TRICYCLAZOLE-CLAY COMPLEXES AS POTENTIAL SMART DELIVERY SYSTEMS: RELEASE IN WATER AND ENVIRONMENTAL FATE IN ALLUVIAL AND SANDY SOILS

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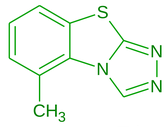
INTRODUCTION

- Tricyclazole is a systemic fungicide used for the control of rice blast caused by *Pyricularia oryzae*
- After its application on paddy fields by aerial fumigation is frequently detected in surrounding waters
- The aim of this work was the modification of natural mineral clays with Fe^{3+} cation or a biopolymer to increase the adsorption capacity for tricyclazole and the preparation of tricyclazole-clay complexes to be used as controlled release formulations (CRFs).

MATERIALS AND METHODS

Fungicide



MW 189,24 g mol^{-1}
Water solubility 596 mg L^{-1}
log Kow 1,4 (pH 7, 20 ºC)

Tricyclazole

Mineral clays

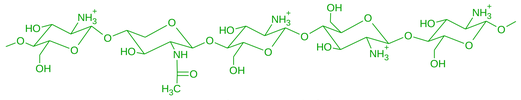
SWy (standard smectite, CEC 76 meq/100g)

CTI (smectite low content mineral, 30-33% smectite)

SH (CEC 44 meq/100g)

Cation and biopolymer

Fe^{3+}

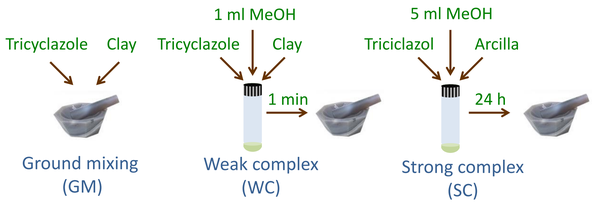


Chitosan (ch)

Soils

Soil	Sand (%)	Silt (%)	Clay (%)	CO (%)	pH	$CaCO_3$ (%)
Alluvial	19,8	43,7	36,4	1,38	8,23	25,9
Sandy	95,7	1,2	3,0	0,27	8,43	3,8

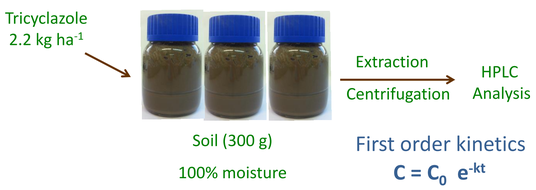
Fungicide-clay complexes



Adsorption-desorption isotherms

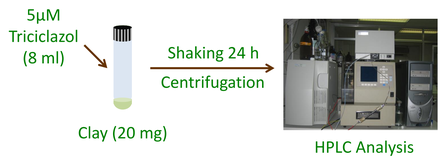
Adsorption C_i = 1,2,5,7, 10 µM
Freundlich equation $C_s = K_f C_e^{Nf}$
Desorption from initial adsorption at 10 mM
Hysteresis index $H = Nf_{des}/Nf_a$

Dissipation studies

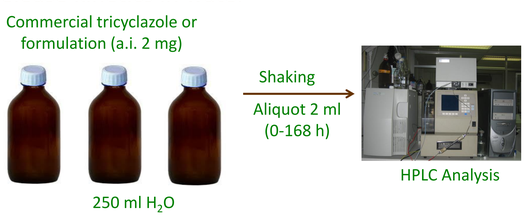


First order kinetics
$C = C_0\ e^{-kt}$

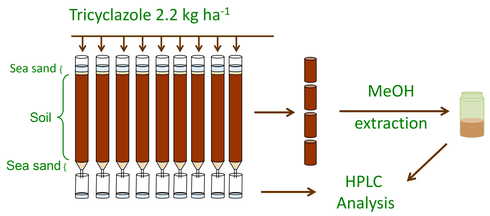
Adsorption at one concentration



Release kinetics in water

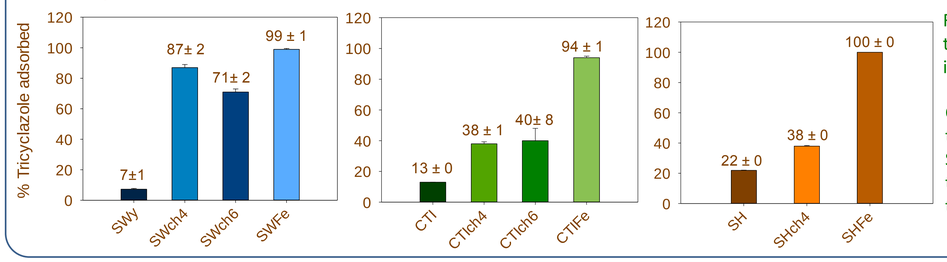


Leaching studies



RESULTS AND DISCUSSION

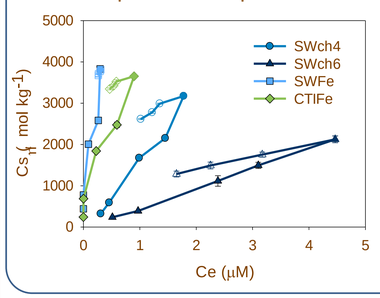
Adsorption at one concentration



Fe^{3+} ions favor the protonation of tricyclazole, being adsorbed at the interlayer; render greatest adsorption

Chitosan modification increased tricyclazole adsortption only on SWch4 because the polymer enters in the interlayer making it available for tricyclazole

Adsorption-desorption isotherms

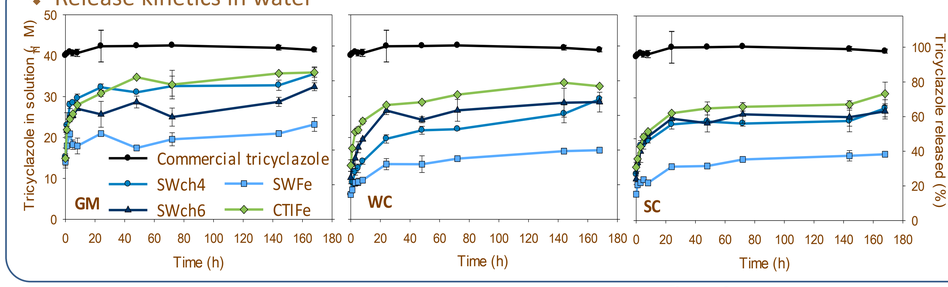


Clay	$K_{f\,a}$ (mmol L^{Nf} kg^{-1})	$N_{f\,a}$	r^2	$Kd_{0.5}$ (Lkg^{-1})	$K_{f\,des}$ (mmol L^{Nf} kg^{-1})	$N_{f\,des}$	r^2	H
SWch4	1517 (1419-1622)[a]	1.3 ± 0.1[b]	0.99	1270	2618 (2571-2666)[a]	0.4 ± 0.1[b]	0.96	0.28
SWch6	448 (430-466)	1.0 ± 0.0	0.99	435	993 (978-1008)	0.5 ± 0.0	0.99	0.48
SWFe	5321 (3500-8089)	0.4 ± 0.2	0.74	7993	4688 (4040-5440)	0.2 ± 0.1	0.53	0.41
CTIFe	3083 (2727-3486)	0.3 ± 0.0	0.95	5185	3715 (3648-3784)	0.1 ± 0.0	0.80	0.38

[a]Numbers in brackets are standard errors of the mean. [b]Mean ± standard error

Tricyclazole adsorption on the modified clays followed the order: SWFe > CTIFe > SWch4 > SWch6
Three different kinds of isotherms were observed: SWch6 (Nf = 1, lineal) due to hydrophobic interactions
SWch4 (Nf > 1)polar and hydrophobic interactions
SWFe and CTI Fe (Nf < 1) polar and ionic interactions

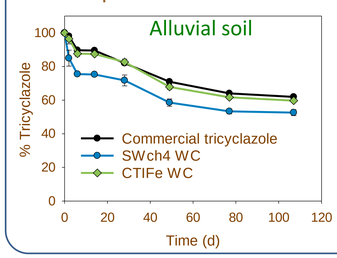
Release kinetics in water



The tricyclazole-smectite complexes assayed showed a slow release profile of the fungicide, but SWFe-tricyclazole released less than 50% of active ingredient

CTIFe GM and WC showed good properties as slow release formulations, tricyclazole release was greater than 80%.

Dissipation studies

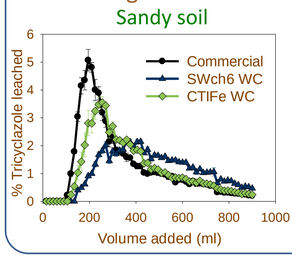


Formulation	$t_{1/2}$ (d)	r^2
Commercial	150 (136-168)[a]	0.936
SWch4 WC	131 (111-160)	0.835
CTIFe WC	141 (127-160)	0.925

[a]Numbers in brackets are standard errors of the mean

No significant differences were observed on tricyclazole half life with the formulation in the alluvial soil

Leaching studies



Tricyclazole leaching decreased in the sandy soil when applied as clay complexes as compared to the commercial product

Tricyclazole was not detectd in the leachates of the alluvial soil and soil depth distribution did not change from commercial to complexes

Leaching studies

Formulation Alluvial soil	% Leached	% Extracted 0-5 cm	% Extracted 5-10 cm	% Extracted 10-15 cm	% Extracted 15-20 cm	% Total recovered
Commercial	0	63 ± 2	11 ± 4	0	0	74 ± 2
SWch4 WC	0	59 ± 1	4 ± 3	2 ± 0	0	65 ± 1
CTIFe WC	0	58 ± 3	7 ± 2	0	0	65 ± 2

The formulations favor the retention of the fungicide to the alluvial soil as compared to the commercial formulation

Formulation Sandy soil	% Leached	% Extracted 0-5 cm	% Extracted 5-10 cm	% Extracted 10-15 cm	% Extracted 15-20 cm	% Total recovered
Commercial	75 ± 1	0	1 ± 0	3 ± 0	5 ± 1	84 ± 1
SWch6 WC	65 ± 2	3 ± 0	4 ± 0	5 ± 1	8 ± 1	85 ± 2
CTIFe WC	69 ± 3	2 ± 0	2 ± 0	3 ± 0	6 ± 0	82 ± 2

Commercial tricyclazol leaches faster in the sandy soil than from the formulations

CONCLUSIONS

- The adsorption of tricyclazole increased in the clays modified with cations. The greatest increase was observed on SWFe, which could be tested as filter to treat contaminated waters, due to its high capacity of adsorption
- For sandy soils, SWch-tricyclazole complexes decreased the tricyclazole leached concentration
- The tricyclazole-smectite complexes with Fe^{3+} or chitosan allow to mantain lower fungicide concentration in the water table on flooded systems for rice cultivations, meanwhile mantaining the soil depth distribution and persistence in the soils.

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