IOSR Journal Of Environmental Science, Toxicology And Food Technology (IOSR-JESTFT)
e-ISSN: 2319-2402,p- ISSN: 2319-2399. Volume 7, Issue 3 (Nov. - Dec. 2013), PP 94-97
www.iosrjournals.org

Remediation of Pesticide chlorpyrifos in solution using Gamma radiation,SilverAg.Nanoparticles and Advanced oxidation method a comparative studies using GC-MSQP2010PLUS.

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***Abstract**: Advanced oxidation process $O3/H_2O_2$ treatment for solution of chlorpyrifos leads to formation of harmful metabolites like 2-Hydroxy 3,5,6 trichloropyridinol or chlorpyrifos oxon which are more toxic than parent chlorpyrifos gets generated. Silver nanoparticles generated by radiolytic reduction of Silver nitrate 300 milli molar solutionof $AgNO_3$ in presence of capping agent polyethylene glycol PEG when made to interact with 100ppmsolution of chlorpyrifos it leads to annihilation of chlorpyrifos completely without forming harmful products as confirmed by GC-MS analysis. Gamma irradiation of Chlorpyrifos in acetonitrile solution also leads to its degradation. However degradation is exponential in nature as shown in Dose vs conc Graph.Technically, it is easier to treat contaminated solution with Ag.nano particles as compared to gamma irradiation in bulk.*
***Key words**: Chlorpyrifos, Pesticides,Remediation,Ag nano particle, Advanced oxidation process.*

I. Introduction:

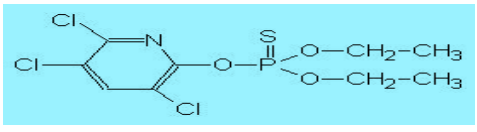
Chlorpyrifos an organophosphate based pesticide which is widely used as pest control for cultivation of different kinds of fruits and vegetables. Chlorpyrifos has an advantage over other products in that it is effective against a wide range of plant-eating insect pests. However residual pesticide remained in soil finally goes to water reservoirs . Since this pesticides are toxic to aquatics ,birds and mammalian species [1] remediation methods like use of advanced oxidation process , Ag. nanoparticles interaction and Gamma Irradiation has been tried and a compared to suit the best method applicable for this particular pesticide remediation in solution.

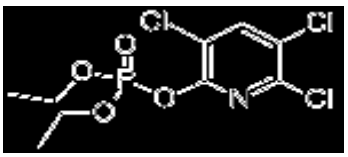
II. Experimental:

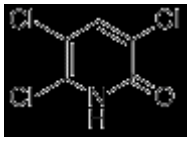
Silver nanoparticle was generated by gamma irradiation of $AgNO_3$ solution[2] in presence of capping agent PEG and isopropanol $OH^{\cdot}$ radical scavenger for absorbed dose of 2kGy. The Ag nano particles has shown plasmon absorption band at 410nm. SHIMADZU GC-MS QP2010Plus was used for monitoring conc. of chlorpyrifos after subjected to addition of silver nano particle solution of milli molar conc.0.2ml added to 1.6 ml of 100ppm solution of Chlorpyrifos.[3] 100ppm solution of chlorpyrifos in acetonitrile was exposed to different conc of O_3 /H2O2 and final products was analyzed using GC-MSQP2010PLUS. GC-MS analysis was done as per method[4]

III. Results and Discussion.

Chemical Formula**:** $C_9H_{11}Cl_3NO_3PS$ **Structure of Chlorpyrifos.**







StrucureI$C_9H_{11}Cl_3NO_3PS$ **strucureII**$C_9H_{11}Cl_3NO_3PO$ **StrucureIII***C5H2Cl3NO*
Structure of Chlorpyrifos Structures of Chlorpyrifos oxon 2-hydroxy3,5,6trichlorPyridine.

StrucutresI, StructuresII and Structures III are shown for chlorpyrifos, chlorpyrifos oxon and 2-hydroxy3,5,6trichlor pyridine in above diagram.

Advanced oxidation process treatment leads to oxidation of sulphur group to oxygen thus becomes Chlorpyrifos oxon. and subsequently cleavage oxygen –phosphorous bonds lead to2-Hydroxy 3,5,6 trichloroPyridine. These metabolites are more toxic as compared to parent compound chlorpyrifos.[5].

Ag.nanoparticles interaction with chlorpyrifos in solution leads annihilation of chlorpyrifos without formation above harmful products. Fig.1 shows GC-MS chromatogram of ozonated chlorpyrifos. The pesticide Chlorpyrifos gets changed to ozonated chlorpyrifos .oxon and 2hydroxy3,5,6trichlor pyridine.

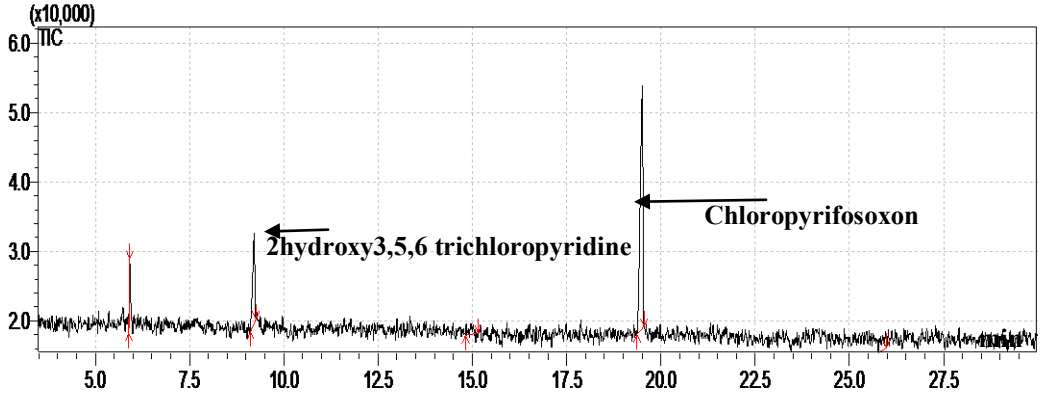


Fig.1GC-MS chromatogram of ozonated Chlorpyrifos

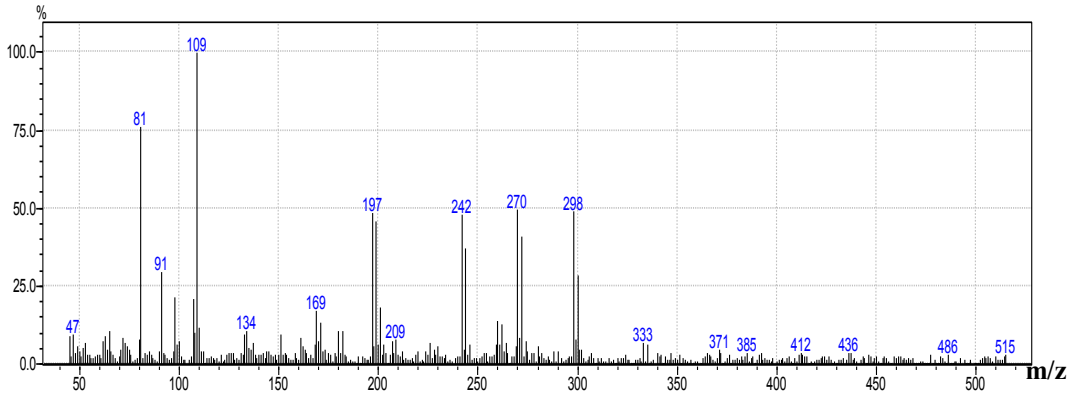


Fig.2 Mass spectrum of Chlorpyrifos oxon. Molwt.333

Fig.2 shows the Mass spectrum of chlorpyrifos oxon and Fig.3 showsMass spectrumof 2hydroxy3,5,6 trichlor pyridine. the

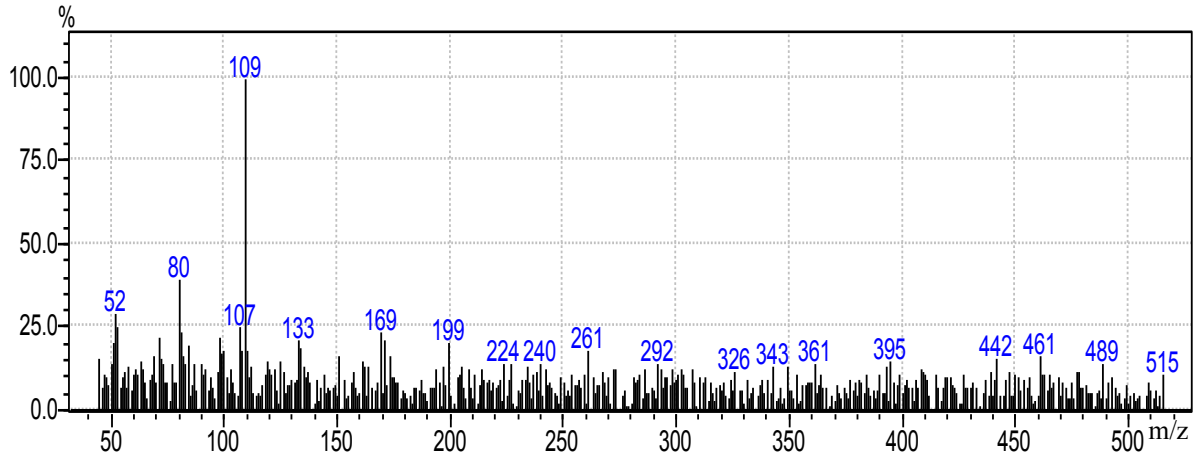


Fig.3 Mass Spectrum of 2hydroxy3,5,6 trichloroPyridine Molwt.197.

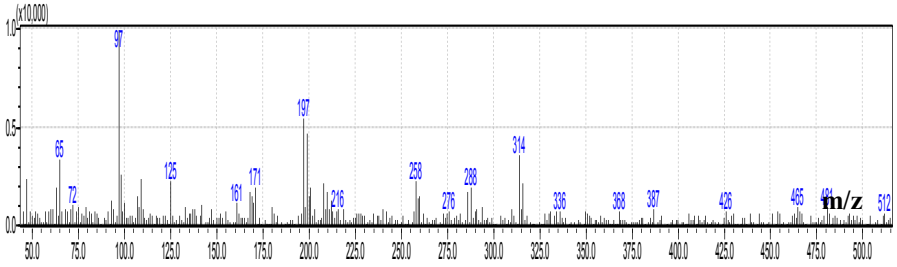


Fig.4Massspectrum of Chlor pyrifos has been shown.

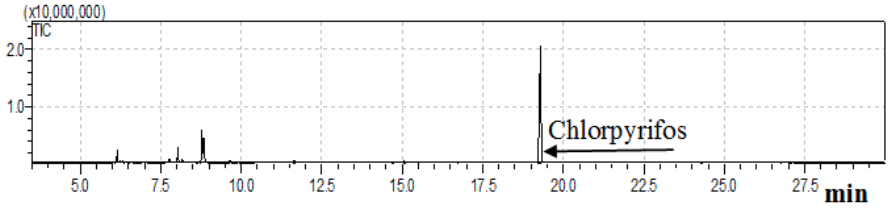


Fig.5GC-MS chromatogram of Chlorpyrifos without Ag.nano particle

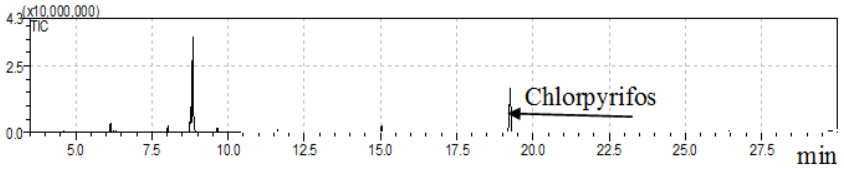


Fig.6GC-MS chromatogram of Chlorpyrifos with Ag nanoparticle

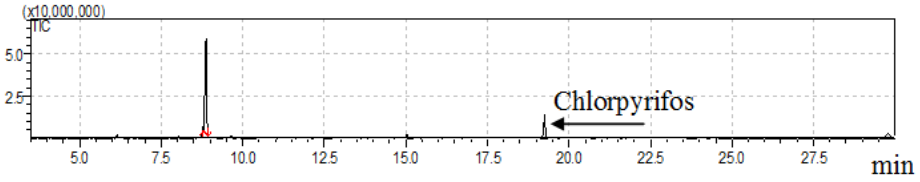


Fig.7GC-MS chromatogram of Chlorpyrifos withAg nano particle

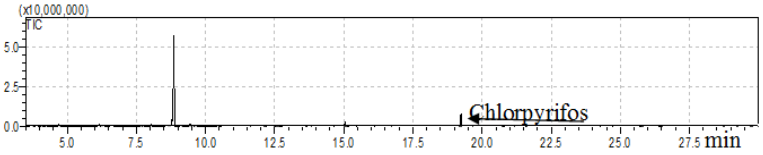
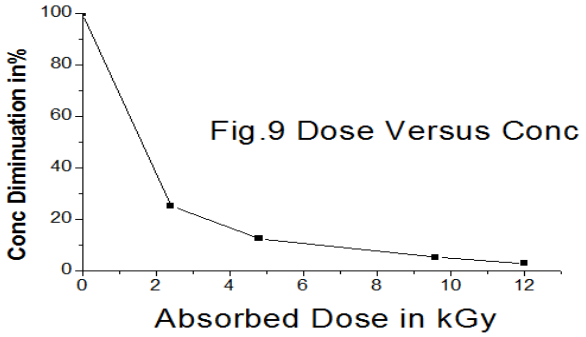


Fig.8GC-MS chromatogram of Chlorpyrifos withAg nano particle.



From Fig.5,6,7 and 8 as shown above it is clear that as we add Ag nano particle solution in Chlorpyrifos solution the peak of chlor pyrifos diminishes as per successive readings. Infact 0.2 millimolar conc of Ag nano particle has been

added to 1.6ml solution of chlor pyrifos of 100ppm concentration. Fig.9 shows the exponetial decay of 100ppm chlorpyrifos solution under Co-60 gamma radiation. Dose rate2.4kGy/hr thus 5 hr irradiation leads to conc. diminuation to 2.97% from initial conc of 100ppm. whereas in case of Ag nano particle it is not even half an hour the conc decreases so fast.

IV. Conclusion.

Thus out of all three methods stated above Ag nano particle interaction appears to be simple to remediate chlorpyrifos.

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