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STUDY OF PHOTOCATALYTIC REMOVAL OF IMIDACLOPRID FROM WATER BY ADVANCED OXIDATION PROCESSES WITH RESPECT TO NANOTECHNOLOGY OF SHAKKAR & PENCH RIVER OF CHHINDWARA DISTRICT (M.P.)

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ABSTRACT:- Environmental contamination due to urbanization, industrialization, anthropogenic activities, heavy metal accumulation, military and agricultural activities etc. is of serious ecotoxicological concern worldwide. In recent years, semiconductor photocatalytic process has shown a great potential as a low-cost, environmental friendly and sustainable treatment technology to align with the “zero” waste scheme in the water/wastewater industry. The ability of this advanced oxidation technology has been widely demonstrated to remove persistent organic compounds and microorganisms in water. In the present research work about photo-degradation of river water by nano catalyst. Photo-degradation is the process of alteration of materials by light, refers to the combined action of light and air. It is usually oxidation and hydrolysis. Nano Catalyst is used for water purification. In this research work we are going to about water purification of Shakkar & Peach river of Chhindwara District. In this study, the kinetics of photocatalytic removal of imidacloprid, a systemic chloronicotinoid insecticide, from water using two advanced oxidation systems (ZnO(normal)/H_2O_2/artificial sunlight and ZnO(nano)/H_2O_2/artificial sunlight) were investigated. Moreover, the effects of pH, insecticide concentration, catalyst concentration, catalyst particle size, and water type on the photocatalytic removal of imidacloprid were evaluated. Furthermore, total mineralization of imidacloprid under these advanced oxidation systems was evaluated by monitoring the decreases in dissolved organic carbon (DOC) concentrations and formation rate of inorganic ions (Cl^- and NO_2-) with irradiation time using total organic carbon (TOC) analysis and ion chromatography to confirm the complete detoxification of imidacloprid in water.

KEYWORDS: - hydroxyl radical, imidacloprid, mineralization, nanocatalyst, removal, water.

INTRODUCTION:-

The planet is mostly composed of water, which is the most crucial component of life. Water is necessary for the existence of all living beings on Earth. It accounts for 71% of the earth's surface (Panchal et al. 2019). Water has the physical traits of being clear, tasteless, odourless, and colourless (Sronsri et al. 2020). It might be polluted by a range of pollutants and pollution sources, including (Aarthye and Suresh kumar 2021). Dangerous substances are used in human activities (industrial wastes, fertilizers, pesticides, etc.) (Akhil et al. 2021) natural minerals and compounds such as arsenic, common salt, and fluorides Pathogens or disease-causing organisms such as amoebas, bacteria, and viruses, as well as pollutants that impact taste, odour, and colour. Water treatment is defined as the process of making water relevant and acceptable for a certain end-use, as well as eliminating and lowering the concentrations of water pollutants to match its intended purpose (Akpe et al. 2020).

Water pollution is the contamination of water bodies such as lakes, rivers, oceans, and groundwater caused by either human activities or industrial activities, which can be harmful to organisms and plants which live in these water bodies. It has always been a major problem to the environment. With industrialization in major areas and an urban city growing the water around them just keeps getting polluted. A lot of water pollution is caused by factories near rivers and lakes doing illegal dumping.

Increasing demand and shortage of clean water sources due to the rapid development of industrialization, population growth and long-term droughts have become an issue worldwide. With this growing demand, various practical strategies and solutions have been adopted to yield more viable water resources. The storage of rainwater for daily activities and increasing the catchment capacity for storm water are just a few examples that could resolve the problems in short-term. Water industries and governments in some arid areas with abundant of sunlight, less rainfall and long-term drought have a challenge to seek viable water resources. It is estimated that around 4 billion people worldwide experience to have no or little access to clean and sanitized water supply, and millions of people died of severe waterborne diseases annually.

Also, new physical and chemical properties emerge when the size of a material is reduced to the nano scale level. The surface energy per nanoparticle increases significantly in the nanorange. This increase in surface energy directly results in an increase in contaminant removal even at low concentrations. The use of nano catalysts also results in less waste generation, especially in post treatment, since less quantity of nanomaterial will be required compared to its bulk form. Furthermore, with the use of nanomaterials, novel reactions can be accomplished at nano scale due to an increase in the number of surface atoms which is not possible with its analogous bulk material, for example, the degradation of pesticides by nanoparticles which cannot be done by the metals in their bulk form.

Pesticides are widely used in agriculture to reduce the loss of production caused by pests; however, they also contribute to pollution of the environment. The presence of pesticide residues in water poses a risk to aquatic organisms as well as to human health. The United Nations has reported that less than 1% of applied pesticides reach their target pests, while the remainder become distributed in different environmental components such as soil, air, and water.

Imidacloprid is a neonicotinoid insecticide registered in more than 140 countries to control many of the sucking insects that affect field crops such as rice, wheat, and cotton. Imidacloprid is also used to control pests in crops grown in greenhouses. This pesticide can be applied as a systemic insecticide to soil and seeds, or by spraying on crops. Imidacloprid is also used as a topical treatment for fleas on domestic pets. Owing to the intensive use of this pesticide, imidacloprid commonly enters water either by spray drift or runoff after application. Because of the high solubility of imidacloprid, it may have adverse effects on aquatic organisms and human health. This paper various aspects of photocatalysis have been published by Castilla-Caballero et al. (2022), Liu et al. (2022a), Wang et al. (2022), and Kajitvichyanukul et al. (2022).

In order to minimize the residues of pesticides in water to levels established by the World Health Organization and the US Environmental Protection Organization, which do not have harmful health effects on humans and the environment, as well as to meet the standards of water quality of pesticides to protect human health, methods of removal of pesticide residues from water must be more effective and highly sensitive. Therefore, the ideal procedures for removing pesticide residues from water are non-selective methods that achieve the rapid and complete destruction of organic pesticides to non-toxic inorganic products that are effective in small-scale remediation units.

In this study, the photocatalytic removal of imidacloprid from water using two advanced oxidation systems (ZnO(normal)/ H_2O_2 and ZnO(nano)/H_2O_2) was investigated. Artificial sunlight (solar simulator) was used in this study to examine the photocatalytic removal of imidacloprid since the sunlight advanced oxidation system is not much studied, compared with the UV light advanced oxidation system. Moreover, the effects of pH, catalyst concentration, insecticide concentration, and water type on the photocatalytic removal of imidacloprid were evaluated.

OBJECTIVES -

The main objective of photodegradation of water of Shakkar and Pench River of Chhindwara district. In this research discussed photocatalytic degradation of pollutants is promising technology due to its advantage of degradation on pollutants instead of their transformation under ambient conditions. The process is capable of removing a wide range of organic pollutants such as pesticides, herbicides, and micropollutants such as endocrine disrupting compounds. Further research to investigate the degradation of the real water constituents is required to better comprehend the process applications.

MATERIAL &METHODS:-

In this research on explaining the some methods by which the research is going to be carried out following description.

Imidacloprid technical standard (99% purity) was obtained from Sigma-Aldrich, USA, as were zinc oxide nanopowder (<100 nm with a specific surface area of 15–25 m3/g) and zinc oxide powder with a purity of 99.99%. Benzene, acetonitrile, and phenol (99.5% purity) were obtained. For TOC analysis, imidacloprid was dissolved directly in Milli-Q water to avoid the influence of methanol on dissolved organic carbon (DOC) levels.

Zinc oxide nanoparticles-

Zinc oxide nanopowder (with a particle size 80 nm and specific surface area of 15–25 m3/g) and zinc oxide powder with a purity of 99.99% (particle size 130 nm and surface area of 5–10 m3/g) were obtained from Sigma Aldrich Company, USA. Fabrication of ZnO oxide nanopowder as reported by the company was conducted by the physical vapor synthesis (PVS) method to produce ZnO nanoparticles with unique characteristics.

Photocatalytic degradation of imidacloprid in water-

This experiment was designed to assess the efficiency of the advanced oxidation process using zinc oxide nanopowder (synthesized) and normal-sized zinc oxide (commercial) to remove imidacloprid from water. River water samples of the chemical composition given in Table 1 were collected from the Shakkar & Pench River of Chhindwara in May of 2022. Water samples were filtered through a glass fiber filter (GC-50, diameter: 47 mm, nominal rating: 0.5 µm, Advantec) before use.

Table 1 - Chemical composition of river water used in photocatalytic degradation of imidacloprid.

Analytical item	Concentration (µM)
Cl^-	1,135.79±10.25
NO_3-	203.42± 2.45
SO_4 --	211.78± 5.47
NH_4+	7.42±0.54
Mg++	193.05± 2.45
Ca++	622.94± 3.87
pH	7.70±1.78
DOC	3.09±0.28 (mg/L)

Irradiation of water samples was conducted using a solar simulator (Oriel, Model 81160-1000) unit equipped with a 300W Xenon lamp (O_3 free) with special glass filters (Oriel, AM0, and AM1.0) that restricted the transmission of wavelengths below 300 nm. The solar simulator provides illumination approximating natural sunlight at the Earth’s surface, and thus the emitted light has been shown to be equivalent to natural sunlight when conducting photodegradation of pesticides in the aquatic environment.

HPLC analysis-

The treated water samples were analyzed directly using an HPLC system with a mixture of acetonitrile and Milli-Q water (30:70) as the mobile phase. The flow rate was maintained at 1.0 ml min_1 and the UV detector wavelength was 270 nm. The detection and quantification limit of imidacloprid in water were 1.2 and 3 µg/L, respectively.

Mineralization experiments-

To evaluate the mineralization rate of imidacloprid inMilli-Q water by the two tested oxidation systems, losses in DOC and formation rate of inorganic ions (Cl^- and NO_2^-) under irradiation using the solar simulator described above in this study were measured using a TOC analyzer and ion chromatography, respectively. For the loss of DOC with different times of solar light exposure (0, 2, 4, 6, and 8 h) a concentration of 3 mg C/L of imidacloprid was used. After exposure to solar light, the water samples were acidified using HCl and injected directly into a TOC analyzer that had been calibrated using standard solutions of potassium hydrogen phthalate.

Data analysis-

For analysis of variance (ANOVA) of obtained data, XLSTAT PRO statistical analysis software (Addinsoft) was used. Fisher's least significant difference (LSD) test was used to separate the mean of each treatment. All analyses were performed at a significance value of $P < 0.05$.

RESULTS:-

Photocatalytic removal of imidacloprid in water-

Photocatalytic degradation of imidacloprid in water using two advanced oxidation systems (ZnO(nano)/H_2O_2/artificial sunlight and ZnO(normal)/H_2O_2/artificial sunlight) was investigated. The effects of imidacloprid concentration, ZnO concentration, solution pH, catalyst particle size (nano and normal), and water type (Milli-Q and river waters) were evaluated to identify the optimum conditions for photocatalytic removal of imidacloprid in water.

Effect of pH-

Photocatalytic degradation of imidacloprid by the two advanced oxidation systems (ZnO(nano)/H_2O_2/artificial sunlight and ZnO(normal)/H2O2/artificial sunlight) under different pH values (5, 7, and 9) was conducted to evaluate the effects of pH on degradation efficiency., the highest degradation rate of imidacloprid was recorded under a pH of 7 followed by 9 and 5, respectively, in both advanced oxidation systems.

Effect of water type on degradation process-

River and Milli-Q water were used to evaluate the effects of water type on the photocatalytic degradation of imidacloprid under examined advanced oxidation systems (H_2O_2/ UV-Vis, ZnO(normal)/H_2O_2/artificial sunlight and ZnO (nano)/H2O2/artificial sunlight) at a pH of 7. For the normal oxidation system (ZnO(normal)/ H2O2/artificial sunlight), imidacloprid half-lives of 85.89 and 123.23 min were observed in Milli-Q and river water, respectively. However, in nano oxidation systems (ZnO(nano)/H2O2/ artificial sunlight), the imidacloprid half-lives were 72.68 and 88.57 min in Milli-Q and river water, respectively. In the case of H_2O_2/artificial sunlight system, imidacloprid half-lives of 135.2 and 154.8 min were observed in Milli-Q and river water, respectively.

Effect of catalyst particle size-

The effects of zinc oxide particle size (normal and nanosized) on the photocatalytic degradation of imidacloprid in Milli-Q and river water were investigated. The results showed that the particle size of zinc oxide catalyst significantly influenced the photocatalytic degradation rate of imidacloprid, with nanosized zinc oxide resulting in faster degradation than normal sized zinc oxide.

Total mineralization of imidacloprid-

The total mineralization of imidacloprid in water was confirmed by the decline in DOC and the yield of inorganic ions (Cl^- and NO_2^-) with irradiation time under both examined advanced oxidation systems. The mineralization of imidacloprid to CO_2 and H_2O was expressed as a reduction in DOC with irradiation time.

DISCUSSION:-

In this study, significant degradation of imidacloprid with a short half-life (41.68 and 26.24) was observed under the examined advanced oxidation systems, ZnO (normal)/ H_2O_2/artificial sunlight and ZnO(nano)/H_2O_2/artificial sunlight, respectively. The effective degradation of imidacloprid by the two examined advanced oxidation systems was due to the high generation rate of highly reactive ^-OH under both oxidation systems.

Investigation of the effects of the initial concentration of imidacloprid on the rate of its degradation using the tested oxidation systems showed that the imidacloprid degradation rate decreased in response to increasing the primary imidacloprid concentration. The observed decrease in the pesticide degradation rate with an increase in its initial concentration may have occurred because a higher concentration of pollutants reduces the rate of hydroxyl radicals formation and thus decreases the rate of degradation in the solution (Patil et al. 2014). Also, in a previous study, Patil & Gogate (2012) found a similar trend in the degradation of methyl parathion. The results revealed that the photocatalytic degradation rate of imidacloprid increased with increasing concentration of ZnO catalyst either at nano or normal size. The results of this study showed that pH is an important factor affecting the photocatalytic degradation of imidacloprid in water, which is consistent with the results reported by Thuyet et al. (2013), who explained that changes in pH in water play an important role in pesticide destruction.

In this study, the degradation and mineralization rates of imidacloprid were enhanced by irradiation under the ZnO(nano)/H_2O_2/artificial sunlight system relative to the ZnO(normal)/H_2O_2/artificial sunlight system. This may have been because the zinc oxide nanocatalyst used in the nano oxidation system had a small particle size that offered much greater surface area and reactivity, leading to a higher rate of -OH generation relative to the normal particles of zinc oxide catalyst (Dhal et al. 2015), and a subsequently higher degradation rate of organic pollutants (Dhal et al. 2015). Moreover, the higher formation rate of -OH under the ZnO(nano)/H_2O_2/artificial sunlight system than the ZnO(normal)/H_2O_2/artificial sunlight system supports this trend. The higher formation rate of -OH in irradiated H_2O_2 solutions in the presence of ZnO compared with H_2O_2 only reflects the significant role of ZnO catalyst in enhancing the formation rate of -OH.

CONCLUSIONS:-

The degradation rate of imidacloprid using the ZnO(nano)/ H_2O_2/artificial sunlight oxidation system was faster than that of the ZnO(normal)/H_2O_2/artificial sunlight oxidation system in Milli-Q or river water. The photoformation rate of -OH using ZnO (nano)/H_2O_2/artificial sunlight was higher than that of the ZnO (normal)/H_2O_2/artificial sunlight system. Some parameters such as water type, pH, catalyst, and pesticide concentration as well as the catalyst particle size significantly affect the efficacy of advanced oxidation processes during imidacloprid removal from water. Total mineralization of imidacloprid was only achieved by using the ZnO(nano)/H_2O_2/artificial sunlight oxidation system, which confirms the complete detoxification of imidacloprid in treated water. Advanced oxidation processes, particularly with zinc oxide nanocatalyst, can be regarded as an effective photocatalytic method for imidacloprid removal from water.

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