10th HELLENIC POLYMER SOCIETY CONFERENCE

with international participation

4 - 6
December 2014
Patras, Greece

The conference is dedicated to the memory of
Prof. ***Anastasios Dondos,***
Prof. ***Ioannis Mikroyannidis*** *and Prof.* ***Nikos Kalfoglou***

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Polymer Synthesis and Macromolecular Design

P67	N. D. Koromilas[1], **Georgia Ch. Lainioti[1]**, G. Bokias[1], J. K. Kallitsis[1,2] *[1]Department of Chemistry, Univ. of Patras, [2]FORTH/ICE-*HT *Synthesis of block antimicrobial copolymers with ionical and immobilized groups*
P68	**Afroditi Moutsi[1]**, N. Koromilas[1], G. Bokias[1], J. Kallitsis[1,2] *[1]Department of Chemistry, Univ. of Patras, [2]FORTH/ICE-HT* *Synthesis and characterization of cationic copolymers based on monomers 4-vinylbenzyl chloride and glycidyl methacrylate*
P69	**Stavroula G. Nanaki[1]**, G. Z. Kyzas[1], D. N. Bikiaris[1], D. A. Lambropoulou[2] *[1]Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle Univ. of Thessaloniki, [2]Laboratory of Environmental Pollution Control, Department of Chemistry, Aristotle Univ. of Thessaloniki* *Effectively designed molecularly imprinted polymers for selective isolation of the drug Metformin*
P70	M.E. Kourti, **Spyridoula-Lida Bitsi**, E.Fega, G. Foteinogiannopoulou and M. Pitsikalis *Department of Chemistry, Univ. of Athens* *Metallocene-mediated cationic copolymerization of methyl- and phenyl, oxazoline*
P71	**Andreas-Philippos Maroudas[1]**, C. Nikovia[1], P. Goulis[1], P. Paraskevopoulou[2], M. Pitsikalis[1] *[1]Industrial Chemistry Laboratory, Department of Chemistry, Univ. of Athens, [2]Inorganic Chemistry Laboratory, Department of Chemistry, Univ. of Athens* *Diblock and Pseudo-diblock copolymers of norbornene and cyclopentene by Ring Opening Metathesis Polymerization*
P72	A. Karatzas, **Panagiotis Christakopoulos**, H. Iatrou, P. Bilalis *Chemistry Department, Univ. of Athens* *Synthesis of diblock copolymers PEO-b-poly(L-histidine) bearing a terminal azide group*
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P75	A. Voege, **Valadoula Deimede**, J. K. Kallitsis *Department of Chemistry, Univ. of Patras* *Synthesis and properties of alkaline stable pyridinium containing anion exchange membranes*
P76	**Margarita Droulia[1]**, V. Asimopoulou-Marinou[1], P. Paraskevopoulou[2], M. Pitsikalis[1] *[1]Industrial Chemistry Laboratory, Department of Chemistry, Univ. of Athens, [2]Inorganic Chemistry Laboratory, Department of Chemistry, Univ. of Athens* *Statistical and block copolymers based on 2-methacryloyloxyethyl ferrocenecarboxylate (MAEFC)*
P77	**Christiana Nikovia[1]**, A.P. Maroudas[1], P. Goulis[1], D. Tzimis[1], P. Paraskevopoulou[2], M. Pitsikalis [1] *[1]Industrial Chemistry Laboratory, Department of Chemistry, Univ. of Athens, [2]Inorganic Chemistry Laboratory, Department of Chemistry, Univ. of Athens* *Statistical ring opening metathesis copolymerization of norbornene and cyclopentene by grubbs [st] generation catalyst*
P78	**George V. Theodosopoulos**, M. Pitsikalis *Industrial Chemistry Laboratory, Department of Chemistry, Univ. of Athens* *Synthesis of well-defined highly-dense norbornene-poly(etheylene oxide) polymer brushes through the combination of anionic polymerization and ROMP*
P79	**Sofia Kakogianni[1]**, S. Aivali[1], A. K. Andreopoulou[1,2], C. Anastasopoulos[1], J. K. Kallitsis[1,2] *[1]Department of Chemistry, Univ. of Patras, [2]FORTH/ICE-HT* *Modified electron donors with functional groups for organic electronics*
P80	S. Kakogianni[1], **Charalampos Anastasopoulos[1]**, A. Andreopoulou[1,2], G. Rassias[1], J. Kallitsis[1,2] *[1]Department of Chemistry, Univ. of Patras, [2]FORTH/ICE-HT*

Effectively designed Molecularly Imprinted Polymers for selective isolation of the drug Metformin

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ABSTRACT SUMMARY:
In the present study, four novel molecularly imprinted polymers with remarkable recognition properties for metformin have been prepared for their selective isolation and removal from aqueous media. The prepared adsorbents were characterized by FTIR, XRD and SEM. The performance of the prepared MIPs was evaluated by the parameter of pH.

INTRODUCTION:
Molecular imprinting is a relatively modern and specific enough technique according to which the selective binding/isolation of target species (molecules or ions/metals) from a mixture can be achieved. Some of the basic application areas of molecular imprinting include separation processes (chromatography, solid-phase extraction, membrane separations), artificial antibodies, and sensors recognition element.
Molecular imprinting is applied using some smart polymeric materials known as Molecularly Imprinted Polymers (MIPs). These polymers are common materials synthesized after classic polymerization reaction (monomer, solvent, initiator, cross-linker), but using both the targets-for-isolation molecule in the polymerization mixture[1]. In this way, the template is imprinted into the polymerization matrix forming numerous imprints in it. The "smart" nature of MIPs is their ability to only selectively rebind (interact/adsorb/isolate) the template for which it was synthesizedeither with covalent bonds or non-covalent ones.
Pharmaceuticals are of scientific and public concern as newly recognized classes of environmental contaminants and are receiving considerable attention with respect to their environmental fate and toxicological properties. Recently, the removal of pharmaceuticals with selective adsorption onto MIPs is characterized as one of the most promising techniques, due to its convenience once applied into current water treatment processes.
Metformin is an antidiabetic drug, conclusively shown to prevent the cardiovascular complications of diabetes. It help sin reduction of LDL cholesterol and triglyceride levels. The drug is not metabolized in humans and the re-adsorbed fraction (about 70%) is excreted unchanged in urine, the rest in feces. Therefore, it is not surprising that high metformin concentrations are present in WWTP influents.
The aim of the present study was to synthesize MIPs that can be used for the absorbance of Metformin. MIPs were characterized using FT-IR, XRD and SEM. Their adsorption capacity was studied in two different pH.

EXPERIMENTAL METHODS:
MIPs were synthesized according to protocol developed in previous study[1]: 2mmol of monomer (2-Hydroxyethyl acrylate-MIP1, Acrylic acid-MIP2, Acrylamide-MIP3, Butyl Acrylate-MIP4), 9 mmol of EGDMA, 2 mmol of the drug were dissolved in 15 mL of the organic solvent DMF. The functional monomer and cross-linker were determined by the ratio of 2:10. After 2 h of stirring, nitrogen sparging (~15 min) followed in order to remove the oxygen. Then, the flask was immediately sealed and stirring was continued at 80^{o}C for 8 h. The polymerization mixture was then removed and washed with Acetic Acid:Methanol 10:90 using a Soxhlet apparatus. In this way, the residual monomers and drug templates were removed, while the formed imprints were allowed to be empty and ready for rebinding.
SEM images were performed with electron microscope (model Zeiss Supra 55 VP, Jena, Germany). FTIR spectra were taken with a FTIR-spectrometer (model FTIR-2000, Perkin Elmer, Dresden, Germany. XRD patterns were taken with a diffractometer (model MiniFlex 600, Rigaku).

Adsorption experiments at two pH were conducted as follow: Conical flasks were placed in temperature-controlled shaking water bath (model Julabo SW-21C, Seelbach, Germany),

having 50 mL of aqueous solutions of GUA (C_0=30 mg/L). Then, 0.05 g of MIP were added and the pH was initially adjusted using aqueous solutions of acid or base (0.01 M HCl and/or 0.01 M NaOH) to reach fixed pH values of 2 and 10. The flasks were stoppered, the agitation speed (N) of shaking bath was adjusted at 150 rpm and its temperature at 25 °C. The flasks were left shaking for 24 h and then the residual drug concentration was estimated after HPLC analysis. Adsorption study conducted in triplicate

RESULTS AND DISCUSSION:

Figure 1 shows SEM photo of MIP2. As seen, MIP2 is smooth in surface without a specific shape. Analogous are SEM photos of the other three MIPs.

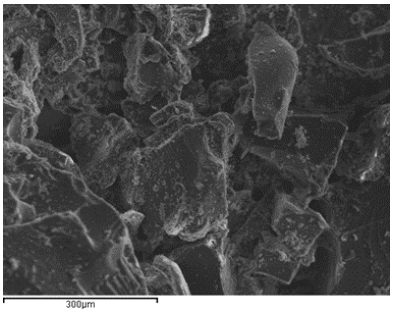

Fig. 1: *SEM photo of MIP2*

FT-IR spectra of the four synthesized MIPs presented in Figure 2. There are present the characteristic peaks; CH_2 bend at 1462cm^{-1}, C=O stretch at 1726 cm^{-1}, C–O stretch at 1160cm^{-1}, C-O bend at 1260 cm^{-1} and C–H stretch at 2960 cm^{-1} [2]. MIP3 showed another two peaks at 3206 and 1670 cm-1 owning to N-H stretch and C=O stretch of amide.

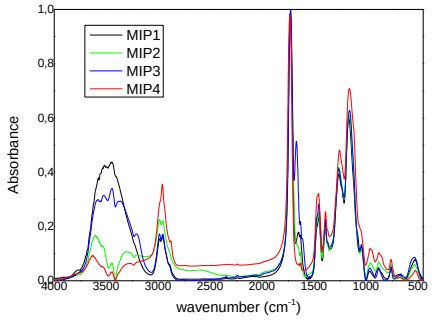

Fig. 2: *FT-IR spectra of MIPs synthesized*

XRD showed that all the synthesized MIPs were amorphous.

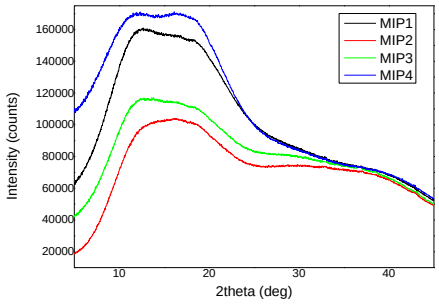

Fig. 3: *XRD patterns of synthesized MIPs*

Adsorption of Metformin studied at two different pH (2 and 10). As seen in Fig. 4 pH 2 found to favour adsorption (an exception was MIP1). Another observation is that MIP2 [poly(acrylic acid)] showed increased adsorption at about 80% while all other three showed adsorption below 40%.

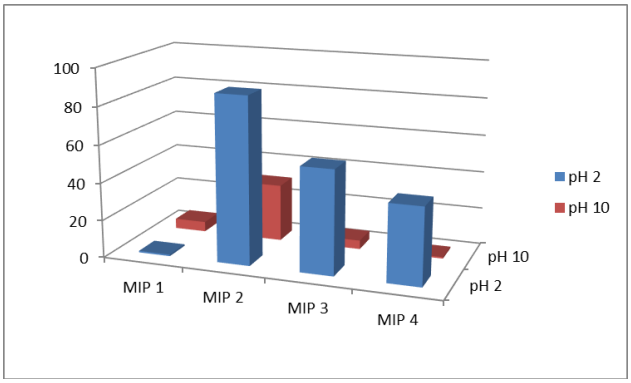

Fig.4: *Adsorption of Metformin at pH 2 & 10*

CONCLUSIONS:

The present work is a preliminary study to reveal if MIPs prepared by acrylates (1&4), acrylic acid (2) and acrylamide (3) are adequate for the adsorption of Metformin. Adsorption studies showed that acidic conditions (pH 2) favors adsorption. Finally, as observed MIP of poly(acrylic acid) showed the best results showing an adsorption of 80% at pH 2.

REFERENCES:

[1] Kyzas GZ, Bikiaris DN, Lazaridis NK. Chem. Eng. J. 149:263-272 (2009a).

[2] Liu Y, Song J, Jiao F, Huang J. . J. Mol. Struct. 1064:100-106 (2014).

ACKNOWLEDGEMENTS:

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.