8th EUROPEAN CONFERENCE ON PESTICIDES AND RELATED ORGANIC MICROPOLLUTANTS IN THE ENVIRONMENT

& 14th SYMPOSIUM ON CHEMISTRY AND FATE OF MODERN PESTICIDES

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Ioannina, 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

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PP32 *ACT1024*

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

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PP33 *ACT1074*

DEVELOPMENT OF NOVEL CATALYTIC BIOSCAVENGERS FOR HERBICIDE DETOXIFICATION

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PP34 *ACT1076*

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

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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

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PP36 *ACT1089*

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

M. M. Laimou-Geraniou[1], G. Z. Kyzas[2], S. G. Nanaki[2], A. I. Koltsakidou[1], D. N. Bikiaris[2], D. A. Lambropoulou[1,*]

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PP37 *ACT1093*

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

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PP36
ACT1089

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Summary

Cross-linked chitosan beads were prepared and evaluated in order to adsorptively isolate a pharmaceutical compound (trimethoprim) from aqueous matrices.

Introduction

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]. Trimethoprim (TMP), a dihydropteroatesynthetase inhibitor, is commonly used in combination with sulfonamides for broad-spectrum antimicrobial therapy. It blocks the folic acid metabolism, and thus produces a synergistic antibacterial activity. The residue of TMP in manure andsoils may affect soil microbial and enzyme activities. Adsorption is a potential technique to remove TMP and overcome the pollution ofantibiotics in the environment. As adsorbent material, a polymeric super-adsorbent has been synthesized namely chitosan. Chitosan (poly-β-(1⊠4)-2-amino-2-deoxy-D-glucose) is an amino-polysaccharide, a cationic polymer produced by the N-deacetylation of chitin. Due to its molecular structure, chitosan exhibits many characteristics that have been the cause of much recent attention, since the range of its applications has enormously expanded in various fields including biotechnology, water-treatment, medicine and veterinary medicine, membranes, cosmetics and food industry. Chitosan presents high swelling degree in aqueous matrices, which usually leads to plugging of columns. In order to overcome this problem chitosan was cross-linked both covalently, by glutaraldehyde (GLA) and ionically, by a polyanion such as tripolyphosphate sodium (TPP).

Synthesis of cross-linked chitosan beads (CCB)

CCB were prepared by initially dissolving chitosan (1.41×10^{-6} moles) in 50 mL of aqueous solution of acetic acid (2% v/v). The solution was added dropwise from a pipette into an aqueous solution of glutaraldheyde (5×10^{-2} mol/L), which also contained tripolyphosphate (1.36×10^{-3} moles) at pH=6, adjusted with an aqueous HCl solution. The formed gelled beads were stirred overnight at room temperature in the aforementioned solution. Then, after filtration and purification by extraction with water in a Soxhlet apparatus for 24 h, a conventional drying at 60 °C was realized. The resulting beads, (CCB) were used for the adsorption experiments.

HPLC Analysis

Identification and quantification of trimethoprim was accomplished with HPLC-DAD and CNW Athena C18, 120 ⊠, 4.6mm *250mm, 5 μm column. Binary gradient mobile phases were used, with water as solvent A and methanol as solvent B. The elution started with 70% methanol and 30% water. All the other parameters remained stable, flow-rate was 1 mL/min, the column temperature was 40 °C and the injection volume was 20 μL. The detection wavelength was set at 287 nm. Further analysis was conducted for linearity, LOD and LOQ, repeatability and reproducibility. The UV spectra and the retention time of trimethoprim standard were used for the identification.

Results and Discussion

SEM showed that Trimethoprim adsorbed on chitosan modified beads wasabout 5μm in size and seemed to be in amorphous phase. This observation noted also from XRD patterns, which showed that Trimethoprim adsorbed is mainly in its amorphous form. However, there are four peaks of the drug present at the adsorbed matrix at 2theta 34.02, 37.84, 39.57 and 44.06 deg indicating that the drug is not completely amorphous. FT-IR was used to examine if bonds between drug and matrix were formed. The spectra of TMP exhibited bands at 3470 and 3319 cm^{-1} corresponds to v(N.H)asy and v(N.H)sy, respectively. These bands were sifted at 3445 and 3262 cm-1 respectively showing that hydrogen bonds with hydroxyl groups of matrix were formed.

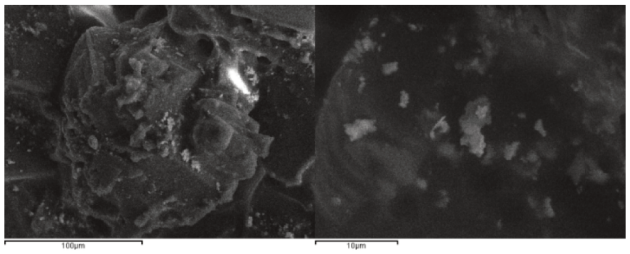

Figure 1. SEM photos of TMP adsorbed.

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 112 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 very quickly (~80 min) after testing the optimum adsorption contact time.

Conclusions

The synthesis of CCB was effectively acted for the isolation (removal) of TMP compound from aqueous matrices, presenting 112 mg/g maximum theoretical adsorption capacity.

Acknowledgments

The support for this study was received from the Greek Ministry of Education (GGET) and through the research program "Excellence II (ESPA2007-2013/EPAN II/Action "ARISTEIA II)" under the title "Advanced microextraction approaches based on novel nano- polymers to measure pharmaceuticals, personal care products and their transformation products in the aquatic environment" (project acronym: PoL-PPCPs-TPs), which is gratefully appreciated.

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[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.

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

Maria M. Laimou-Geraniou[1], George Z. Kyzas[2], Stavroula G. Nanaki[2], Anastasia I. Koltsakidou[1], Dimitrios N. Bikiaris[2], Dimitra A. Lambropoulou[1,*]

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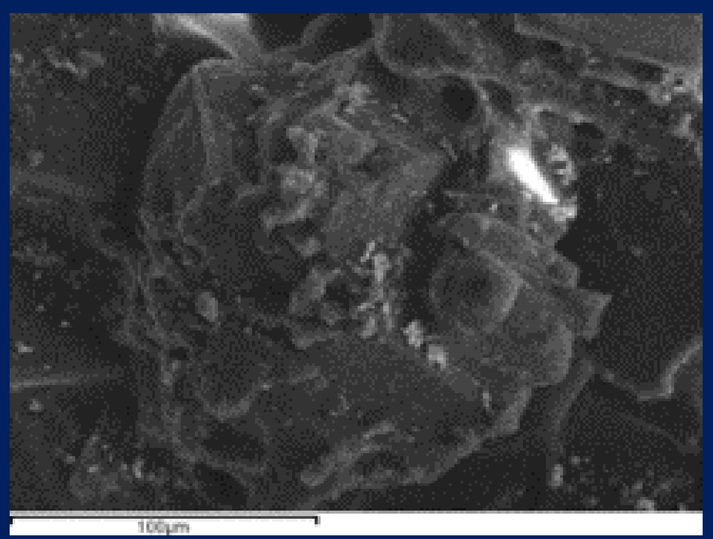
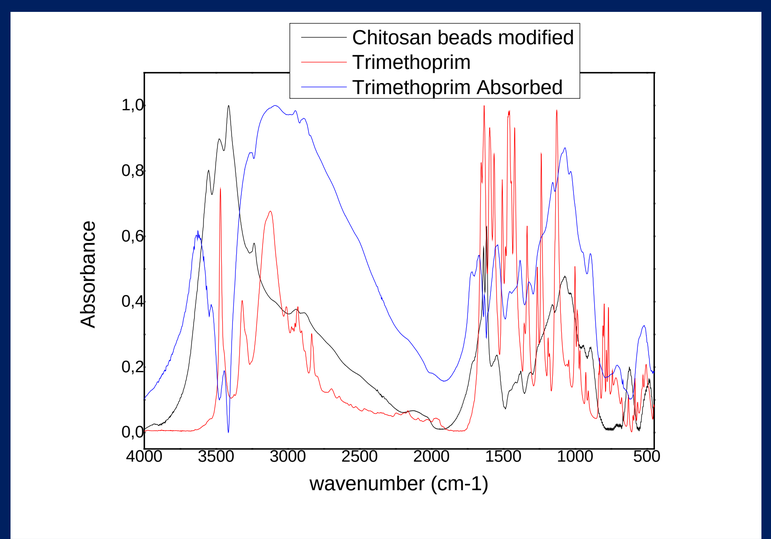


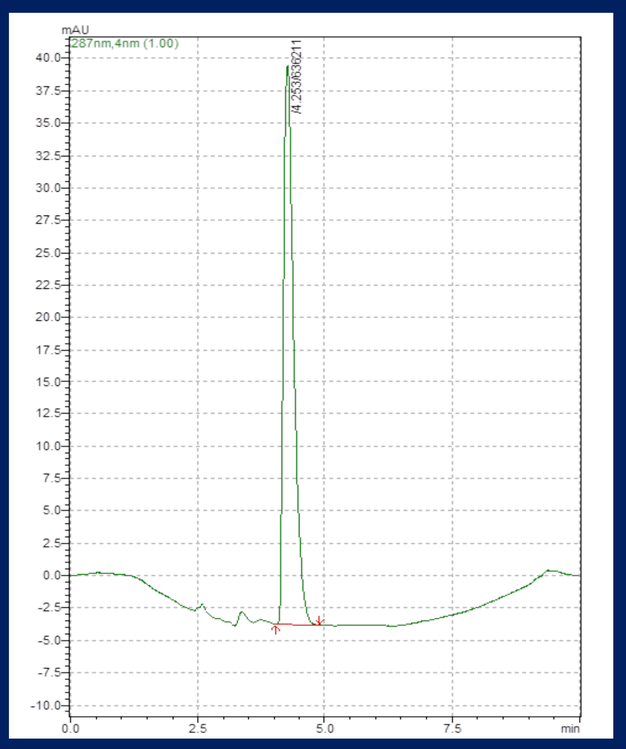
SEM micrographs of trimethoprim adsorbed



FT-IR spectra of the trimethoprime adsorbed

SEM was used to examine the morphology of the drug after adsorption. It was found that trimethoprim adsorbed on chitosan modified beads was about 5µm in size and seemed to be in amorphous phase.

FT-IR spectra of trimethoprim adsorbed showed that amino groups of the drug forms hydrogen bonds with hydroxyl groups of polymer matrix during adsorption studies.



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Adsorption experimental procedure

Experiments were carried out using 1 g/L of adsorbent each time and samples were taken at predetermined time intervals and filtered using 50 µm pore size filtration membrane.

- For the pH-effect experiments the solution pH was initially adjusted with aqueous solutions of acid or base (0.01 mol/L of HCl and/or 0.01 mol/L NaOH) to reach pH values of 2-12.

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 112 mg/g at 25 oC. The latter was found after fitting to the combinational isotherm model of Langmuir-Freundlich. The adsorption was reached at equilibrium very quickly (~80 min) after testing the optimum adsorption contact time.

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The support for this study was received from the Greek Ministry of Education and Religious Affairs through Operational Program “Education and Lifelong Learning” of the National Strategic Reference Framework (NSRF) - Research Funding Program “Excellence II (Aristeia II)” under the title “Advanced microextraction approaches based on novel nano- polymers to measure pharmaceuticals, personal care products and their transformation products in the aquatic environment”, which is gratefully appreciated.

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Ioannina, Greece September 18-21, 2014

"Karolos Papoulias" Conference Center
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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.

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Department of Chemistry
University of Ioannina