SORPTION OF IONIC MODEL HERBICIDES ON POLYMERIN

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INTRODUCTION

The problem of olive mill wastewaters (OMW) disposal has stimulated many researchers to study methods for their exploitation. To this end, the polymeric organic fraction named *polymerin* was isolated from OMW and characterized. It is an organic-metal mixture with humic-like properties. Previously, we demonstrated that polymerin exhibits strong sorption properties for heavy metals. Therefore, we decided to study the sorption on polymerin of two ionic model herbicides, paraquat and 2.4-D.

AIM

The aim of this work was to study a sorption model for the potential employment of the polymerin as biofilter for decontamination of polluted waters by ionic herbicides and general ionic pesticides.

MATERIALS AND METHODS

Sorption as a function of pH

The pH experiments were carried out in a range from 3.0 to 8.0 at concentration of 0.27 mmol L^{-1} for paraquat, and from 2.0 to 5.0 adding 0.22 mmol L^{-1} for 2.4-D.
All the experiments were conducted at solid/liquid ratios of 0.5, 1.25 and 2.5.

Sorption kinetics

Kinetic studies, carried out varying the incubation time from 0 to 48 h, were performed using the same concentrations of herbicide as above reported at polymerin native pH (5.7) for paraquat and at pH 3.0 for 2.4-D.

Isotherms

Sorption isotherms were carried out with initial concentrations of pesticide ranging from 0.1 to 4.0 mmol L^{-1} at pH 5.7 for paraquat and from 0.1 to 1.0 mmol L^{-1} at pH 3.0 for 2.4-D. Samples were stirred for 4 h and 24 h for paraquat and 2.4-D, respectively.

Separation of the liquid phase

Polymrin was separated from the solution using three different systems: i) ultrafiltration (cell equipped with a 1000 Da cut-off membrane), ii) Amicon Centricon (simultaneous centrifugation and filtration through a horizontal membrane), iii) Amicon Ultra (simultaneous centrifugation and filtration through two transversal membranes).

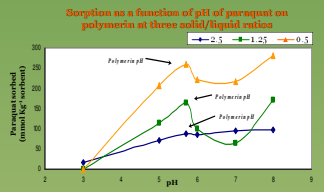
RESULTS

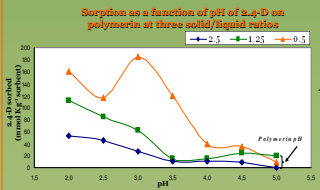
SYSTEMS OF SEPARATION	Paraquat sorbed (mmol Kg^{-1} sorbent)	
Ultrafiltration	770*	770**
Amicon Centricon	319*	410**
Amicon Ultra	652*	1082**

* The amount of Paraquat added was 1,0 mmol L^{-1}
** The amount of Paraquat added was 4,0 mmol L^{-1}

Amicon Ultra was the most rapid, low cost and reproducible system.

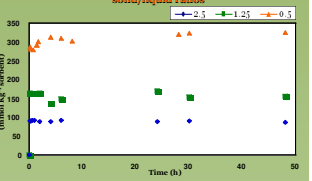
Paraquat sorption was greatest at polymerin native pH (5.7).

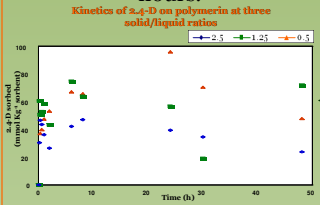




Sorption of 2.4-D increased at low pH values.

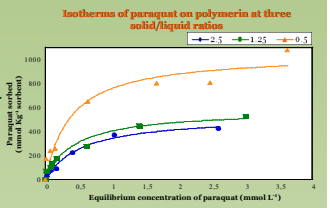
Paraquat kinetics show a fast reaction time, reaching plateau after 4 hours.

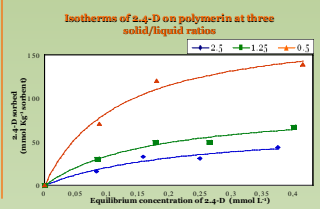




2.4-D is very slowly adsorbed, reaching the maximum after 24 hours.

Highest amounts of paraquat adsorbed (1082 mmol Kg^{-1}) were observed at solid/liquid ratio of 0.5.





At solid/liquid ratio of 0.5 polymerin adsorbed 140 mmol Kg^{-1} of 2.4-D.

CONCLUSIONS

✓ Paraquat shows a sorption kinetic very fast (4 h) at polymerin native pH (5.7). 2.4-D interacts slowly with the polymerin (24 h) at acid pH (3.0).

✓ Highest amounts of paraquat and 2.4-D adsorbed were observed at solid/liquid ratio of 0.5, probably as a consequence of a conformational variation of the matrix that lead to increase amount of its sorption sites.

✓ Polymerin exhibits different sorption capacity between cationic and anionic herbicides, due to the ionic exchange in the first case, and the H-bonding interactions in the second.

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