

Abstract

# Hybrid Cryogels with Advanced Adsorbent Properties for Penicillin<sup>†</sup>

Marinela-Victoria Dumitru<sup>1,2,\*</sup>, Teodor Sandu<sup>1</sup>, Iulia Elena Neblea<sup>1</sup>, Horia Iovu<sup>2</sup>, Anita-Laura Chiriac<sup>1</sup>, Ionut Cristian Radu<sup>2</sup>, Andrei Sarbu<sup>1</sup> and Tanta Verona Iordache<sup>1,\*</sup>

<sup>1</sup> National Institute for Research and Development in Chemistry and Petrochemistry-ICECHIM, 202 Spl. Independenței, 060021 Bucharest, Romania; teodor.sandu@icechim.ro (T.S.); iulia.neblea@icechim.ro (I.E.N.); anita-laura.radu@icechim.ro (A.-L.C.); andrei.sarbu@icechim.ro (A.S.)

<sup>2</sup> Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, 1-7 Gh. Polizu Street, 011061 Bucharest, Romania; horia.iovu@upb.ro (H.I.); radu.ionutcristian@gmail.com (I.C.R.)

\* Correspondence: marinela.dumitru@icechim.ro (M.-V.D.); tanta-verona.iordache@icechim.ro (T.V.I.)

<sup>†</sup> Presented at the 17th International Symposium “Priorities of Chemistry for a Sustainable Development” PRIOCHEM, Bucharest, Romania, 27–29 October 2021.

**Keywords:** hybrid cryogels; penicillin; chitosan; clay; water purification

In recent years, natural polymers (chitosan and biocellulose) have sparked interest, especially when it comes to medical uses (wound healing, excipients for drug administration), due to their great biocompatibility and low toxicity [1–3]. However, the poor mechanical properties of chitosan limit its use to some extent. For this reason, in this study, chitosan was used in a mixture with a natural clay, i.e., kaolin. The choice of kaolin was made considering both its low toxicity and the occurrence of hydroxyl groups, which make it suitable for hybrid cryogels with advanced adsorbent properties. Since 1941, penicillin has been used to cure infectious diseases, but it may be also involved in food preservation. The presence of antibiotic residues in wastewater poses toxicity issues, requiring measures to reduce this pollution effect [4,5]. In this study, hybrid super-adsorbent cryogels were developed, capable of retaining penicillin from aqueous samples. In order to develop the desired hybrids, two types of chitosan were used: commercial chitosan (CC) and chitosan prepared in a laboratory from shrimp shells (CS). Other reagents were as follows: acetic acid, used in a mixture with water, for chitosan dissolution; a crosslinking agent; kaolin;  $\gamma$ -methacryloxypropyltrimethoxysilane, the organophilization agent; and penicillin G, the antibiotic. The issues related to the rather limited compatibility between inorganic kaolin and organic chitosan require organic modification of kaolin, in which case MAPTES was used. In order to confirm the organophilization and the structure of super-adsorbent materials, samples were characterized using various modern techniques (FTIR, BET, SD, UV-Vis). FTIR spectra confirmed the occurrence of characteristic bands of the involved raw materials. The developed hybrids possess adjustable porosity according to BET. The UV-Vis results confirmed that hybrid cryogels posed great retention capacity for penicillin in aqueous solutions.

Innovative super-adsorbent cryogels based on natural polymers and clays were successfully prepared. These materials showed great adsorption capacity, mainly because of the high swelling capacity of chitosan. The use of kaolin yielded improved mechanical properties.

**Author Contributions:** Conceptualization of the paper by T.-V.I.; Methodology by M.-V.D. and A.-L.C.; Formal analysis by S.T., I.E.N. and I.C.R.; Investigation by M.-V.D. and A.-L.C.; Writing of Original Draft was done by M.-V.D. and T.-V.I.; Writing—review and editing by T.-V.I.; Supervision by H.I., A.S. and T.V.I.; Project administration by A.-L.C. and T.-V.I.; All authors have read and agreed to the published version of the manuscript.



**Citation:** Dumitru, M.-V.; Sandu, T.; Neblea, I.E.; Iovu, H.; Chiriac, A.-L.; Radu, I.C.; Sarbu, A.; Iordache, T.V. Hybrid Cryogels with Advanced Adsorbent Properties for Penicillin. *Chem. Proc.* **2022**, *7*, 61. <https://doi.org/10.3390/chemproc2022007061>

Published: 2 April 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

**Funding:** This research was funded by EU, JPI Oceans and the Romanian National Authority for Scientific Research and Innovation UEFISCDI, in the framework of the collaborative international consortium (BIOSHELL, contract no. 157/2020) financed under the ERA-NET Cofund Bluebio 2019 Call.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Konovalova, M.V.; Markov, P.A.; Durnev, E.A.; Kurek, D.V.; Popov, S.V.; Varlamov, V.P. Preparation and biocompatibility evaluation of pectin and chitosan cryogels for biomedical application. *J. Biomed. Mater. Res.* **2017**, *105*, 547–556. [[CrossRef](#)] [[PubMed](#)]
2. Jayakumar, R.; Menon, D.; Manzoor, K.; Nair, S.V.; Tamura, H. Biomedical applications of chitin and chitosan-based nanomaterials—A short review. *Carbohydr. Polym.* **2010**, *82*, 227–232. [[CrossRef](#)]
3. Piacham, T.; Ayudhya, C.I.N.; Prachayasittikul, V. A simple method for creating molecularly imprinted polymer-coated bacterial cellulose nanofibers. *Chem. Pap.* **2014**, *68*, 838–841. [[CrossRef](#)]
4. Yeşilova, E.; Osman, B.; Kara, A.; Özer, E.T. Molecularly imprinted particle embedded composite cryogel for selective tetracycline adsorption. *Sep. Purif. Technol.* **2018**, *200*, 155–163. [[CrossRef](#)]
5. Urraca, J.L.; Hall, A.J.; Maria, C.; Bondi, M.; Sellergren, B. A Stoichiometric Molecularly Imprinted Polymer for the Class-Selective Recognition of Antibiotics in Aqueous Media. *Angew. Chem.* **2006**, *118*, 5282–5285. [[CrossRef](#)]