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The Study of Stability of Imazethapyr in the Presence of Some Ions in Water and Milk Samples

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Abstract

This study was carried out to evaluate the stability of imazethapyr in different chemical and physical conditions such as temperature, ionic strength, pH, presence of metallic ions (Ag^+, Cu^{+2}, Na^+, Mg^{+2}) in water and milk matrix. The results were shown that temperature and pH have no effect on degradation or interaction of imazethapyr and only copper ion have selective interaction with imazethapyr. The copper ion can form complex with imazethapyr. Monitoring of imazethapyr was performed using liquid chromatography system.

Keywords:* *Imazethapyr; Copper ion; Milk; High performance liquid chromatography

Introduction

Agricultural, industrial and urban development has caused damage to human health and to the environment due to the high pollution rates, especially in water. The current wide spread use of a range of herbicides in agriculture as a means of controlling weed has been contributing to a growing concern with the contaminations of surface and groundwater bodies. Imazethapyr ((R,S)-5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid) is herbicide, and belongs to a class of chemicals known as imidazolinones. Imazethapyr (IM) is systemic with contact and residual activity. Imazethapyr kills unwanted plants and absorbed by the foliage and roots, with rapid translocation in the xylem and phloem to the meristematic regions, where it accumulates Acetolactate Synthase (ALS) inhibitor [1]. The acute oral Lethal Dose (LD 50) for technical imazethapyr was reported to be>5000 mg/kg for rats. The acute inhalation LC 50 for rats exposed to imazethapyr is 3.27 mg/L. The dermal LD 50 for rabbits exposed to technical imazethapyr was>2000 mg/kg. It was found to be slightly irritating to the rabbit eye, with complete recovery in 7 days.

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The technical material was found to be slightly irritating to the skin of male rabbits. Formulated product: The oral LD 50 of a 110 g/L liquid formulation of imazethapyr was also>5000 mg/kg for the rat and rabbit. The LC 50 was>2.67 mg/L. The dermal LD 50 was>5000 mg/kg. The liquid formulation was non-irritating to the rabbit eye and skin [2].

The behavior of imazethapyr under field conditions is influenced by factors such as physical and biological processes. The IM can interact with Bovine Serum Albumin (BSA) through a static quenching process. Some studies have shown that co-exposure of two different contaminants in the environment may influence their environmental fate, bioavailability and toxicity [3].

In toxicology, depending on the presumed modes of action of the components in a mixture, two concepts are used to predict the effects of mixtures: Concentration Addition (CA) and Independent Action (IA). The effects of the mixture can be additive but if the observed responses are stronger or weaker than expected, then the combined effect is described as being either antagonistic or synergistic, respectively. The occurrence of interactions between heavy metals and organic contaminants (such as pesticides) could have important environmental significance. The impact of such interactions on the toxicity of pesticides in aquatic environments raises new questions regarding the assessment of the combined toxicity of pesticides and heavy metals. The metal ions have the most important effect through stabilization of IM by complexation [4].

It is known that different environment contains different chemical and physical conditions, for the bio-degradation of herbicides. The purpose of this study was to investigate the effect of some parameters such as, pH, temperature and metal ion on the stability of imazethapyr [5].

Materials and Methods

Chemicals

Imazethapyr (99.0% purity) was purchased from Sigma-Aldrich corporation. All solvents employed were of HPLC grade. A stock standard solution (1000.0 mg L^{-1}) of imazethapyr was prepared in water. Water was distilled and purified by a direct-Q3 UV with a pump system (Millipore, Molshein, France). Copper (II) sulfate, sodium chloride, magnesium (II) nitrate, sodium hydroxide and hydrochloric acid were supplied from Merck. Desired solutions were prepared by dissolving a weighed quantity of them in 10.0 mL of water [6].

Apparatus

Analysis of samples was performed using a Model 2695 waters liquid chromatography system (waters, Milford, MA, USA) consisted of auto sampler, an in-line degasser, a 600 E pump, and PDA detector. A Millennium 32 workstation (Waters) was utilized to control the system and for the acquisition and analysis of the data. A Nova Pak C 18 column (3.9 id × 150 mm, 5.0 µm) prepared from waters (Ireland) and was used for separations. For determination of imazethapyr, the mobile phase was a mixture of 0.5% w/v phosphoric acid in water-acetonitrile (70:30, V/V), the flow rate was set at 1.0 mL min^{-1}, and the detection wavelength was set at 254 nm [7].

Sample preparation

To 1.0 mL of sample (milk or water), 2.0 mL of acetonitrile was added in a polypropylene centrifuge tube and then and one gram of NaCl was added and then the sample mixture was vortexes for 1 min. The tube was centrifuged at 3000 rpm for 5 min at room temperature. Acetonitrile (extraction solvent) was separated at the top of centrifuge tube and was drawn out by a Hamilton syringe and transferred to a conical vial and 20.0 µL was injected to HPLC/UV for quantification [8,9].

Effect of acidity and temperature

In the acidity studies, 10 mL of water solution containing 100 mg L^{-1} of imazethapyr at various concentration of sodium hydroxide or hydrochloric acid were used and finally the obtained solution diluted in 1:1 ratio with 0.5% w/v of phosphoric acid and was injected to HPLC. As you can see, IM is stable in the pH range of 0-14 and no new byproduct form under these conditions. It is important to be note that temperature has no effect on stability of IM in the range of 25ºC-65ºC (FIG.1) [10].

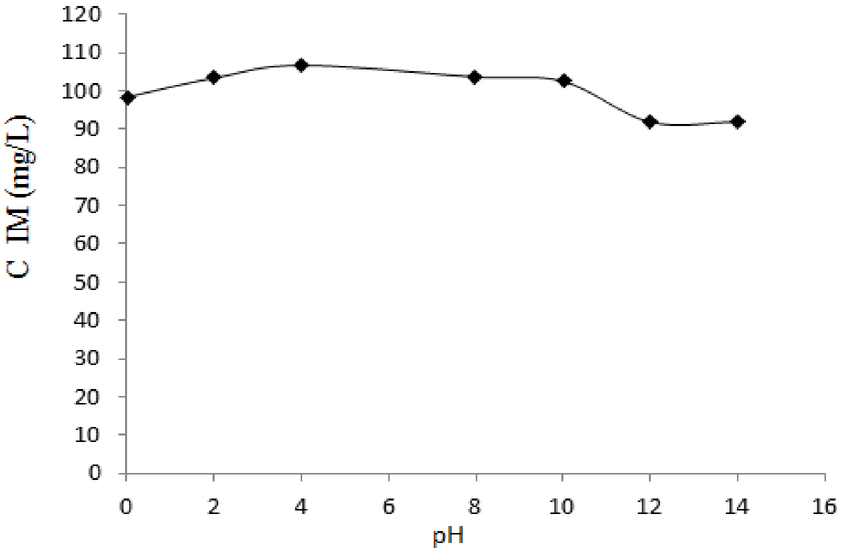

FIG.1. **Effect of pH on stability of imazethapyr. (Conditions: Concentrations of IM (100 mg L^{-1}, Temperature: 25ºC).**

IM is an amphoteric herbicide, having a carboxylic acid and a basic pyridine functional group. Its structure comprises the pyridine group with carboxylic acid and basic functionality. Imazethapyr is a weak acid with pka 1=2.1 and pka 2=3.9. It is weakly acidic compound that may occur in cationic, neutral, or anionic form.

Its ionic state depends upon the pH conditions of the medium: At neutral or high pH, the anionic form predominates causing very low or negative adsorption of the herbicide due to the repulsion of the anions from the negatively charged clay and organic surfaces (FIG.2) [11].

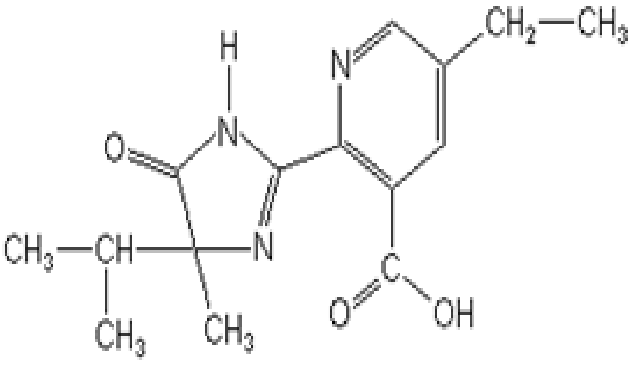

FIG.2. **Structure of imazethapyr.**

Results

Interaction between IM and cations

Fixed concentrations of IM (100 mg L^{-1}), and various concentration of Na, Mg, Ag, and Cu ions were mixed in test tube and used to study the interactions. The results show that only Cu has interaction with IM. The presence of metal ions such as copper (II) stabilizes IM by means of a strong chelating effect. HPLC method was used to determine the interactions between Cu and IM. IM retention time is 6.5 min and it was found that the retention time of IM went changes when Cu was added into the solution. The results also showed that when IM (100 mg L^{-1}) was added to different concentrations of Cu (0.1% w/v, 0.2% w/v, 0.3% w/v, 0.5% w/v and 1% w/v, the concentration of new compound (retention time=2.1 min) and concentration of IM was increased and decreased linearity related to concentration of Cu, respectively. The retention time of IM:Cu complex shifted towards lower time that means probably has positive charge and the new structure is more hydrophilic than IM. Thus, the presence of metal ions such as copper (II) stabilizes IM by means of a strong chelating effect (FIG. 3-FIG. 6) [12].

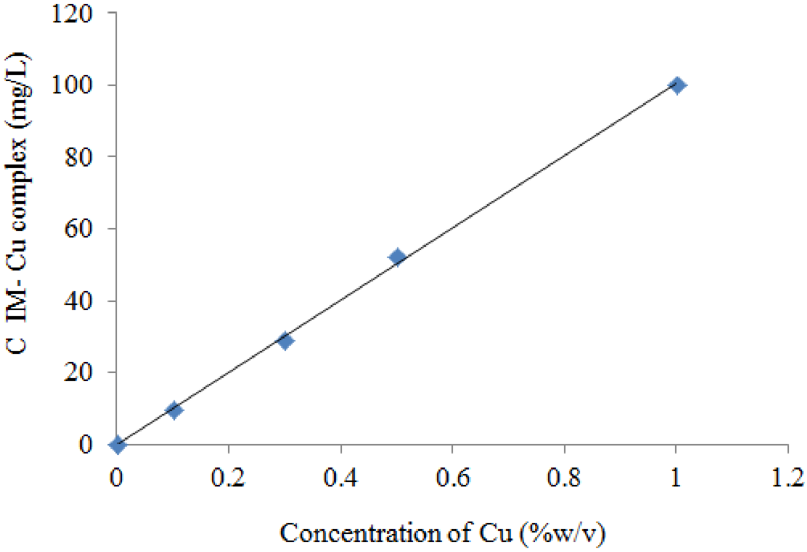

FIG.3. **Effect of copper concentration on IM in water sample. (Conditions: Concentrations of IM (100 mg L^{-1}, Temperature:25°C). Note: y=100.71x-0.1675, R^2=0.9992.**

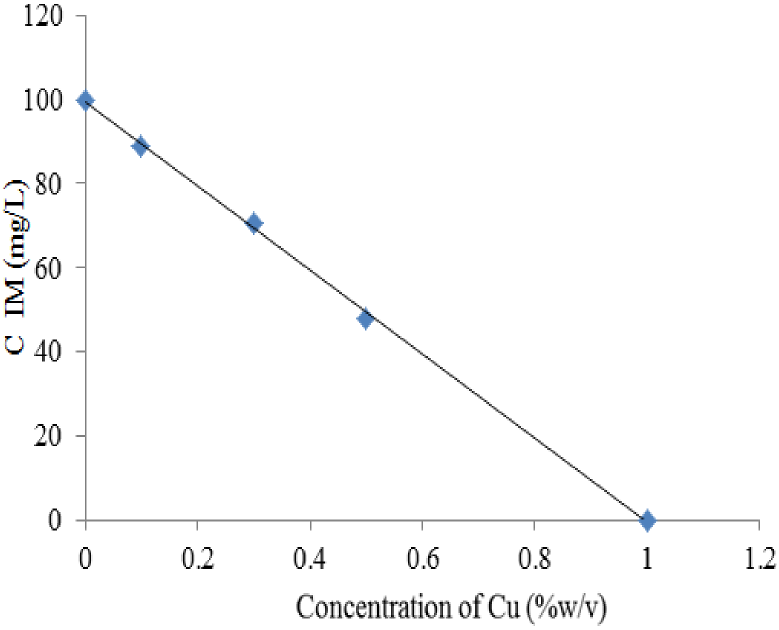

FIG.4. **Effect of copper concentration on IM:Copper complex in water sample. (Conditions: Concentrations of IM (100 mg L^{-1}, Temperature: 25°C). Note: y=-100.04x+99.594, R^2=0.9994.**

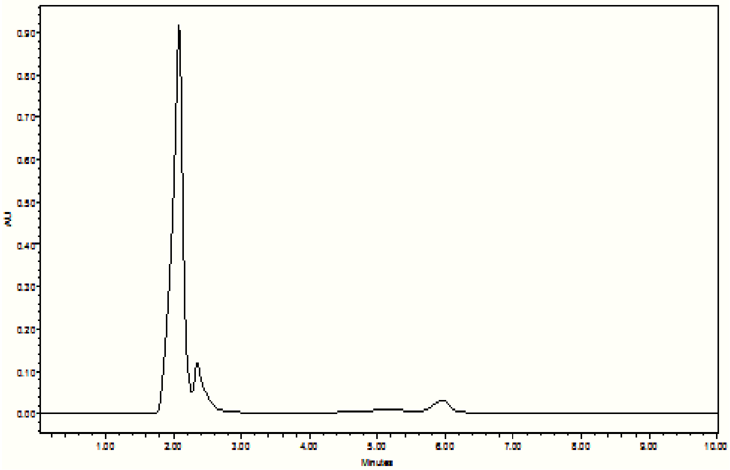

FIG.5. **Chromatogram obtained for imazethapyr at 100 mg L^{-1} Concentration (low) at 25ºC in water.**

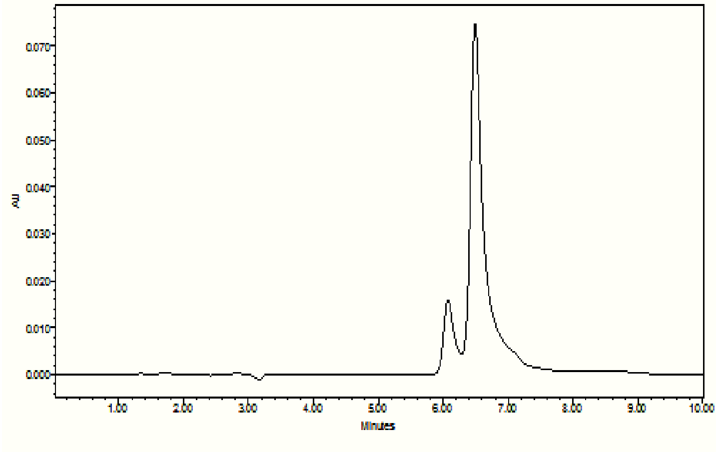

FIG.6. **Chromatogram obtained for IM:Copper complex (RT=2.1 min) (up) at 25ºC in water.**

Discussion

Although, the degradation of the pesticides governed by the factors likes microbial composition, pH, temperature etc. But some pesticides were not degraded and have different behavior. But in milk, the addition of different concentration of copper to IM produces four new byproducts at different retention times (2.1 min, 2.3 min, 6.1 min and 6.8 min) that show some compounds in milk can interact with copper or IM (FIG.7, FIG.8) [13].

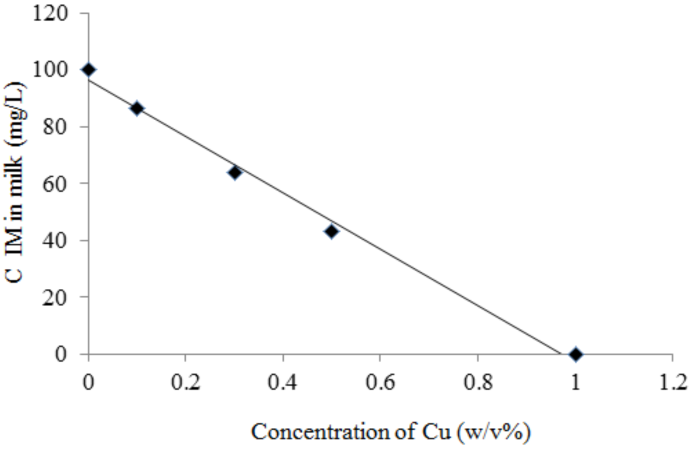

FIG.7. **Effect of copper concentration on IM in milk sample at 25ºC. Note: y= -98.953x+96.347, R^2=0.9935.**

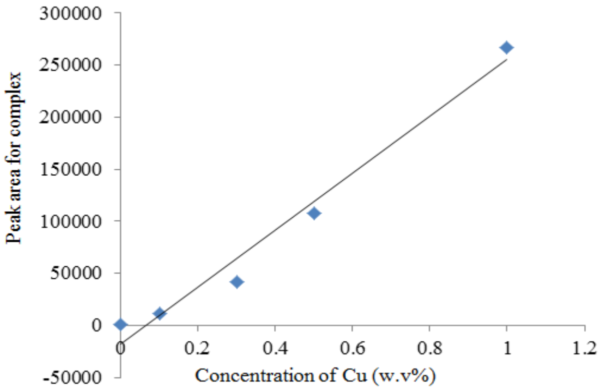

FIG.8. **Effect of copper concentration on IM: Copper Complex (RT=2.1 min) in milk sample at 25ºC. Note: y=273952x-18329, R^2=0.9778.**

Our research results showed that the herbicide IM can form IM-Cu complex. Several researchers have been studying the complexation of copper and imidazolinone herbicides. It was shown that possible binding mechanism can be created between the ions Cu^{+2} and the two nitrogen atoms 1 and 2 of the imidazolinone molecules. Some researcher reported that imazapyr, an herbicide from imidazolinone family, can form the complex $Cu(IM)_2$ with copper up to pH (TABLE1) [14-15].

TABLE.1. **Retention time obtained for IM in water and milk matrix in the presence of 1% Cu solution.**

Type of solution	**RT (min)**				
	2.1	**2.25**	**6.1**	**6.5**	**6.8**
IM solution	No peak	No peak	No peak	Peak	Peak
IM solution + Cu+2 in water	No peak	Peak	No peak	Peak	Peak
IM solution + Cu+2 in milk	Peak	Peak	Peak	Peak	Peak

Conclusion

This study shows that the ions such as (Ag^+, Na^+, Mg^{+2}), pH and temperature has no effect on imazethapyr stability and only Cu^{+2} has interaction with imazethapyr. Our work has shown that Cu^{+2} ions have effect through stabilisation of imazethapyr by complexation. This process can use for detoxification of imazethapyr and Cu^{+2}. Although this study does not predict exactly the behaviour of pesticides under environmental conditions, it shows the potential importance of metal salts (Cu^{+2}) in pesticide persistence.

References

1. Pacheco ME, Bruzzone L. Interactions between imazethapyr and bovine serum albumin: Spectrofluorimetric study. J Lumin. 2012;132:2730-2735.

2. Quivet E, Faure R, Georges J, et al. Influence of metal salts on the photodegradation of imazapyr, an imidazolinone pesticide. Pest Manag Sci. 2006;62:407-413.

3. Reimche GB, Machado SL, Oliveira MA, et al. Imazethapyr and imazapic, bispyribac-sodium and penoxsulam: Zooplankton and dissipation in subtropical rice paddy water. Sci Total Environ. 2015;514:68-76.

4. Wen Y, Zhang L, Chen Z, et al. Co-exposure of silver nanoparticles and chiral herbicide imazethapyr to Arabidopsis thaliana: Enantioselective effects. Chemosphere. 2016;145:207-214.

5. Kim KH, Kabir E, Jahan SA. Exposure to pesticides and the associated human health effects. Sci Total Environ. 2017;575:525-535.

6. Chen H, Sheng X, Wen Y, et al. New insights into the effects of the herbicide imazethapyr on Cu (II) ecotoxicity to the aquatic unicellular alga *Scenedesmus obliquus*. Aquat Toxicol. 2013;140:407-414.

7. Jia S, Zhou Y, Li J, et al. Highly selective enrichment and direct determination of imazethapyr residues from milk using magnetic solid-phase extraction based on restricted-access molecularly imprinted polymers. Anal Methods. 2021;13:426-435.

8. Rohit JV, Kailasa SK. Simple and selective detection of pendimethalin herbicide in water and food samples based on the aggregation of ractopamine-dithiocarbamate functionalized gold nanoparticles. Sens Actuators B Chem. 2017;245:541-550.

9. Tarley CR, Suquila FA, Casarin J, et al. Development of selective preconcentration/clean-up method for imidazolinone herbicides determination in natural water and rice samples by HPLC-PAD using an imazethapyr imprinted poly (vinylimidazole-TRIM). Food chem. 2021;334:127345.

10. Casarin J, Gonçalves Jr AC, Segatelli MG, et al. Poly (methacrylic acid)/SiO_2/Al_2O_3 based organic-inorganic hybrid adsorbent for adsorption of imazethapyr herbicide from aqueous medium. React Funct Polym. 2017;121:101-109.

11. Casarin J, Junior AC, Segatelli MG, et al. Insight into the performance of molecularly imprinted poly (methacrylic acid) and polyvinylimidazole for extraction of imazethapyr in aqueous medium. Chem Eng J. 2018;343:583-596.

12. Urseler N, Bachetti R, Morgante V, et al. Groundwater quality and vulnerability in farms from agricultural-dairy basin of the *Argentine Pampas*. Environ Sci Pollut Res Int. 2022:1-9.

13. Speltini A, Scalabrini A, Maraschi F, et al. Newest applications of molecularly imprinted polymers for extraction of contaminants from environmental and food matrices: A review. Anal Chim Acta. 2017;974:1-26.

14. Lubomirsky E, Padro JM, Reta MR. Development of a dispersive liquid-liquid microextraction technique for the analysis of aryloxyphenoxy-propionate herbicides in soy-based foods. Microchem J. 2016;129:63-70.

15. Van Emon JM, Gerlach CL, Bowman K. Bioseparation and bioanalytical techniques in environmental monitoring. J Chromatogr B Biomed Sci Appl. 1998;715:211-228.