]. The worldwide consumption of the pesticide is nearly 2 million tons per year, of which 3.75% is consumed in the India

[6]. A total consumption of the pesticide in India during 2005-06 to 2009-10 is nearly 210600 MT [7]. The Indian state wise consumption of the total pesticides is shown in **Figure 1**.



Figure 1 Total consumptions of pesticides in states of India [7]

There are different types of the pesticides are used in India such as fungicides, insecticides, herbicides, rodenticides, molluscicides and nematicides. A total of 234 pesticides have been registered in India by Central Insecticides Board and Registration Committee (CIBRC). Out of these, 19 are World Health Organization (WHO) class I pesticides and 76 are WHO class II pesticides [7,8].

Pollution and health impact of pesticides

Pesticides / Agrochemicals are mainly used in the agriculture and public health sector. In agriculture pesticides use to increase the crop yield [6]. Due to increase in population, crop yield must be needed to increase. But the exposure of the pesticide both occupationally and environmentally causes a range of human health problems because pesticides are toxic in nature [2]. The most important portion of contamination due to pesticide / Agrochemical wastewater is observed in agricultural areas and in surface waters that come from agricultural areas. The major pollution of the pesticide wastewater is released from pesticide/ agrochemical manufacturing industry wastewater [9].

Pesticide wastewater distinguishes itself because of its toxic and persistent nature in the environment. This wastewater depicts a wide variation in its characteristics based on the pesticide product; raw materials used and water consumption and wastewater flow [9]. The general characteristics of the pesticides / Agrochemical manufacturing industry wastewater and its Central Pollution Control Board (CPCB) limits are shown in **Table 1**. The WHO limits of the pesticide residue in water to 0.1 µg/L for an individual and to a total of 0.5 µg/L for all pesticides [11]. As per Bureau of Indian Standards (BIS) the total pesticides should be absent in drinking water and permissible limit up to 0.001 mg/L in surface water. [6,12]. The pesticide contamination level as high as 500 mg/L in the wastewater from agricultural industries and pesticide manufacturing or formulation plants [13]. In addition Central Pollution of Control Board (CPCB) of government of India gives the following standards for pesticides in wastewater of pesticides manufacturing and formulation industry: Benzene Hexachloride, Carbonyl, DDT, Endosulfan, Fenitrothion, Malathion, Phorate, Methyl Parathion and Pyretrums (10 mg/L); Copper Sulphate (50 mg/L); Dimethoate (450

mg/L); Zirum (1000 mg/L); Sulphar (30 mg/L); Proponil (7300 mg/L); Paraquat (2300 mg/L); All other pesticides (0.1 mg/L) [10].

| Parameters | Characteristic value [5,9] | CPCB limits [10] |
|----------------|----------------------------|--|
| pН | 8.98 - 12.95 | 6.5 - 8.5 |
| BOD 3days 27°C | 184 - 685 | 30 – formulation unit & 100-Technical grade unit |
| COD | 6000-7000 | 250 |
| TDS | 12000-13000 | 100 |
| TSS | 250 - 300 | 100 |
| Phosphates | 12 - 81 | 5 |
| Cyanide (CN) | 0.4-0.7 | 0.2 |
| Copper (Cu) | 1.07 – 29.86 | 1 |
| Nickel (Ni) | 0.47 – 0.9 | 3 |
| Chromium (Cr) | 0.48 - 1.16 | 0.1 |
| Zinc (Zn) | 0.87 - 6.15 | 1 |
| Lead (Pb) | 0.61 – 1.19 | 0.1 |
| Iron (Fe) | 1.15 - 42.62 | 3 |

Table 1 General characteristics of pesticide wastewater and its CPCB limits

Note: The unit of all values is mg/L except for pH value

The overall impact of a pesticide depends on its behavior in the environment, its toxicity and amount applied. Different pesticides pose different type of risks of the human and aquatic life. [14,15]. Some pesticides are commonly used in India and its health effect on the human life is explained in the **Table 2**.

Treatment Technologies

There are various treatment methods are available for the treatment of pesticide wastewater such as thermal, chemical, physical and biological methods. The most commonly used technique under thermal method is incineration [6]. Under Chemical method, the treatment techniques are ozonation/ UV radiation [16], fenton-oxidation [16], electro-oxidation, electro-coagulation [2], phytoremediation [6] and photo-catalytic degradation [17]. The techniques under the physical method are adsorption [18], reverse osmosis [19], nano filtration [9] electro dialysis and [19] membrane distillation [20-22]. The biological method used biodegradation technique [6] for treatment of pesticides wastewater. But these techniques are neither cost effective, nor eco-friendly, nor involving low concentration. Each technique provides a different and unique approach and perhaps provides certain advantages over others for a particular situation. However, when large volumes of water containing toxic elements are to be treated, it would be of great advantages if the method would provide reliable results without involving much cost and working efforts. The description and disadvantages of each technique for pesticide wastewater treatment are explained in **Table 3**.

Table 2 Most commonly used pesticides in India and their Health effects [7]

| Pesticide | Health impacts |
|-------------------------|--|
| DDT | Chronic liver damage, endocrine and reproductive disorder, breast cancer, polyneuritis etc. |
| Endosulfan | Effects on kidney, developing fetus, decrease in the quality of semen, increase in testicular and prostate cancer, etc. |
| Benzene Hexachloride | Chronic liver damage, reproductive disorders, breast cancer, polyneuritis. |
| Carbonyl | It may damage kidneys and nervous systems, brain cancer, genetic changes in living cells etc. |
| Fenitrothion | It causes eye effects, frontal lobe impairment and neurological deficits. |
| Melathion | Delayed neurotoxin, allergic reactions, behavioral effects, ulcers, eye damage and abnormal brain waves. |
| Phorate | It causes the neurological and neuromuscular effects. |
| Methyl Parathion | Loss of consciousness, dizziness, tremors, blurred vision, diarrhea, effects on nerve function and sweating. |
| Pyretrums | Mimicking the female hormones, estrogen lowered sperm count, abnormal growth of breast tissue. |
| Copper sulphate | Irritating effects on the gastrointestinal tract, burning pain in the chest, nausea, diarrhea, vomiting, and injury to brain, stomach, liver and kidney. |
| Dimethoate | Birth defects, reproductive toxicity and mutagenic effects. |
| Sulphar | Disturbance of blood circulation, reproductive failure, damage of liver, kidney, immune system, heart, neurological and dermatological effects. |
| Paraquat | Parkinson's and Alzheimer's diseases. |
| Altrazine | Cancer of testes |
| 2, 4-D | Non Hodgkins Lymphoma |
| Aldrin | Lung cancer, liver diseases. |

In recent years, membrane technologies such as nanofiltration, reverse osmosis, electrodialysis has become a more attractive for water treatment as compared to the conventional purification [36,39,40]. These are the pressure-driven separation technologies and only membrane distillation (MD) is a thermal-driven separation process [36,41]. MD separation process is driven by the vapor pressure difference across the porous hydrophobic membrane surfaces. It is a non-isothermal membrane separation process, in which feed water is heated to increase its vapor pressure, which generates the difference between partial pressure on both sides of the membrane. MD is supposed to have a great potential due to lower energy requirement, low cost, low operational pressure as compared to RO and distillation [36,37]. It utilizes low grade waste steam / heat from power stations. It allows a theoretical 100% separation factor of non-volatile solute. Due to the number of such advantages, MD is an interesting and growing technology in water treatment

| Technique | Description | Disadvantages | Ref. |
|-----------------------------|---|--|------------------|
| Incineration | It is a high temperature oxidation process. Pesticides are converted into inorganic gases. >99.9 % organic pesticide removal is possible. The use of ozone and UV radiation to | Operated higher than 1000 ^o C; Formation of corrosive and toxic gases | [16,19] |
| Ozonation / UV radiation | enhance the oxidation of aromatic compounds. Ozonation is more effective in the presence of UV light because it can form hydrogen radicals, which are very effective oxidizing agents. | High energy consumption; Initial equipment cost is high | [16,23- 25] |
| Fenton-Oxidation | It can be used as a part of an oxidative system to treat and degrade pesticides. It consists of hydrogen peroxide and iron salts at low pHs. Organic pollutants are oxidatively degraded by hydroxyl radicals generated from hydrogen peroxide in the presence of iron ions as a catalyst. | It may result in the formation of other toxic or unwanted products | [26-28] |
| Electro-Oxidation | It is an electrochemical method. It consists of carrying out the oxidation reaction at the anode where pollutants are transferred into non-toxic substances. The final products mainly CO_2 and H_2O . | It is useful especially in small scale facilities; formation of unwanted products; costly process | [29] |
| Electro- Coagulation | It includes coagulation, adsorption, precipitation and flotation. It utilizes iron anode to produce iron hydroxide flocks by the reaction at the anode followed by electrolysis | Costly and energy intensive process | [2,9,30] |
| Phytoremediation | In this method plants are used to contain and remove harmful environmental contaminants from groundwater. | It is a time consuming process; Application of this is limited to surface and subsurface soil | [6,16,31 32] |
| Photocatalytic degradation | The organic contaminants destroyed in a relatively short time when the contaminated soils mixed with TiO2 and exposed to stimulate solar radiation. | Useful for small scale and low concentration of pesticides | [18] |
| Adsorption | Pollutants are adsorbed on the surface of adsorbate using activated carbon, inorganic and organic material and naturally available material. | Byproducts for disposal; No destruction involved | [4,17,33, 34] |
| Reverse Osmosis | Impurities are separated by a semi- permeable membrane at a pressure greater than the osmotic pressure caused by the dissolved solids. | It is an expensive process; membrane fouling is a major issue | [19] |

 Table 3 Innovative pesticide wastewater treatment techniques

| Electrodialysis | Semi permeable ion selective membranes used. Electrical potential applied between the two electrodes causes a migration of cations and anions towards respective electrodes. | Formation of metal hydroxide, which clog the membrane; Expensive process | [19] |
|--------------------------|---|---|---------|
| Nanofiltration | It is a recent membrane filtration method. Nano porous membranes are suitable for a mechanical filtration with extremely small pores smaller than 10 nm. | It is a very efficient but costly process | [35] |
| Membrane distillation | It is a thermal, vapor-driven transportation process through micro porous hydrophobic membranes. The feed water is heated to increase its vapor pressure, which generates the difference between the partial pressure at both sides of the membrane. Hot water evaporates through non-wetted | It has a great potential due to lower energy requirement, low cost, low operational pressure as compared to RO and distillation | [36,37] |
| Biodegradation | pores of hydrophobic membranes It relies on the ability of microorganisms to convert organic contaminants in simple and harmless compounds to the environment. | High cost; formation of the unwanted products; relatively slow process | [16,38] |

Conclusions

In India the consumption of the pesticides in the application of agriculture for increasing crop yield is very high. Also, the pesticide manufacturing, industrial wastewater is also added to the water. Hence it needs to remove the pesticide from water due to the toxicity of the pesticides. It can adversely affect on the human health and living organism. In this paper, various treatment methods are used for the removal of pesticides from the wastewater include: incineration, ozonation/ UV radiation, Fenton-oxidation, phytoremediation, electro-coagulation, electro oxidation, photo catalytic degradation, adsorption, reverse osmosis, nanofiltration, electro dialysis, membrane distillation and biodegradation. Some of these methods are an expensive and suffer from variability of effectiveness. MD in the membrane technology is an effective technique can be used for pesticide removal from the wastewater. Hence a further study has been planned for pesticide removal mainly focusing on membrane distillation.

References

- [1] I. Ali, M. Asim, A. Tabrez, J Environ Managm 2012, 113, 170-183.
- [2] B.R. Babu, K.M. Seenimira, P. Venkatesan, Sustain Environ Res 2011, 21(6), 401-406.
- [3] C. Ozdemir, S. Sahinkaya, M. Onucyildiz, Asian J of Chemistry 2008, 20(5), 3795-3804.
- [4] V.K. Singh, R.S. Singh, P.N. Tiwari, J.K. Singh, F. Gode, Y.C. Sharma, J Water Resource and Protection 2010, 2, 322-330.
- [5] P.U. Singare, S.S. Dhabarde, Int Letters of Chem, Phy, and Astronomy 2014, 3, 8-15.
- [6] R. K. Pathak, A.K. Dikshit, Int Conf on Life Sci and Tech (IPCBEE) Singapore 2011, 3.
- [7] Web information: http://www.indiaforsafefood.in/farmingindia.html, Pesticide use in India, 2012.
- [8] C. Bhushan, A. Bhardwaj, S. Mishra, State of Pesticide regulation in India, Centre of Science and Environment, New Delhi, India 2013.
- [9] R. Misra, S. Satyanarayan, N. Potle, Int J Chem and Phy Sci 2013, 2, 39-51.
- [10] Ministry of Environment and Forest Notification, New Delhi 13th June 2011

- [11] Guidelines for drinking water quality, Geneva, Switzerland: World Health Organization, 1984, vol. 1.
- [12] J.M. Mauskar, Status of groundwater quality in India-Part-I, Central Pollution Control Board, Ministry of Environment and Forest, India 2007.
- [13] S.Chiron, A. Fernandez-Alba, A. Rodriguez, E. Garcia-Calvo, Water Res 2000, 34(2), 366-377.
- [14] D. Fatta, C. Michael, S. Canna-Michaehdou, M.Christodoulidou, N.Kythreotou, M. Vasquez, Desalination 2007, 215, 233-236.
- [15] A. Zaleska, J. Hupka, Waste Managm Res 1999, 17(3), 220-226.
- [16] M.T. Al Hattab, A.E. Ghaly, J Environ Protection 2012, 3, 431-453.
- [17] D. Dong, P. Li, X. Li, Q. Zhao, Y. Zhang, C. Jia, and P. Li, J Hazardous Material 2010, 174, 859-863.
- [18] B. Srivastava, V. Jhelum, D.D. Basu, P.K. Patanjali, J Scientific & Ind Res 2009, 68, 839-850.
- [19] N. Ahalya, T.V. Ramchandra, R.D. Kanamadi, Res. J Chem.and Enviro 2003, 7(4), 71-74.
- [20] B.L. Pangarkar, M.G. Sane, S.B. Parjane, M. Guddad, Desalination and Water Treatment 2013
- [21] A. Criscoli, P. Bafaro, E. Diroli, Desalination 2013, 323, 17-21.
- [22] J.K. Singh, S. Upadhyaya, S.P. Chaurasia, Int J of Chem & Chem Engg 2013, 3(3), 209-214.
- [23] P. C. Kearney, Q. Zeng, J. M. Ruth, ACS Symposium Series 1984, 259, 195-209.
- [24] W. H. Glaze, Environ Sci and Tech 1987, 21(3), 224-230.
- [25] G. R. Peyton, W. H. Glaze, ACS Symposium Series 1987, 327, 76-88.
- [26] K. Barbusinski, K. Filipek, Polish J Environ Studies 2001, 10(4), 207-212.
- [27] Y. Sun, J. J. Pingnatello, J of Agri Food Chem 1992, 40 322-327.
- [28] C. Ozdemir, S. Sahinkaya, M. Onucyildiz, Asian J Chem 2008, 20 (5), 3795-3804.
- [29] S.B. Dimitrijevic, S.P. Dimitrijevic, M.D. Vukovic, 17th Int. Research/ Expert Conf., Trends in the Development of Machinary & Associated Technology, Istabul, Turkey 2013.
- [30] S.A. Abdel-Gawad, A.M. Baraka, K.A. Omran, M.M. Mokhtar, Int J Electrochem Sci 2012, 7, 6654-6665.
- [31] US EPA, Pesticides and Pesticide Containers, US Environ. Protection Agency, Municipal Environ. Res. Lab., Cincinnati 2011.
- [32] C. V. Hall, J. Baker, P. Dahm, L. Freiburger, G. Gor- der, US Environ. Protection Agency, Municipal Environ. Res. Lab., Cincinnati 1981.
- [33] P.C. Mishra, R.K. Patel, J Hazardous Materials 2007, 07, 91-97.
- [34] G. Satpathy, Y.K. Tyagi, R.K. Gupta, J Agricultural Sci 2012, 4(2), 69-77.
- [35] K. Padmaja, J. Cherukuri, M.A. Reddy, Int J Innovative Res in Sci 2014, 3(2) 9375-9385.
- [36] T. Mohammadi, M. Ali Safavi, Desalination 2009, 249, 83-89.
- [37] Z. Jin, D. Yang, S. Zhang, X. Jian, J Membrane Sci 2008, 310, 20–27.
- [38] A. S. Felsot, K. D. Racke, D. J. Hamilton, Reviews of Environmental Contamination and Toxicology 2003, 177, 123-200.
- [39] M. Busch, R. Chu, U. Kolbe, Q. Meng, S. Li, Desalination and Water Treatment 2009, 10, 1-20.
- [40] C. Bartels, M. Hirose, S. Rybar, R. Frabks, Desalination and Water Treatment 2009, 10, 21-26.
- [41] Z. Jin, D. Yang, S. Zhang, X. Jian, J Membr Sci 2008, 310, 20–27.

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