SERVIÇO PÚBLICO FEDERAL - MINISTÉRIO DA EDUCAÇÃO

UNIVERSIDADE FEDERAL DE ALFENAS

Rua Gabriel Monteiro da Silva, 700. Alfenas, MG. CEP 37130-001
Telefone: (35) 3701-9000

PROGRAMA DE ENSINO DE DISCIPLINA

(Rascunho sem validade oficial)

Turma: 1 - Special Topics in Chemistry II: Crystal Engineering: A Short Course in Fundamentals and Applications (Special Topics in Chemistry II: Crystal Engineering: A Short Course in Fundamentals and Applications) (QUI137)
Curso: Doutorado em Química (210)
Carga Horária Total: 30h | Ano / Semestre: 2025 / Segundo
Distribuição da Carga Horária: Teórica - 30h
Ementa: This course explores the fundamental principles and practical applications of crystal engineering. Key topics include the historical background of the field, advanced techniques for solid-state investigation, and in-depth analysis of intermolecular interactions. Students will examine various crystal forms, crystal polymorphism, crystallization techniques, solvates, hydrates, co-crystals, and chirality. The course also delves into modern materials such as metal-organic frameworks (MOFs) and hydrogen-bonded organic frameworks (HOFs), concluding with an integration of database analysis and structure prediction tools.
Objetivo Geral: The course aims to provide students with a comprehensive understanding of crystal engineering. Emphasis is placed on the theoretical and experimental aspects of crystallization and structural design, with applications in pharmaceuticals, materials science, and intellectual property. Students will gain the ability to identify, characterize, and manipulate different crystal forms, and explore their impact on functionality and performance. Special focus is given to the design of multicomponent systems, chiral resolution, and the potential of MOFs and HOFs in industrial and optoelectronic applications.
Metodologia de Ensino: Lectures and seminars
Competências:
Habilidades:
Observações: 1) The course will be delivered in English and condensed into an intensive five-day format delivered by foreign lecturers. 2) The evaluation phase will take place during the two weeks following the classes given by the foreign professors. 3) Responsible Professors: • Prof. Dario Braga (Emeritus Professor) – 7.5 hours Email: dario.braga@unibo.it Profile: https://www.unibo.it/sitoweb/dario.braga • Prof. Fabrizia Grepioni (Full Professor) – 7.5 hours Email: fabrizia.grepioni@unibo.it Profile: https://www.unibo.it/sitoweb/fabrizia.grepioni • Prof. Antonio Carlos Doriguetto (Full Professor) – 15 hours Profile: http://lattes.cnpq.br/4581537476491370
Responsável: Antônio Carlos Doriguetto

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CONTEÚDO PROGRAMÁTICO

UNIDADE I

-INTRODUCTION

-Historical background and origins of crystal engineering

-Overview of solid-state investigation techniques: IR and Raman spectroscopies, solid-state NMR, X-ray diffraction, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA)

OBJETIVOS ESPECÍFICOS:

-To present the historical background and foundations of crystal engineering, highlighting its scientific evolution and significance. Additionally, to provide a comprehensive overview of key solid-state characterization techniques, including infrared (IR) and Raman spectroscopies, solid-state nuclear magnetic resonance (NMR), X-ray diffraction, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA).

UNIDADE II

-INTERMOLECULAR INTERACTIONS

-Molecular crystals and amorphous substances

-Hydrogen bonds, halogen bonds, sigma-hole interactions, and coordination bonds in the construction of superstructures

OBJETIVOS ESPECÍFICOS:

-To explore the structural and functional properties of molecular solids, with emphasis on crystalline and amorphous substances, highlighting the principles that govern their organization and behavior. The course also aims to examine the role of key intermolecular interactions—such as hydrogen bonds, halogen bonds, sigma-hole interactions, and coordination bonds—in the design and construction of superstructures, emphasizing their importance in crystal engineering and the rational development of functional materials.

UNIDADE III

-CRYSTAL FORMS

-Diversity of crystal forms for a single compound

-Polymorphism, hydrates, solvates, salts, co-crystals, and their polymorphs

OBJETIVOS ESPECÍFICOS:

-To investigate the diversity of crystal forms exhibited by single chemical compounds, with a focus on the phenomena of polymorphism and the formation of crystal variants such as hydrates, solvates, salts, co-crystals, and their respective polymorphs.

UNIDADE IV

-CRYSTAL POLYMORPHISM

-Identification, characterization, and applications of polymorphs

-Pharmaceutical relevance and intellectual property considerations

-Enantiotropic vs. monotropic systems; case studies

OBJETIVOS ESPECÍFICOS:

-To analyze the identification, characterization, and practical applications of polymorphs in solid-state chemistry, emphasizing their pharmaceutical significance and implications for intellectual property. The course will explore the distinctions between enantiotropic and monotropic systems through case studies, highlighting how polymorphic behavior impacts drug formulation, stability, and regulatory strategy.

UNIDADE V

-CRYSTALLIZATION TECHNIQUES

-Crystallization from solution and melt

-Kinetic challenges and strategies for achieving thermodynamic stability

OBJETIVOS ESPECÍFICOS:

-To examine crystallization techniques used in the preparation of solid-state materials, with an emphasis on crystallization from solution and melt. The course aims to address kinetic limitations encountered during crystallization and to explore strategic approaches for achieving thermodynamically stable crystal forms. Through this study, students will gain insight into how processing conditions influence crystallinity, purity, and material properties.

UNIDADE VI

-SOLVATES AND HYDRATES

-Dynamic vapor sorption, solubility, and stability

-Crystallization methods, solvent removal, and phase interconversion

-Thermodynamic and calorimetric aspects; case study: Rifaximin

OBJETIVOS ESPECÍFICOS:

-To investigate the structural, thermodynamic, and physicochemical aspects of solvates and hydrates in solid-state systems. The course will cover techniques such as dynamic vapor sorption for evaluating solubility and stability, and will explore crystallization strategies, solvent removal processes, and phase interconversion phenomena. Special emphasis will be placed on thermodynamic and calorimetric analyses, illustrated through a detailed case study of Rifaximin.

UNIDADE VII

-CO-CRYSTALS

-Preparation via solution, thermal, and solid-state methods

-Mechanochemical techniques

-Intellectual property, patentability, and case studies

-Ionic co-crystals in pharmaceuticals and agriculture

OBJETIVOS ESPECÍFICOS:

-o explore the preparation, characterization, and practical relevance of co-crystals in the context of solid-state chemistry and material science. The course will address methods of co-crystal formation—including solution-based, thermal, and solid-state approaches—as well as mechanochemical techniques. Students will examine the implications of co-crystals for intellectual property and patentability through case studies, and will analyze the role of ionic co-crystals in pharmaceutical development and agricultural innovation.

UNIDADE VIII

-CHIRALITY IN CRYSTALS

-Molecular vs. crystal-level chirality

-Racemic mixtures, conglomerates, and racemates

-Chiral resolution strategies; case studies

OBJETIVOS ESPECÍFICOS:

-o examine the principles and manifestations of chirality in crystalline materials, distinguishing between molecular and crystal-level chirality. The course will explore the structural characteristics and implications of racemic mixtures, conglomerates, and racemates, while also presenting strategies for

chiral resolution through real-world case studies. Emphasis will be placed on the relevance of chirality to solid-state properties and its applications in pharmaceutical development and chemical synthesis.

UNIDADE IX

-METAL-ORGANIC FRAMEWORKS (MOFS)

-Coordination chemistry and network design: spacers and nodes

-MOF properties and applications: gas storage, catalysis, molecular sieving

-Adsorption/desorption behavior; case studies

OBJETIVOS ESPECÍFICOS:

-To explore the design, structure, and functionality of Metal-Organic Frameworks (MOFs) through the lens of coordination chemistry and network architecture, focusing on the roles of spacers and nodes. The course will examine key physicochemical properties of MOFs and their diverse applications in gas storage, catalysis, and molecular sieving. Additionally, students will analyze adsorption and desorption behavior through case studies, gaining insight into performance optimization and material innovation.

UNIDADE X

-HYDROGEN-BONDED ORGANIC FRAMEWORKS (HOFS)

-Synthesis and applications of porous hydrogen-bonded networks

OBJETIVOS ESPECÍFICOS:

-To investigate the synthesis, structural characteristics, and functional applications of Hydrogen-Bonded Organic Frameworks (HOFs), with particular emphasis on porous hydrogen-bonded networks. The course will explore the principles governing their self-assembly, stability, and tunable porosity, highlighting their potential applications.

UNIDADE XI

-INTEGRATION WITH STRUCTURAL DATABASES

-Use of databases such as CSD and ICSD

-Fundamentals of crystal structure prediction (CSP)

-Applications beyond pharma/agro: conductive materials, proton conductivity, photoreactivity, and luminescence

OBJETIVOS ESPECÍFICOS:

-To introduce the integration of structural databases—such as the Cambridge Structural Database (CSD) and the Inorganic Crystal Structure Database (ICSD)—into solid-state research workflows. The course will cover the fundamentals of crystal structure prediction (CSP) and demonstrate how database-driven insights contribute to the discovery and design of advanced functional materials. Special emphasis will be placed on applications extending beyond pharmaceutical and agricultural domains, including electrically conductive systems, proton-conducting frameworks, photoreactive compounds, and luminescent materials.

BIBLIOGRAFIA BÁSICA

Bolla, G.; Sarma, B.; Nangia, A. Crystal Engineering of Pharmaceutical Cocrystals in the Discovery and Development of Improved Drugs. CHEMICAL REVIEWS 2022. DOI: 10.1021/acs.chemrev.1c00987.

Braga, D.; Casali, L.; Grepioni, F. The Relevance of Crystal Forms in the Pharmaceutical Field: Sword of Damocles or Innovation Tools? INTERNATIONAL JOURNAL OF MOLECULAR SCIENCES 2022, 23 (16). DOI: 10.3390/ijms23169013.

Desiraju, G. Crystal engineering: A holistic view. ANGEWANDTE CHEMIE-INTERNATIONAL EDITION 2007, 46 (44), 8342-8356. DOI: 10.1002/anie.200700534.

Desiraju, G. Crystal Engineering: From Molecule to Crystal. JOURNAL OF THE AMERICAN CHEMICAL SOCIETY 2013, 135 (27), 9952-9967. DOI: 10.1021/ja403264c.

DESIRAJU, G. SUPRAMOLECULAR SYNTHONS IN CRYSTAL ENGINEERING - A NEW ORGANIC-SYNTHESIS. ANGEWANDTE CHEMIE-INTERNATIONAL EDITION IN ENGLISH 1995, 34 (21), 2311-2327. DOI: 10.1002/anie.199523111

LEHN, J. PERSPECTIVES IN SUPRAMOLECULAR CHEMISTRY - FROM MOLECULAR RECOGNITION TOWARDS MOLECULAR INFORMATION-PROCESSING AND SELF-ORGANIZATION. ANGEWANDTE CHEMIE-INTERNATIONAL EDITION IN ENGLISH 1990, 29 (11), 1304-1319. DOI: 10.1002/anie.199013041.

Moulton, B.; Zaworotko, M. From molecules to crystal engineering: Supramolecular isomerism and polymorphism in network solids. CHEMICAL REVIEWS 2001, 101 (6), 1629-1658. DOI: 10.1021/cr9900432.

Nangia, A.; Desiraju, G. Crystal Engineering: An Outlook for the Future. ANGEWANDTE CHEMIE-INTERNATIONAL EDITION 2019, 58 (13), 4100-4107. DOI: 10.1002/anie.201811313.

Sun, L.; Wang, Y.; Yang, F.; Zhang, X.; Hu, W. Cocrystal Engineering: A Collaborative Strategy toward Functional Materials. ADVANCED MATERIALS 2019, 31 (39). DOI: 10.1002/adma.201902328.

The Cambridge Crystallographic Data Centre. Available at: https://www.ccdc.cam.ac.uk/. Accessed on: June 23, 2025.

BIBLIOGRAFIA COMPLEMENTAR

Other various journals in the fields of crystallography, crystal engineering, and supramolecular

chemistry to be accessed via the CAPES Journal Portal.

SISTEMA DE AVALIAÇÃO

	Data	Valor	Peso
Evaluative seminars and assignments will be coordinated by Prof. Antonio Carlos Doriguetto, in accordance with the content delivered by the guest lecturers.	a combinar	10.0	1.0
Prova Especial	a combinar		

(*) Datas de avaliação sujeitas à alteração posterior.

Programa de ensino em fase de elaboração