# EUROPEAN CONFERENCE ON PESTICIDES AND RELATED ORGANIC MICROPOLLUTANTS IN THE ENVIRONMENT

14th Symposium on Chemistry and Fate of Modern Pesticides

http://www.pesticides2014.gr

info@pesticides2014.gr

### **loannina, Greece** September 18-21, 2014

"Karolos Papoulias"
Conference Center
University of Ioannina

**FINAL PROGRAMME** 



#### Organized by:



EUROPEAN AND MEDITERRANEAN
ASSOCIATION FOR ENVIRONMENTAL
EDUCATION ASSESSMENT AND PROTECTION



DEPARTMENT OF CHEMISTRY SCHOOL
OF SCIENCES UNIVERSITY OF IOANNNNA





GRUPPO DI RICERCA ITALIANO FITOFARMACI E AMBIENTE





INTERNATIONAL ASSOCIATION OF ENVIRONMENTAL ANALYTICAL CHEMISTRY

1964 -2014 Celebrating the



50TH ANNIVERSARY

PP32 ACT1024

#### DISSIPATION OF PESTICIDES IN AN AMENDED SOIL AT TWO RATES AND ITS IMPACT ON THE SOIL MICROBIAL COMMUNITY

<u>A. Álvarez-Martin<sup>1,2</sup>\*,</u> G. Bending<sup>2</sup>, S. L. Hilton<sup>2</sup>, M.S. Rodríguez-Cruz<sup>1</sup>, M.J. Sánchez-Martín<sup>1</sup>

<sup>1</sup>Instituto de Recursos Naturales y Agrobiología de Salamanca (IRNASA-CSIC), Cordel de Merinas 40-52, 37008 Salamanca, España:

PP33 ACT1074

#### DEVELOPMENT OF NOVEL CATALYTIC BIOSCAVENGERS FOR HERBICIDE DETOXIFICATION <u>F. Pouliou</u>, F. Perperopoulou, N. E. Labrou\*

Laboratory of Enzyme Technology, Department of Agricultural Biotechnology, Agricultural University of Athens, Greece

**PP34** ACT1076

#### GLOBAL SENSITIVITY ANALYSIS OF PESTICIDE LOSSES IN STRUCTURED TILE-DRAINED SOIL

R. Dairon<sup>1,2</sup>, C. Lauvernet<sup>2</sup>, B. Cheviron, N. Carluer<sup>2</sup>

<sup>1</sup> Arvalis-Institut du végétal, 3 rue Joseph et Marie Hackin 75016 Paris

<sup>2</sup>Irstea, UR MALY, 5 rue de la Doua, F-69626 Villeurbanne, France

PP35 ACT1086

#### FATE OF CYPRODINIL AND FLUDIOXONIL RESIDUES IN STORED APPLES AT OZONE-ENRICHED ATMOSPHERE

#### A. Papadi-Psyllou, D. Tsouris, G. Mergialis, N. G. Tsiropoulos

Department of Agriculture, Crop Production & Rural Environment, Analytical Chemistry and pesticides Laboratory, University of Thessaly, 38446 Nea Ionia - Volos, Greece

PP36 ACT1089

#### REMOVAL OF TRIMETHOPRIM AS ORGANIC MICROPOLLUTANT IN AQUEOUS MATRICES USING MODIFIED CHITOSAN SUPER-ADSORBENT BEADS

M. M. Laimou-Geraniou<sup>1</sup>, G. Z. Kyzas<sup>2</sup>, S. G. Nanaki<sup>2</sup>, A. I. Koltsakidou<sup>1</sup>, D. N. Bikiaris<sup>2</sup>, <u>D. A. Lambropoulou<sup>1,\*</sup></u>

<sup>1</sup>Laboratory of Environmental Pollution Control, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece

<sup>2</sup> Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece

PP37 ACT1093

#### SYNTHESIS OF MOLECULARLY IMPRINTED POLYMERS (MIPS) FOR THE SELECTIVE REMOVAL OF IBUPROFEN FROM BIOMEDICAL WASTEWATERS

G. Z. Kyzas\*, D. N. Bikiaris

Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece

<sup>&</sup>lt;sup>2</sup>School of Life Sciences, University of Warwick, Coventry CV4 7AL, United Kingdom

# SYNTHESIS OF MOLECULARLY IMPRINTED POLYMERS (MIPS) FOR THE SELECTIVE REMOVAL OF IBUPROFEN FROM BIOMEDICAL WASTEWATERS

#### George Z. Kyzas\*, Dimitrios N. Bikiaris

Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece

#### **Summary**

Molecularly Imprinted Polymers (MIPs) were prepared for the selective isolation of ibuprofen (pharmaceutical compound) from aqueous matrices of biomedical wastewaters.

#### Introduction

One of the most hot-topics of recent research is the reuse of some compounds existed as pollutants in environment. These compounds (molecules, ions, complexes, etc) are of high-added value and it will be ideal to selectively bind them with any environmental application and reuse them in their initial or modified form. The latter can be achieved using molecular imprinting. The whole process is based on adsorption technology, which is already one of the most successful techniques for pollutants removal. Pharmaceuticals are of scientific and public concern as newly recognized classes of environmental pollutants and are receiving considerable attention with respect to their environmental fate and toxicological properties over the last 15 years [1,2]. Ibuprofen is a nonsteroidal anti-inflammatory drug (NSAID) used for relieving pain, helping with fever and reducing inflammation. Ibuprofen has an antiplatelet effect, though it is relatively mild and somewhat short-lived compared with aspirin or prescription antiplatelet drugs. In general, ibuprofen also has a vasodilation effect.

#### Synthesis of (IBU-MIP)

For the preparation of IBU-MIP, 2mmol of MAA, 10 mmol EGDMA, 1.6 mmol IBU and 0.05 g AIBN were dissolved in 50 mL of the organic solvent DMF. The functional monomer and cross-linker were determined by the ratio of 2:10. The mixture of reagents was stirred for 2 h, followed by nitrogen sparging (~5 min) to remove oxygen. After then, the flask was immediately sealed and stirring was continued at 75 °C for 12 h. The flask was then smashed and the monolithic polymers obtained, were ground in a laboratory mortar and pestle. Next, the obtained particles were washed with acetone and hot water, followed by extraction in a Soxhlet apparatus using methanol, in order to remove residuals of the monomers and template molecules. The extraction lasted for 16 h, a sum of 30-35 solvent cycles (each cycle lasts approximately 30 min). At the end of the 16-h period, the higher percentage of template molecules (97%) was removed from the polymer matrix, giving that for noncovalent imprinting 85-95% was reported to be the ideal range of the template extraction from the polymer. Non-imprinted polymers (NIPs) were prepared with the same procedure just in the absence of the template molecule.

#### **Results and Discussion**

SEM showed that the surface of MIPs was not smooth but it had many channels and cavities.

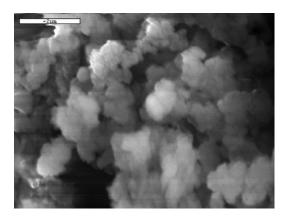


Figure 1. SEM photos of IBU-MIP adsorbed.

The experiments for the pH effect showed that the optimum value was at alkaline conditions (pH=10), while the maximum theoretical adsorption capacity was found to be 54 mg/g at 25 °C. The latter was found after fitting to the combinational isotherm model of Langmuir-Freundlich. The adsorption was reached at equilibrium slowly (~6 h) after testing the optimum adsorption contact time. The selectivity tests with other similar pharmaceutical compounds showed extremely large selectivity to IBU molecules, revealing the excellent use of this material as selective adsorbent.

#### **Conclusions**

The synthesis of IBU-MIPs was effectively acted for the isolation (removal) of ibuprofen compound from aqueous matrices, presenting 54 mg/g maximum theoretical adsorption capacity and very high selectivity degrees.

#### **Acknowledgments**

The support for this study was received from the State Scholarships Foundation (IKY) of Greek Ministry of Education and Religious Affairs (in the framework of the Hellenic Republic - Siemens Settlement Agreement) through the research program "IKY Fellowships of Excellence for Postgraduate Studies in Greece - Siemens Program" under the title "Advanced Molecularly Imprinted Polymers (MIPs) as materials for the selective binding and recovery of various high-added value environmental targets with application to industrial-scale adsorption columns", which is gratefully appreciated.

#### References

- [1] K. Kümmerer, Antibiotics in the aquatic environment A review Part I, Chemosphere, 75 (2009) 417-434.
- [2] D. Fatta-Kassinos, S. Meric, A. Nikolaou, Pharmaceutical residues in environmental waters and wastewater: Current state of knowledge and future research, Analytical and Bioanalytical Chemistry, 399 (2011) 251-275.

# Synthesis of Molecularly Imprinted Polymers (MIPs) for the selective removal of Ibuprofen from biomedical wastewaters

George Z. Kyzas and Dimitrios N. Bikiaris

Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, Greece

# Abstract / Aim / Novelty

One of the most hot-topics of recent research is the reuse of some compounds existed as pollutants in environment. These compounds (molecules, ions, complexes, etc) are of high-added value and it will be ideal to selectively bind them with any environmental application and reuse them in their initial or modified form. The latter can be achieved using molecular imprinting. The whole process is based on adsorption technology, which is already one of the most successful techniques for pollutants removal. Pharmaceuticals are of scientific and public concern as newly recognized classes of environmental pollutants and are receiving considerable attention with respect to their environmental fate and toxicological properties over the last 15 years. Ibuprofen is a nonsteroidal anti-inflammatory drug (NSAID) used for relieving pain, helping with fever and reducing inflammation. Ibuprofen has an antiplatelet effect, though it is relatively mild and somewhat shortlived compared with aspirin or prescription antiplatelet drugs. In general, ibuprofen also has a vasodilation effect.

# Synthesis of adsorbent

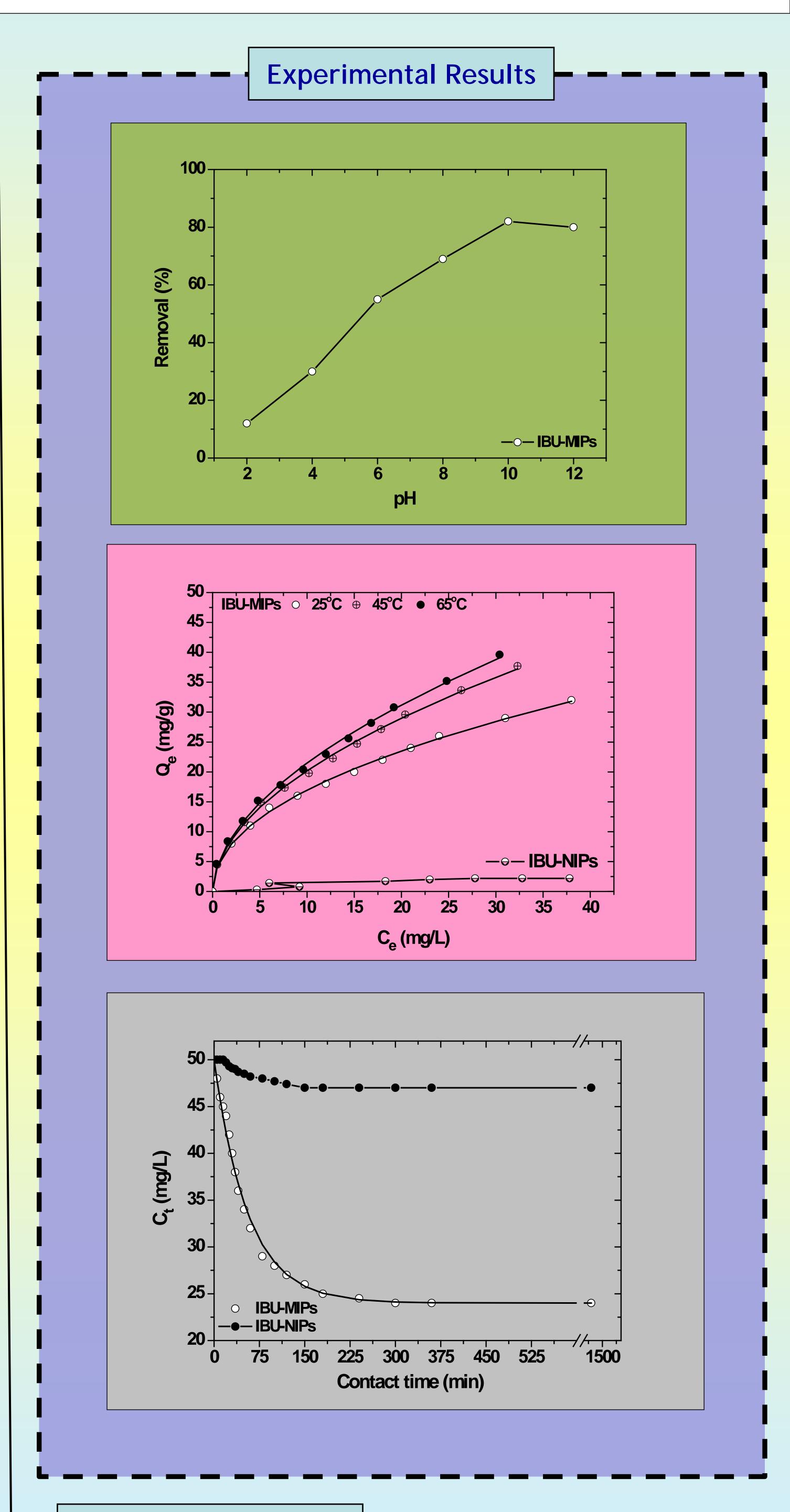
For the preparation of IBU-MIP, 2mmol of MAA, 10 mmol EGDMA, 1.6 mmol IBU and 0.05 g AIBN were dissolved in 50 mL of the organic solvent DMF. The functional monomer and cross-linker were determined by the ratio of 2:10. The mixture of reagents was stirred for 2 h, followed by nitrogen sparging (~5 min) to remove oxygen. After then, the flask was immediately sealed and stirring was continued at 75 °C for 12 h. The flask was then smashed and the monolithic polymers obtained, were ground in a laboratory mortar and pestle. Next, the obtained particles were washed with acetone and hot water, followed by extraction in a Soxhlet apparatus using methanol, in order to remove residuals of the monomers and template molecules. The extraction lasted for 16 h, a sum of 30 - 35 solvent cycles (each cycle lasts approximately 30 min). At the end of the 16-h period, the higher percentage of template molecules (97%) was removed from the polymer matrix, giving that for non-covalent imprinting 85 – 95% was reported to be the ideal range of the template extraction from the polymer. Non-imprinted polymers (NIPs) were prepared with the same procedure just in the absence of the template molecule.

Figure 1. SEM photos of IBU-MIP adsorbed.

# ~2<u>µm</u>

# Acknowledgment

The support for this study was received from the State Scholarships Foundation (IKY) of Greek Ministry of Education and Religious Affairs (in the framework of the Hellenic Republic - Siemens Settlement Agreement) through the research program "IKY Fellowships of Excellence for Postgraduate Studies in Greece - Siemens Program" under the title "Advanced Molecularly Imprinted Polymers (MIPs) as materials for the selective binding and recovery of various high-added value environmental targets with application to industrial-scale adsorption columns", which is gratefully appreciated.



# Conclusions

The synthesis of IBU-MIPs was effectively acted for the isolation (removal) of ibuprofen compound from aqueous matrices, presenting 54 mg/g maximum theoretical adsorption capacity and very high selectivity degrees.



EUROPEAN AND MEDITERRANEAN
ASSOCIATION FOR ENVIRONMENTAL
EDUCATION ASSESSMENT AND PROTECTION





**FITOFARMACI E AMBIENTE** 

INTERNATIONAL ASSOCIATION OF ENVIRONMENTAL ANALYTICAL CHEMISTRY





14th SYMPOSIUM ON CHEMISTRY AND FATE OF MODERN PESTICIDES

Ioannina, Greece September 18-21, 2014

**"Karolos Papoulias"** Conference Center **University of Ioannina** 

# Certificate of Attendance

This is to certify that

## **KYZAS GEORGE**

attended the

8th European Conference on Pesticides and Related Organic Micropollutants in the Environment &

the 14th Symposium on Chemistry and Fate of Modern Pesticides

which was held in Ioannina, Greece, on September, 18-21, 2014.

The Conference Chairman

**Albanis Triantafyllos** 

Professor

Department of Chemistry University of Ioannina