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Various Techniques for Atrazine Removal

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Abstract—**Atrazine [2-chloro-4(ethylamino)-6(isopropylamino) -s-triazine; CAS 1912-24-9; ATZ] is one of the most widely used herbicides in the world for the control of broadleaf weeds in corn and sorghum. Due to its low vapor pressure, longer half life (180 to 360 days), apparent biodegradability, low pKa value and extensive use, atrazine has led to the contamination of terrestrial ecosystems and has been detected in ground and surface waters in many countries beyond permissible limits. Many techniques like incineration, adsorption using activated carbon, reduction-oxidation, photolysis, dechlorination, hydrolysis, deamination, reverse osmosis and chemical degradation have been tried for atrazine removal. These methods are either very costly producing other toxic substances or are not feasible. Biological treatment has been recently reported for atrazine removal due to its ability to use microorganisms for effective remediation. Some novel approaches like phytoremediation, biodegradation and biosorption also have been reported. Several fungi, bacteria and algae have been already reported as effective biosorbents for removal of dyes, metals and even pesticides. Our future study on atrazine removal shall mainly focuses on biosorption owing to its low cost, non-toxic approach, regeneration capability and high efficiency for pollutant uptake.**

Keywords-Atrazine; Biosorption; Biosorbent; Herbicide; Fungus

I. INTRODUCTION

Agricultural development continues to remain the most important objective of Indian planning and policy. Since land availability has not increased with the population, efforts have been made to increase the crop yield. This has led to complete transformation of conventional forms of agriculture. In the process of development of agriculture, pesticides have become an important tool as a plant protection agent for boosting food production. The main uses of pesticides in India are in agriculture and public health sector to combat the various pests and diseases that affect man, respectively. However, exposure to pesticides both occupationally and environmentally causes a range of human health problems.

The worldwide consumption of pesticides is about 2 million tonnes per year, of which 24% is consumed in the USA alone, 45% in Europe and 25% in the rest of the world. India's share is just 3.75%. The usage of pesticides in India is only 0.5 kg/ha, while in Korea and Japan, it is 6.6 and 12.0 kg/ha, respectively. Currently, the pesticides are being used on 25% of the cultivated area.

India is the largest producer of pesticides in Asia (Figures 1 and 2) and ranks twelfth in the world for the use of pesticides [1]. A vast majority of the population in India is engaged in agriculture and is, therefore, exposed to the pesticides used in agriculture. Although, Indian average consumption of pesticide is far lower than many other developed economies, the problem of pesticide residues is very high in India.

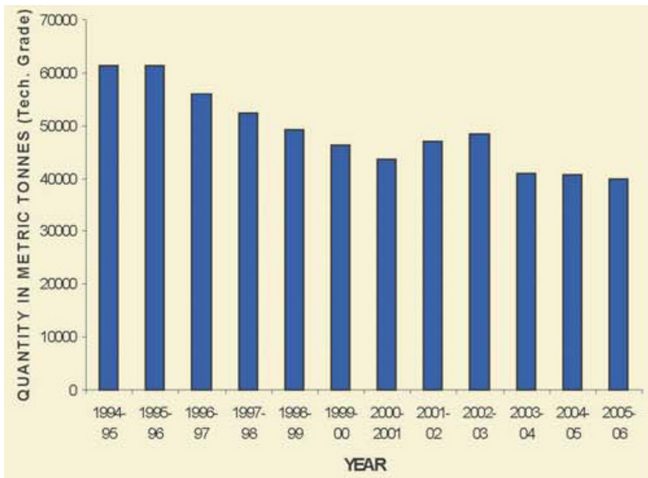

Figure 1. Yearwise Consumption of Chemical Pesticides in India (Source: Adapted from http://dacnetnic.in/lpmweb /lpmhome/lpmpest_ main.htm)

There has been a growing body of data regarding the presence of residual pesticides in the water, air and soil environment since 1960s. The monitoring results obtained show that traces of pesticides may undergo long range transport and be deposited considerable distances away from the treatment areas. These pesticides, then, undergo a variety of transformations that provide a complex pattern of metabolites and pose a threat to human health and the environment including remote areas such as the Arctic and Antarctic regions [2, 3].

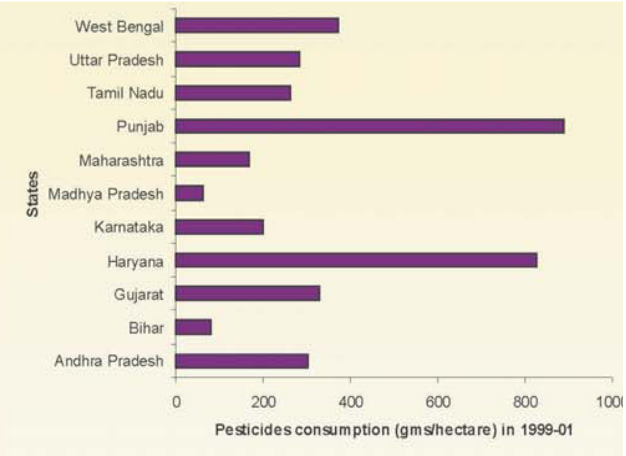

Figure 2. Statewise Consumption of Pesticide in India (Source: Adapted from FAO statshttp://www.fao.org)

The ICMR study has found large amounts of pesticide residues in wide variety of food including fruits, vegetables, pulses, grains, rice, wheat flour, eggs, meat, fish, poultry and milk [4]. Some of the pesticides have been reported to be persistent, toxic, mutagenic, carcinogenic and tumorogenic. Pesticide residues in food can cause numerous health complications like cancer, genetic defects and impotency.

The World Health Organization limits the pesticides' residue in water to 0.1 µg/L for an individual pesticide and to a total of 0.5 µg/L for all pesticides [5]. As per BIS (Bureau of Indian Standards), the pesticide residue should be absent in drinking water and should not exceed 0.005 mg/L in surface waters [6, 7].

Given the major health issues related to pesticide use in the country, it is important to study the removal and degradation methods for such chemicals. In the present work, efforts will be made to develop biosorbent based on the biomass obtained from the dead micro-fungus, which will help in removal of atrazine from water sources.

II. ATRAZINE AND ITS HELATLH EFFECTS

A. *Atrazine*

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1, 3, 5-traiazine) is among the most widely used herbicides in USA, Europe and rest of the world. It was first registered in 1958 as an herbicide.

The chemical structure of Atrazine is given in Figure 3 while Table I shows the important physical and chemical properties of Atrazine.

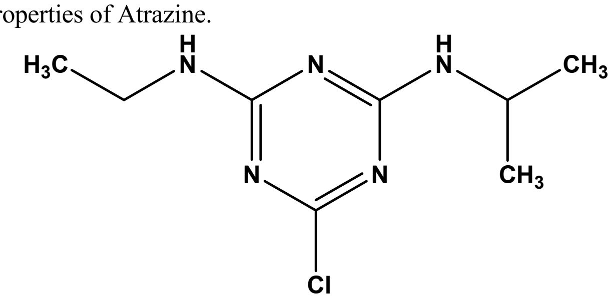

Figure 3. Structure of Atrazine

TABLE I. BASIC CHEMICAL AND PHYSICAL DATA

Empirical formula	$C_8H_{14}ClN_5$
Rel. molecular mass	215.69 g
Density	1.2 g/cm^3
Boiling point	not distillable
Melting point	173-175°C
Vapour pressure	4 x 10^{-5} Pa
Solvolysis/ solubility	Approx. 70 mg/L in water, 12 g/L (20°C) in ether, 18 g/L (at 27°C) in methanol, 36 mg/L (27°C) in n-pentane, 52 g/L (27°C) in chloroform

Atrazine was first synthesized in 1948 [8]. Atrazine is synthesized from cyanuric chloride (A) and iso-propyl amine. This reaction is performed in xylene or toluene in the presence of water as shown in Figure 4. This reaction leads to an intermediate (B) that is further converted under the same reaction conditions with iso-propylamine. In the final step of the reaction, sodium hydroxide is added and separation of the product (C) is performed.

B. *Uses*

Globally, atrazine is used in the production of maize, sorghum, sugar cane, pineapples, chemical fallows, grassland, macadamia nuts, conifers, and for industrial weed control, with its biggest market in maize production.

Atrazine is applied worldwide – in 1998, it was the most widely used maize herbicide in the US, applied to 69% of the maize acreage. The world market for atrazine is worth over $400 million at the user level. In Europe, atrazine consumption has dropped markedly since 1989 due to restrictions on its use and competition from newer, less-persistent herbicides. In the UK, atrazine is not widely applied, however, it still find significant uses in maize production for general weed control, for which there are no alternatives.

C. *Health Effects*

The health effects of atrazine due to its presence in water and food are classified in three types: developmental, reproductive and cancerous. More details are provided in Table II [9].

TABLE II. HEALTH EFFECTS OF ATRAZINE

Effects	Description
Developmental	Post-implantation losses, decreases in fetal body weight, incomplete bone formation, neuro-development effects, delayed puberty, and impaired development of the reproductive system.
Reproductive	Pre-term delivery, miscarriage, and various birth defects.
Cancerous	Non-Hodgkin's lymphoma, prostrate, brain, testes, breast, and ovarian cancer.

III. Treatment Technologies

There are several technologies available for the removal of atrazine from water, wastewater and contaminated soil. Among these, the most commonly used techniques are chemical treatment, incineration, adsorption, phytoremediation and biodegradation.

Most commonly employed chemical methods for the remediation of atrazine bearing wastewaters are photolysis, hydrolysis, dehalogenation and oxygenation.

Table III presents details and disadvantages of various physico-chemical techniques while Table IV lists various methods used in 2010.

Sorption by dead or live cells through metabolism independent processes is termed biosorption. It is an energy-independent, growth independent and surface-binding phenomenon. The special surface properties of bacteria, yeasts, fungi and algae enable them to adsorb different kinds of pollutants from solutions. In comparison to live cells, dead cells are more efficient in technical and economical aspect in most of the cases.

The most commonly used biosorbent materials are based on fungi, yeast, bacteria and algae. Microbial biomass, such as fungi, would be particularly cost effective as there are many food-processing plants in many countries that could provide wastewater as substrate at a very low cost for the cultivation of these. Important fungal biosorbents include *Aspergillus*, *Penicillium* and *Rhizopus*. The anionic functional groups present in the peptidoglycan, teichoic acids and teichuronic acids of Gram-positive bacteria, and the peptidoglycan, phospholipids and lipopolysaccharides of Gram-negative bacteria are reported to be the components primarily responsible for the pollutant binding capability of the cell wall [10].

TABLE III. VARIOUS PHYSIO-CHEMICAL TECHNIQUES FOR ATRAZINE UPTAKE

Methods	Application	Disadvantage	Reference
Incineration	More than 99.9% destruction of organic pesticide is possible.	Formation of corrosive and toxic gases.	[10]
Reverse osmosis	Impurity is separated by a semi-permeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids.	Expensive.	[10]
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 hydroxides, which clog the membrane.	[10]
Chemical degradation	Includes photolysis, hydrolysis, oxygenation etc.	May result in formation of other toxic or unwanted products, costly.	[10]
Immobilized enzyme based technology	Use of two fusion proteins which dechlorinate atrazine while being firmly bound to an insoluble cellulose matrix.	Costly, affects stability of enzymes and diffusion problems.	[10]
Phytoremediation	Poplar trees seemed to be effective in rapid assimilation of ring leveled atrazine (90%) from sandy soil in less than 9 days	Application limited to surface and subsurface soils, time consuming process.	[11]

TABLE IV. RECENT METHODS FOR ATRAZINE REMOVAL

Method used	Applications	References
De-oiled two-phase olive mill waste	Effects of de-oiled two-phase olive mill applied to soil for sorption	[12]
Ultrasonic destruction	The use of high power ultrasound to destroy pesticide contaminants like DDT, chlordane, atrazine, 2,4,5-T and endosulfan in sand slurries	[13]
Photocatalytic degradation	Photocatalytic degradation of pyrene on soil surfaces using nanometer anatase TiO_2 under UV irradiation. The organic contaminants destroyed in a relatively short time when the contaminated soils containing atrazine, 2-chlorophenol, 2,7 dichlorodibenzodioxin mixed with TiO_2 and exposed to simulated solar radiation.	[14]
Dissipation	The dissipation of herbicide O-methyl-O-(2,4-dimethyl-6-nitrophenoxy)-N-isopropyl phosphoramidothioate (H-9201) in soil.	[15]

IV. Conclusion

Based on literature review, biosorption appears to be low cost and non-toxic approach having regeneration capability and high efficiency for pollutant uptake. Hence, the further study has been planned on atrazine removal mainly focusing on biosorption.

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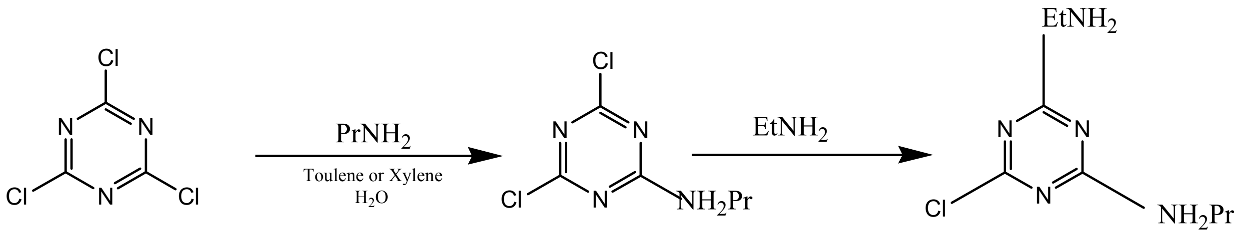

(A) (B) (C)

Figure 4. Synthesis of Atrazine [8]