C. R. Chimie xxx (2018) 1–6

Contents lists available at ScienceDirect

Comptes Rendus Chimie

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Imidazolinone and triazine herbicides in soils in relation to the complexes formed with Cu(II) ions

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ARTICLE INFO

Article history:
Received 26 March 2018
Accepted 15 May 2018
Available online xxxx

Keywords:
Imidazolinone herbicides
Triazine herbicides
Copper complexes
Stability constants
Heavy metal pollution

ABSTRACT

Imidazolinone and triazine herbicides are used in many countries and may have a great impact on metal biocycles in soil. This article deals with the dynamics of imidazolinone and triazine herbicides in soils related to the formation of complexes with Cu(II) ions, which can be very stable. The stability constants of the complexes formed by five imidazolinone herbicides and ten triazine herbicides with Cu(II) ions are determined by means of fast, easy, and inexpensive measurements performed by ultraviolet–visible spectroscopy, for imidazolinones, and voltammetry (cyclic and differential pulse), for triazines. Because of the occurrence of dissociation reactions, the determinations were performed at three pH values for imidazolinones and at one pH value for triazines. In aqueous solutions of $5 < pH < 10$ (corresponding to the majority of soils of agricultural use), the herbicides form very stable complexes with the Cu(II) ions, the complexes being integrated by two ligands (herbicides) and one copper ion. In conclusion, crops treated with such herbicides in conjunction with Cu(II) salts experience a decrease in its persistence and effectiveness. In addition, the herbicides and the copper ions may pass to the phreatic layer of the soil, increasing the chance of pollution.

1. Introduction

In past few years, public awareness of environmental protection is increasing. Ecofriendly agriculture implies the control of plant protection products. These are tools to obtain high crop yields but their uncontrolled use in conjunction with inorganic salts, such as copper nitrate and sulfate, could cause negative impacts to the ground, water, and living organisms.

Pesticides and their metabolites are usual contaminants of groundwater [1] but imidazolinone herbicides (imazapyr, imazapic, imazethapyr, imazamox, and imazaquin) present low toxicity for humans, being an alternative to phenoxy herbicides, such as 2,4-D and 2,4,5-T, or to triazine herbicides, especially those of the atrazine family.

In a previous article [2], the speciation of imidazolinone herbicides in aqueous media was studied from ultraviolet–visible (UV–vis) and potentiometric measurements. The effect of pH in the natural dynamics of these herbicides was discussed. Triazines are pesticides belonging to the group of herbicides used to control weed growth. The action of triazines is most based on the first stages of the plant growth, because they destroy a wide variety of plants in the first days of germination (10–15 days). They are used in agriculture in an extended way and are of pre-emergence and postemergence type. They also make the

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https://doi.org/10.1016/j.crci.2018.05.007
1631-0748/

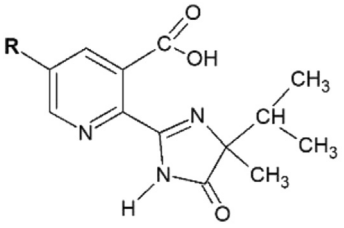
photosynthesis largely impossible, because many of them are absorbed by the root system and are accumulated in the leaves of the plant.

Herbicides may have a great impact on metal biocycles in soil [3,4], interacting with clay components. These heterocyclic compounds form complexes with metal ions as Co(III), Mn(II), Ni(II), Cu(II), and so forth [3–8]. These complexes have been studied mainly in solid state by EPR, IR or FTIR, and ESI mass spectrometry, but their behavior in aqueous solutions is poorly known.

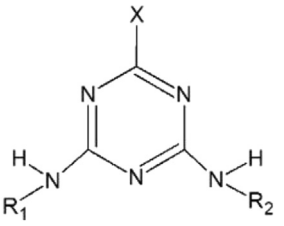
Copper derivatives are commonly used on crop foliage to control fungal disease [8,9], being an essential metal for plants, and playing a key role in photosynthesis [10,11].

The aim of this work is, first, to determine the stability constants of the complexes formed by the imidazolinone and triazine herbicides when they interact with Cu(II) ions, by means of rapid, easy, and nonexpensive measurements performed by UV–vis spectroscopy, for the imidazolinone herbicides, and by electrochemical measurements, for the triazine herbicides, and second, to relate the stability of these complexes with the dynamics of the herbicides and the copper ions in the soils.

The structures of the herbicides are



Imidazolinone herbicides



Triazine herbicides

2. Materials and methods

In all cases, Merck analytical grade reagents were used with the exception of imidazolinone herbicides, which were from Riedel de Haën (analytical standards). All other reactants were used without further purification. Solutions were prepared using ultrapure water type I (resistivity 18.2 MΩ cm at 25 °C) obtained by an ultrapure water system Millipore Simplicity.

Spectrophotometric studies were performed using a double beam Varian Cary 100BIO spectrophotometer. Hanna quartz cuvettes of 1 cm path length were used. Electrochemical measurements were performed with an Autolab PGSTAT302N potentiostat using the software package NOVA 1.7. A three-electrode cell equipped with a Pt wire counter electrode and a BAS MF-2079 $Ag/AgCl_3$ M KCl reference electrode was used. The working glassy carbon electrode of 38.5 mm^2 area was polished with a silicon carbide paper, followed by diamond (0.25 μm) slurry and alumina (0.3 and 0.05 μm) slurries. Residual polishing material was removed from the surface by sonication of the electrode in water bath for 30 min. Solutions were purged with purified nitrogen and the temperature was kept at 25 ± 0.1 °C.

3. Results and discussion

3.1. Imidazolinone herbicides

Imidazolinone herbicides present three pK values corresponding to acid–base equilibria [2], which means that the possible copper complexes formed depend on the pH, i.e. on the protonation state of the herbicide.

The lowest pK values (pK_1) correspond to the simultaneous protonation–dissociation equilibria of the pyridinic (or quinolinic) nitrogen and the carboxyl group. The following pK (pK_2) corresponds to the iminium nitrogen and the basic pK (pK_3) to the dissociation of the imido nitrogen. The pK values are presented in Table 1.

At pK_1 < pH < pK_2 (below pH 6 and until pH ca. 2.5), the predominant form of the herbicide in the solution is a zwitterion having both positive and negative charges (see Scheme 1). In addition, the herbicides will be negatively charged at pH greater than pK_2 and lower than ca. 11, which includes virtually all of the soils. These pK values are important in the discussion of the effect of pH in the natural dynamics of imidazolinone herbicides. This is especially true in the case of the soil sorption of the herbicides, because of the possible occurrence of interactions with the soil colloids. So, three pH values were selected to investigate the complex formation (1, 2.8, and 6.8), at which the predominating forms of the herbicides are shown in Scheme 1.

The stability constants of the complexes of imidazolinone herbicides with Cu(II) ions were obtained by spectroscopic measurements. First, the UV–vis spectra of both

Table 1
pK values of the protonation–dissociation reactions of the imidazolinone herbicides in acidic media [2].

Herbicide	R	pK_1	pK_2	pK_3
Imazapyr	H	1.9	3.6	10.8
Imazapic	$-CH_3$	2.1	3.9	11.1
Imazethapyr	$-CH_2-CH_3$	2.1	3.9	10.5
Imazamox	$-CH_2-O-CH_3$	2.09	5.04	10.8
Imazaquin	Quinoline	1.8	3.7	11.03

Please cite this article in press as: M.T. Moreno, et al., Imidazolinone and triazine herbicides in soils in relation to the complexes formed with Cu(II) ions, Comptes Rendus Chimie (2018), https://doi.org/10.1016/j.crci.2018.05.007