NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
POLITEHNICA BUCHAREST
DOCTORAL SCHOOL OF "CHEMICAL ENGINEERING AND BIOTECHNOLOGIES"
FIELD OF DOCTORAL RESEARCH: CHEMICAL ENGINEERING

DOCTORAL THESIS

Coloured materials with controlled absorbance and emission

Materiale colorate cu absorbanță și emisie controlată

Summary of the thesis

Scientific coordinator: Prof. Dr. Eng. Ioan CĂLINESCU

Author: Eng. Diana-Ioana BULIGA

BUCHAREST

2025

TABLE OF CONTENTS

RESEARCH JUSTIFICATION

In the context of concerns regarding the negative environmental impact of the textile industry, caused by using synthetic dyes that require large amounts of material and energy resources, recent research has highlighted the ecological alternatives offered by natural dyes. These are extracted from plant, animal, or mineral sources, and currently, there is a focus on utilizing non-agricultural fields for crops intended for the extraction of natural dyes, to reduce pressure on arable ground designated for food production. Although there is a global trend toward adopting natural products, the replacement of synthetic dyes with natural ones is not yet fully feasible due to challenges related to dyeing processes and variability in results between batches.

Research in this field contributes to the development of sustainable solutions for using natural pigments in industrial applications, creating a solid foundation for developing efficient methods of extraction, stabilization, and controlled use. Additionally, considering the progress made in stabilizing and optimizing extraction processes, these studies open new perspectives for integrating natural dyes in fields such as the textile industry, cosmetics production, and the biomedical sector. In these contexts, the use of natural dyes is expected to become a viable alternative to synthetic dyes, helping to reduce environmental impact and promote more responsible resource consumption.

The study presented in this doctoral thesis demonstrates that research on natural dyes can significantly contribute to the development of ecological, economic, and sustainable solutions for the textile industry and beyond. Improving the extraction, stabilization, and application processes of these dyes can open promising prospects for the gradual replacement of synthetic dyes, thereby reducing the negative environmental impact and promoting a more responsible and eco-friendly industry

The paper is organized into two parts:

Theoretical Aspects: Structured over three chapters, the first part provides an overview of the history of natural dyes and the role they have played. It presents a classification of extraction methods, both conventional and unconventional, as well as methods for separating and stabilizing natural dyes. Furthermore, the influence of environmental factors on the

properties of natural dyes is discussed. In particular, the history, structure, location, function, and uses of chlorophyll, curcumin, and phycocyanin are emphasized.

Original Contributions: This part presents the author's own research on the possibilities of extracting and stabilizing chlorophyll, curcumin, and phycocyanin. The efficiency of conventional and unconventional extraction methods was studied comparatively. The stabilization of natural dyes was carried out using various methods published in the literature or of original design. Photodegradability studies are presented for textile materials printed with ink made from natural source pigments through screen printing or impregnation. Additionally, the production of alginate-based hydrogels enriched with extracts of natural dyes with antioxidant properties, with potential medical applications, was also explored.

IV. OBJECTIVES

The research study aimed to optimize extraction processes, improve the resistance of natural dyes to environmental factors, and highlight their potential direct applications.

Based on these considerations, the presented thesis had the following general objectives, also shown in Scheme IV.1:

O1. Study and optimization of extraction processes for natural dyes.

O2. Study of stabilization methods and improvement of dye fastness by converting them into insoluble products and using them as pigments in textile printing processes.

O3. Study of the efficiency of stabilization methods in terms of degradability through light exposure.

The specific objectives of the study are:

- Extraction of bioactive compounds (chlorophyll, curcumin, phycocyanin) from plant material using conventional methods (maceration, reflux) and unconventional methods (microwave-assisted extraction and ultrasound-assisted extraction, both direct and indirect);
- Study of the influence of parameters (stirring speed, time, extraction temperature, and power) in the extraction methods used;

- Obtaining phycocyanobilin from phycocyanin extract derived from *Spirulina platensis*;
- Stabilization of the extracted compounds by forming complex combinations or encapsulating them in a silica matrix, and characterization of the physicochemical properties of the obtained products;
- Study of the influence of stabilization methods through encapsulation of natural dyes on their photodegradability;
- Production of textile inks based on natural-source pigments obtained through stabilization processes, and their application on textile materials via screen printing or impregnation;
- Study of the photodegradability property of materials printed with natural dyes;
- Use of phycocyanin in the formulation of alginate-based hydrogels with applications in biomedical controlled-release systems.

CHAPTER V – EXTRACTION AND STABILITION OF CHLOROPHYLL FROM GREEN LEAVES

V.2. Materials and methods

V.2.1. Materials

For the extraction of chlorophyll, fresh raw materials such as dill, parsley, spinach, and patience dock, purchased from a local store, were used. Frozen spinach leaves were also used. Ethanol (96%) and acetone (99% analytical purity) were purchased from Chemical Company SA (Iași, Romania) and used as extractive solvents. Tetraethyl orthosilicate (TEOS) (Aldrich), 3-aminopropyltriethoxysilane (APTES) (Aldrich), cetyltrimethylammonium bromide (CTAB) (Aldrich), and sodium hydroxide (NaOH) (Fluka) were of analytical purity. In addition, Hydra Clear 77 printing paste (a transparent and flexible polyurethane base designed for pigmentation) and white tercot (20% polyester and 80% cotton) with a specific weight of 195 g/m² were used. Also, 37% hydrochloric acid (HCl), 0.1 M copper nitrate solution ($Cu(NO_3)_2$), and pure chlorophyll were used.

- Unconventional extraction methods

Among the known methods, the extraction of chlorophyll from spinach leaves was carried out using direct ultrasound treatment. For this purpose, the UP200H ultrasound probe was used. It was inserted into a cylindrical vessel with a jacketed volume of 100 mL, positioned 3 cm from its bottom. A magnetic stirrer with heating, model ARE, manufactured by VELP SCIENTIFICA, was used. The temperature of the mixture was maintained by circulating cooling water through the jacket of the vessel.

Figure V.7 UAE equipment: Hielsher UP200H sonotrode, jacketed reactor, electric plate with controlled heating and stirring

The process was optimized using the Design of Experiments (DOE) technique to find the best working parameters. The Response Surface Methodology (RSM) Box-Behnken, which uses the least squares method, was employed. The variables introduced were of two types: continuous on an interval (solid/solvent ratio – between 0.1 and 0.5 – and stirring speed – between 500 and 1500 rpm) and discrete (ultrasound power (US) – 40, 60, 80, 100, 120 W). These were used to determine the optimal conditions for maximizing the concentration of chlorophyll extracted from spinach leaves. The experimental design was carried out with the

JMP software (Cary, N.C., USA). The parameters used for the 15 initial experiments are presented in Table V.1.

Table V.1. Introduced variables

No. exp.	Solid-liquid ratio, x_1	US power, W, x_2	Stirring rate, rpm, x_3
1	0.1	40	500
2	0.1	60	1000
3	0.1	100	1500
4	0.1	120	500
5	0.236	40	1500
6	0.3	60	1000
7	0.3	80	500
8	0.3	100	1000
9	0.3	100	1000
10	0.378	120	1500
11	0.402	60	500
12	0.5	40	790
13	0.5	60	1500
14	0.5	100	1000
15	0.5	120	500

The responses, or output variables, evaluated in the experimental set were the concentrations of chlorophyll-a and chlorophyll-b. The levels of the evaluated factors were also determined, representing the specific variations of each factor (input variable) in an experiment and are essential for the analysis and optimization of a process.

V.3. Results and discussions

V.3.1. Chlorophyll extraction from green leaves

A. Conventional extraction of chlorophyll

For the extraction of chlorophyll from spinach leaves using modern methods direct ultrasound treatment was employed. The solvent used was ethanol and the aim of this stage was to optimize the extraction process using the DOE technique. The experimental trials in Table V.1 were performed and analyzed in triplicate. The output variables, namely the concentrations of chlorophyll-a and chlorophyll-b, are illustrated in Table V.2, along with the influence of the parameters on them.

Tabel V.2 Obtained chlorophyll concentrations

No. exp.	Chlorophyll-a concentration, mg/mL	Chlorophyll-a concentration -b, mg/mL
1	0.062	0.025
2	0.085	0.038
3	0.073	0.025
4	0.099	0.038
5	0.086	0.035
6	0.094	0.047
7	0.079	0.042
8	0.125	0.053
9	**0.149**	0.066
10	0.098	**0.088**
11	0.032	0.025
12	0.04	0.047
13	0.041	0.061
14	0.043	0.060
15	0.027	0.028

The maximum concentration of chlorophyll-a (0.149 mg/mL) was obtained using a solid-solvent ratio (x_1) of 0.3, an ultrasound power (x_2) of 120 W, and a stirring speed (x_3) of

1000 rpm. The mathematical model was generated according to equation (V.6) and describes the empirical relationship between the three parameters and the desired responses (in this case, the maximum chlorophyll concentration).

$$\begin{aligned} Conc_{clorofila-a} = {} & 0{,}11369072 + (-0{,}024003994) * \frac{x_1 - 0{,}3}{0{,}2} + 0{,}0160507036 * \frac{x_2 - 80}{40} \\ & + \frac{x_2 - 80}{40} * \frac{x_2 - 80}{40} * 0.013491454 + 0{,}0074291106 * \frac{x_3 - 1000}{500} + \frac{x_1 - 0{,}3}{0{,}2} \\ & * \frac{x_1 - 0{,}3}{0{,}2} * (-0{,}043350139) + \frac{x_1 - 0{,}3}{0{,}2} * \frac{x_2 - 80}{40} * (-0{,}005728985) \\ & + \frac{x_1 - 0{,}3}{0{,}2} * \frac{x_3 - 1000}{500} * 0{,}012081002 + \frac{x_2 - 80}{40} * \frac{x_3 - 1000}{500} \\ & * (-0{,}003296513) + \frac{x_3 - 1000}{500} * \frac{x_3 - 1000}{500} * (-0{,}031036143) \end{aligned} \quad \text{(V.6)}$$

For chlorophyll-b, the maximum concentration (0.088 mg/mL) was obtained for x_1=0.378, x_2=120 W, and x_3=1500 rpm. Similarly, the mathematical model was generated and is presented in the form of equation (V.7).

$$\begin{aligned} Conc_{clorofila-b} = {} & 0{,}055133058 + 0{,}0108066783 * \frac{x_1 - 0{,}3}{0{,}2} + 0{,}0100351407 * \frac{x_2 - 80}{40} + \frac{x_2 - 80}{40} \\ & * \frac{x_2 - 80}{40} * 0{,}0071193196 + 0{,}098802809 * \frac{x_3 - 1000}{500} + \frac{x_1 - 0{,}3}{0{,}2} * \frac{x_1 - 0{,}3}{0{,}2} \\ & * (-0.011096342) + \frac{x_1 - 0{,}3}{0{,}2} * \frac{x_2 - 80}{40} * (-0{,}001310845) + \frac{x_1 - 0{,}3}{0{,}2} \\ & * \frac{x_3 - 1000}{500} * 0{,}0144959741 + \frac{x_2 - 80}{40} * \frac{x_3 - 1000}{500} * 0{,}0060538288 \\ & + \frac{x_3 - 1000}{500} * \frac{x_3 - 1000}{500} * (-0{,}011518656) \end{aligned} \quad \text{(V.7)}$$

The model examination was performed through analysis of variance (ANOVA). The quality of the model was expressed by the coefficient of determination, R^2. The value of the multiple correlation coefficient, $R > 0.90$ (see Figure V.13), indicates a strong positive correlation between the observed and estimated values. The predicted profiles provide the optimal parameters, with a desirability of 0.96. The optimal parameters are $x_1 = 0.23$, $x_2 = 120$ W, and $x_3 = 1000$ rpm. By adhering to these parameters, the maximum concentrations of chlorophyll-a (0.148 mg/mL) and chlorophyll-b (0.067 mg/mL) can be obtained.

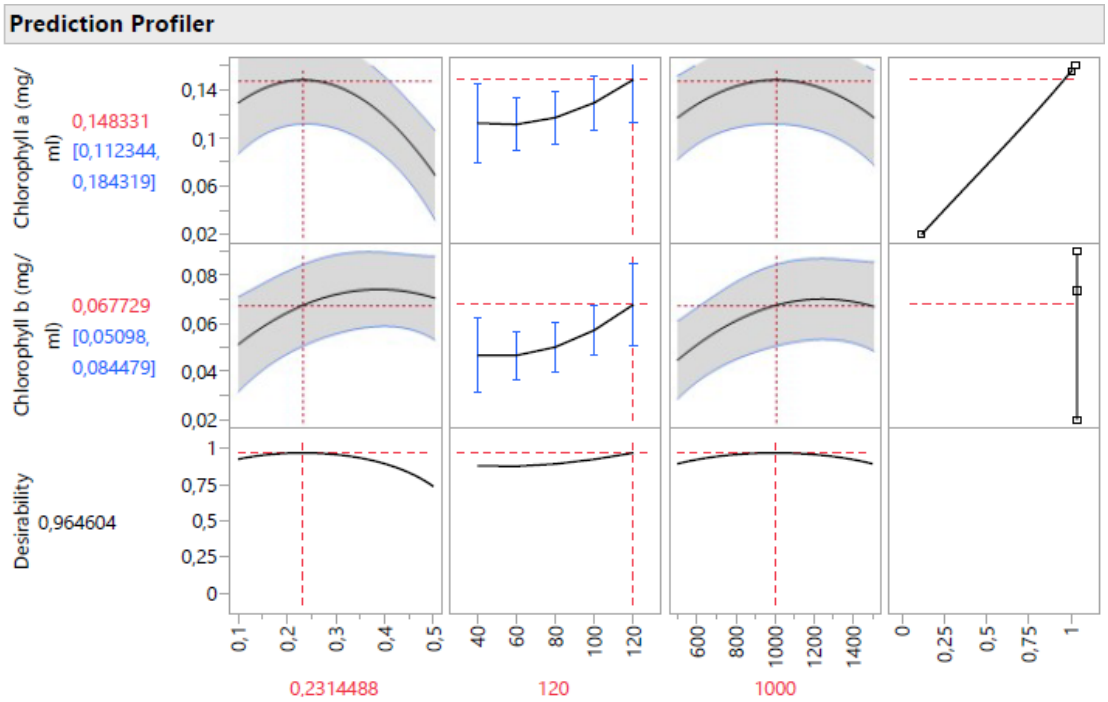

Figure V.13. Optimal parameters regarding the chlorophyll extraction from fresh spinach leaves using UAE

CHAPTER VI. EXTRACTION AND STABILISATION OF CURCUMIN

VI.3. Results and discussion

VI.3.2. Curcumin stabilization by encapsulation

A. Stabilization/encapsulation with NaOH

The absorption spectra of the samples corresponding to this method are presented in Figure VI.15. As observed, sample P I-3, which has the lowest encapsulation efficiency (86.33%) and the lowest curcumin content, exhibits the lowest absorption peaks. Also, for similar encapsulation efficiency values (P I-1 96.13%, P I-2 91.97%), an increase in absorption can be observed for sample P I-2 compared to P I-1, even though a larger amount of curcumin extract was used in the latter. The characteristics of sample P I-1 can be explained by the large volume of ethanol present in the system, which can lead to a decrease in the stability of the

particles, resulting in larger particles due to a change in the particle growth stage. During this process, curcumin can be fixed in a larger quantity inside the capsules, leading to a lower absorption peak than that corresponding to P I-2.

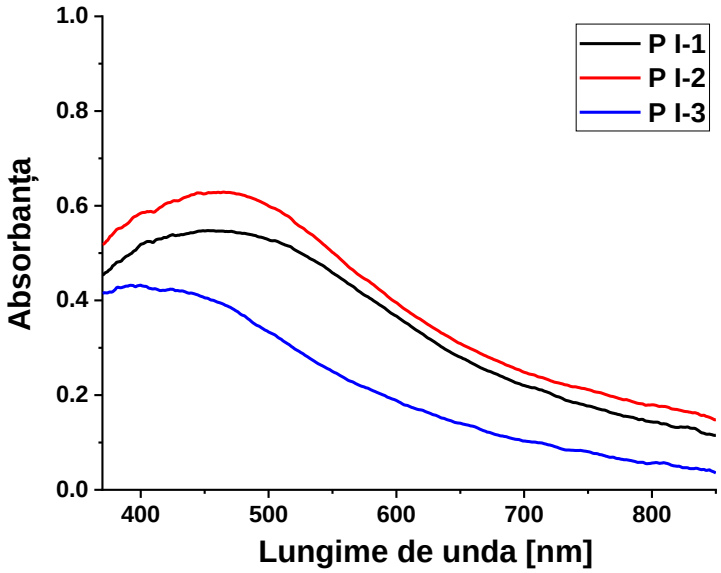

Figure VI.15 Absorption spectra for curcumin encapsulated by the first method (hydrolysis/condensation catalyzed by NaOH)

The results regarding the amount of encapsulated curcumin per gram of silica and the fluorescence properties of the samples are presented in Figure VI.16. Thus, it can be observed that a very good dispersion of the dye was obtained, as, despite the concentration differences between the three samples, the fluorescence properties are similar, with P I-3 having the highest emission peak, while the curcumin concentration loaded is the lowest. Additionally, there is a slight bathochromic shift in the emission peak of samples P I-2 and P I-1, which can be attributed to the formation of curcumin aggregates in the silica particles. The formation of curcumin aggregates is more easily observed in the normalized spectra. It is known that a high concentration causes the aggregation of nanoparticles in solution, leading to the beforementioned bathochromic shift. This is why samples P I-1 and P I-2 have a peak at 568 nm, compared to P I-3 at 559 nm. Aggregation occurs in the presence of a high curcumin content; however, in this case, a maximum aggregation is reached at 32 mg of dye per gram of silica.

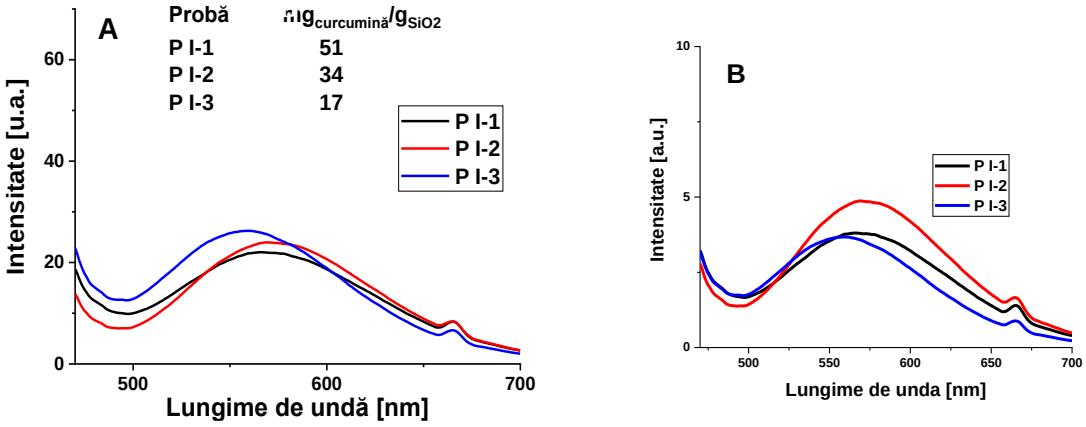

Figure VI.16 A - Fluorescence spectra for curcumin encapsulated by the first method (hydrolysis/condensation catalyzed by NaOH); B – normalized fluorescence spectra

The morphology of the particles was investigated by Scanning Electron Microscopy (SEM), and the results are presented in Figure VI.17. The SEM analysis revealed that the first encapsulation method (hydrolysis/condensation catalyzed by NaOH) leads to individual, spherical, and porous capsules, all with similar encapsulation efficiencies. The size of the silica particles decreases as the amount of ethanol solution of Si-curcumin introduced into the reaction decreases, which is consistent with the previous examples. The variation in particle size can also justify the results of the UV-Vis analysis. The lower absorption in the case of P I-1 can be explained by a thicker silica layer covering the curcumin, so only a part of the loaded curcumin absorbs light. Furthermore, the fluorescence results suggest that for P I-1 and P I-2, curcumin aggregates are formed, and this can be facilitated by the increase in particle size.

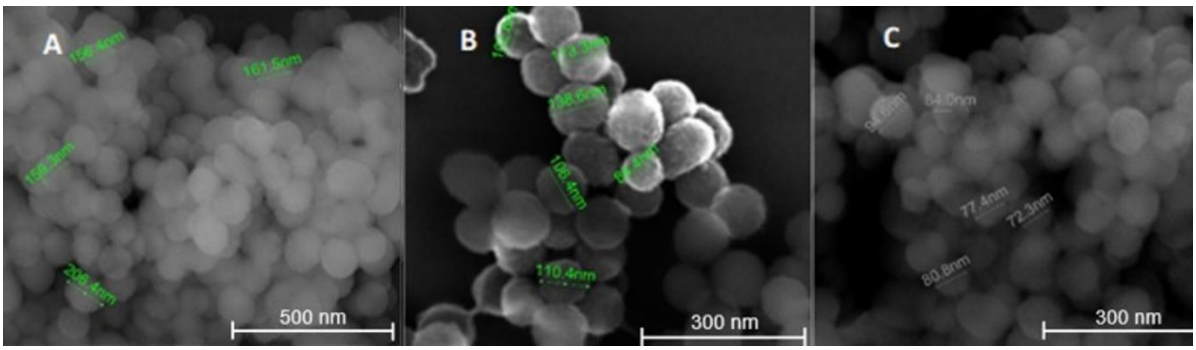

Figure VI.17 SEM images of silica particles loaded with curcumin through the first method (hydrolysis/condensation catalyzed by NaOH) (A – P I-1; B – P I-2; C – P I-3)

CHAPTER VII. PHYCOCYANIN EXTRACTION AND THE STABILISATION OF THE NATURAL DYE

VII.2 Materials and methods

VII.2.1 Materials

Spirulina powder was used and purchased from the S.C. Herbalvit S.R.L. company in 200 g packages, lot 200616, and Blue Spirulina (lot 23163) distributed by Dragon Superfoods®. A 0.1 M phosphate-buffered solution (PBS) with pH ≈ 7.4 was used as the extractive solvent. Methanol (MeOH), distilled water, and ammonium sulfate ((NH4)2SO4) from Sigma-Aldrich were used for phycocyanobilin separation. For determining antioxidant activity, copper chloride, CuCl2 (99%, Sigma-Aldrich), ammonium acetate, NH4CH3COOH (97%, Sigma-Aldrich), neocuproine, Nc (98%, Sigma-Aldrich), and 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (TROLOX) (97%, Sigma-Aldrich) were used. Hybrid silica-based materials required TEOS, phenyl triethoxysilane (PTES), tetrahydrofuran (THF), ethanol, citric acid, 0.1 N HCl, and calcium chloride (CaCl2), all from Sigma-Aldrich. For the synthesis of alginate-based hydrogels, polyvinyl alcohol (PVA, average molecular weight 85,000 – 124,000 g/mol, hydrolyzed 87-89%), sodium alginate, acrylamide (AM), N,N'-methylenebis(acrylamide) (MBSA), and ammonium persulfate (APS, purified by recrystallization in ethanol) were used, all obtained from Sigma-Aldrich.

A. Analysis methods

a) Release of phycocyanin from alginate-based polymer hydrogels

A volume of 30 mL of simulated body fluid (SBF) with pH = 7.45 was placed in a 50 mL plastic flask and used as the release medium. Before adding the phycocyanin-loaded hydrogel, the flask was placed for 24 hours in a dry bath (HCM100-PRO Thermo Mix) set at 37 °C and 250 rpm. The same parameters were maintained for the controlled release of phycocyanin-loaded hydrogels over a period of 9 hours. Samples of 3 mL were collected every 10 minutes during the first 2 hours, every 30 minutes during the next 3 hours, and every 60 minutes until 9 hours. The removed release medium volume was replenished with PBS to

maintain a constant volume of 30 mL. The samples were stored at 4–8°C before being analyzed spectrophotometrically.

The amount of released phycocyanin was calculated according to the equation *(VII.11)*:

$$CC_{t=n} = \sum_{t=0}^{n-1} CC + Conc_{t=n} * 30 \quad \text{(VII.11)}$$

VII.3 Results and discussion

VII.3.4 Alginate Polymer-Based Hydrogels

D. Controlled Release of Phycocyanin from Alginate Polymer-Based Hydrogels

To characterize the release profile of phycocyanin from alginate polymer-based hydrogels, four mathematical models were considered: zero-order kinetics, first-order kinetics, the Higuchi model, and the Korsmeyer-Peppas model. These were selected because they are the most used kinetic models for the release mechanism of substances from polymeric matrices [258-260].

Thus, phycocyanin-loaded hydrogel discs were analyzed for controlled release over 9 hours at two different pH values, 7.45 and 6.5. The experimental results were graphically represented based on the zero-order model, first-order model, Higuchi model, and Korsmeyer-Peppas model, presented in Figure VI.35 (pH = 7.45) and Figure VII.36 (pH = 6.5).

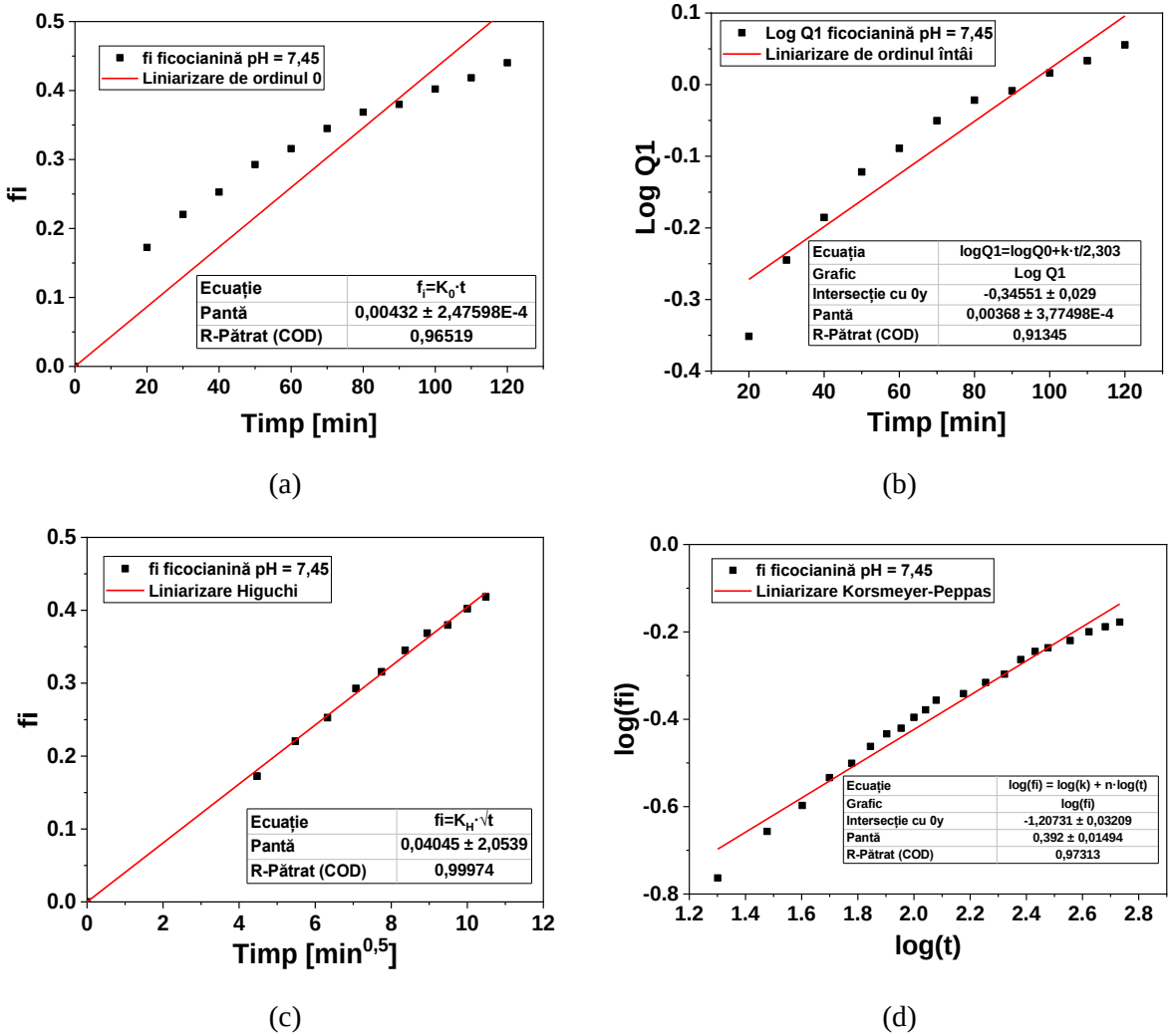

Figure VII.35 Graphical representation of zero-order kinetics (a), first-order kinetics (b), Higuchi kinetics (c), and Korsmeyer-Peppas kinetics for the release of phycocyanin at pH = 7.45

In this study, the release of phycocyanin at pH 7.45 (Figure VII.35) was best described by the Higuchi model, characterized by the highest regression coefficient (R^2 = 0.9997) compared to the other models: zero-order (R^2 = 0.9651), first-order (R^2 = 0.9131), and Korsmeyer-Peppas (R^2 = 0.9731). When the pH value was lowered to 6.5, the Higuchi model again provided the best result, with an R^2 of 0.9872 (Figure VII.36-c), compared to zero-order (R^2 = 0.9181), first-order (R^2 = 0.8802), and Korsmeyer-Peppas (R^2 = 0.9811). However, the R^2 value at the higher pH was significantly higher, being very close to 1, indicating a superior fit. According to the Higuchi model, the polymer-based system is characterized by a hydrated layer that appears on the surface edge, where the release medium is present, based on a Fickian diffusion process [261]. In general, as the contact time of the hydrogel with the medium

increases, the active compound encapsulated or loaded in the PAM/APV-alginate matrix (in this case, phycocyanin) diffuses into this layer and dissolves in the medium [262].

GENERAL CONCLUSIONS

The research completed during the doctoral studies demonstrates the potential of natural dyes—chlorophyll, curcumin, and phycocyanin—was demonstrated in terms of their extraction and stabilization through innovative methods, with applicability in various fields such as the textile industry, polymer material colouring, and the pharmaceutical industry. The main objectives included optimizing extraction methods, improving colour stability, and enhancing resistance to environmental factors.

The key conclusions can be summarized as follows:

- Efficient extraction methods were identified for chlorophyll, curcumin, and phycocyanin, using both conventional techniques (maceration, reflux extraction) and modern ones (UAE, MAE).
- For chlorophyll, maceration in acetone (0.24 mg/mL for Chl-a and 0.25 mg/mL for Chl-b) provided better results than maceration in ethanol (0.11 mg/mL Chl-a and 0.08 mg/mL Chl-b), while reflux with ethanol led to smaller quantities due to the thermal lability of chlorophyll (0.02 mg/mL Chl-a and 0.03 mg/mL Chl-b). Modern methods, such as ultrasound-assisted extraction (UAE), optimized the process using parameters: solid-solvent ratio 0.23, US power of 120 W, and agitation speed of 1000 rpm, with a desirability of 0.96.
- Curcumin was efficiently extracted by refluxing with acetone (2.85 ± 0.07 mg/mL). Similar concentrations were obtained in a shorter time using microwave-assisted extraction (2.73 ± 0.09 mg/mL).
- Phycocyanin was extracted with a higher yield through UAE in continuous mode (29.31 ± 0.33 mg/mL) compared to conventional techniques (13.19 ± 0.47 mg/mL) and MAE (13.82 ± 0.01 mg/mL). However, high-purity extracts (0.5 ± 0.002) resulted from microwave treatment.
- An original method was developed to isolate phycocyanobilin from the obtained extracts, resulting in a high-purity compound. Using 5 g of spirulina powder, 0.54 ± 0.015 mg/mL of phycocyanobilin was obtained, representing 10.7 mg/g of plant. Additionally, antioxidant activity was determined using the CUPRAC method, yielding 2.2 mg TE/mL extract.

- Regarding stabilization, the resistance of chlorophyll was improved through two approaches: changing the central ion and encapsulation. Textiles dyed with Chl-Cu showed superior light resistance compared to those dyed with pure chlorophyll. Encapsulation improved colour stability over time, reducing degradation by 24.57% for Chl-a and 14.06% for Chl-b compared to non-stabilized samples.
- For curcumin, encapsulation in a silica matrix ensured uniform dispersion, increased light stability, and improved resistance, with notable results for methods using NaOH and lysine. Encapsulation in the presence of NaOH offered good dimensional control and excellent light stability, while the biphasic encapsulation process formed porous aggregates, yet with similar resistance.
- The light resistance of textiles impregnated with phycocyanin was addressed. The natural dye was effectively protected by using sodium alginate as a solvent and covering with nanosol, demonstrating improvements in light resistance and promising colour stability.
- Given the antioxidant properties of phycocyanin, an innovative method was approached for formulating alginate-based hydrogels with potential applications as wound dressings. The controlled release behaviour at pH 6.5 and 7.45 was studied. The Higuchi model best described the release mechanism, with regression coefficients up to $R^2 = 0.9997$.

These studies contribute to the development of sustainable solutions for using natural pigments in industrial applications, laying the foundation for efficient extraction, stabilization, and controlled use methods. The results obtained open promising perspectives for integrating these natural dyes into fields such as the textile industry, cosmetics production, and the biomedical industry.

PERSPECTIVES

Future research will explore additional methods for stabilizing natural pigments, such as encapsulation in different types of nanomaterials (polymer nanoparticles, liposomes, etc.) to enhance their resistance to environmental factors, including exposure to light, temperature, and oxygen. New stabilization technologies through bioconservation processes or the use of natural additives to protect the dyes over time will also be investigated. An interesting direction will be the study of interactions between natural pigments and various materials and polymer matrices to obtain products with improved functional characteristics, such as more durable textures, increased resistance to light, water, or mechanical factors. Additionally, the behaviour of these dyes in different environments (aqueous, acidic, alkaline) will be analyzed to develop a wide range of applications.

Given the antioxidant and anti-inflammatory properties of natural pigments, future research will continue to explore their use in biomedicine. One example is the study of using extracts of phycocyanin, curcumin, or chlorophyll in treatments for inflammatory diseases, cellular protection, or even promoting tissue regeneration. Their applications as therapeutic agents in anti-aging treatments or as support for skin regeneration will also be explored.

In the context of transitioning to more eco-friendly solutions, future studies will explore the ecological impact of using natural pigments in industrial processes. These studies may include life cycle analysis (LCA) of the pigment, evaluating resource consumption, carbon emissions, and waste generated in the production process, to ensure the sustainable implementation of these dyes in industries such as textiles, food, and cosmetics.

These research directions could contribute to expanding knowledge on the potential of natural pigments, promoting their use across a variety of industrial, medical, and ecological fields.

PUBLISHED WORK

Scientific articles

1. D.-I. Buliga, A. Mocanu, E. Rusen, A. Diacon, G. Toader, O. Brincoveanu, I. Călinescu, A.C. Boscornea, 2024, *Phycocyanin-Loaded Alginate-Based Hydrogel Synthesis and Characterization*, Marine Drugs.; 22(10):434. (**IF – 4.9, Q1**) – ISSN: 1660-3397, WOS: 001342463500001

2. A.-M. Draghici-Popa, **D.-I. Buliga**, I. Popa, S.T. Tomas, R. Stan, A.C. Boscornea, 2024, *Cosmetic Products with Potential Photoprotective Effects Based on Natural Compounds Extracted from Waste of the Winemaking Industry*, Molecules, 29(12), 2775. (**IF – 4.2, Q2**) – ISSN: 1420-3049, WOS: 001255844200001

3. A.-M. Roșca, **D.-I. Buliga**, A.C. Boscornea, 2023, *Optimisation Of Hypericin Ultrasound Assisted Extraction: A Mathematical Model Approach*, UPB Scientific Bulletin, Series B: Chemistry and Materials Science, 85(4), 45-56. (**IF – 0.5, Q3**) – ISSN:1454-2331, WOS: 001126670800023

4. D.-I. Buliga, I. Popa, A. Diacon, C.A. Boscornea, 2022, *Optimization of Ultrasound-Assisted Extraction of Chlorophyll Using Design of Experiments and Stability Improvement via Encapsulation*, UPB Scientific Bulletin, Series B: Chemistry and Materials Science, 84(4), 59-72. (**IF – 0.5, Q3**) – ISSN:1454-2331, WOS: 000897670000005

5. D.-I. Buliga, A. Diacon, I. Calinescu, I. Popa, E. Rusen, A. Ghebaur, O. Tutunaru, C. A. Boscornea, 2022, *Enhancing the light fastness of natural dyes by encapsulation in silica matrix* Journal of Photochemistry and Photobiology A: Chemistry, 432, Article No. 114085. (**IF – 5.141, Q2**) – ISSN: 1010-6030, WOS: 000826687700003

6. I. Asofiei, I. Călinescu, V. Staicu, **D.-I. Buliga**, A. I. Gavrilă, 2021, *A STRATEGY FOR ENHANCING THE EXTRACTION YIELD OF POLYPHENOLS FROM SEA BUCKTHORN LEAVES*, UPB Scientific Bulletin, Series B: Chemistry and Materials Science, 83(2), 37-44. (**IF – 0,5, Q3**) – ISSN:1454-2331, WOS: 000661663200004

International conferences

1. Conference **Chemistry World Conference 2021**, Roma, Italy - **Diana-Ioana Buliga**, Aurelian Cristian Boscornea, Ioan Calinescu, Aurel Diacon, Ioana Popa, *Optimization of ultrasound-assisted extraction of chlorophylls from spinach by-products using response surface methodology and stabilization of the extracted pigments by encapsulation*.

2. Workshop **NeXT-Chem 2021**, Bucharest, Romania - **Diana-Ioana Buliga**, Aurelian Cristian Boscornea, Ioana Popa, Ana-Maria Draghici-Popa, Ioan Calinescu, *Phycocyanin – a possible solution for natural blue pigments*.

3. Conference **AdFoodChem 2021**, Bucharest, Romania - Stefan Theodor Tomas, Ana-Maria Draghici-Popa, Ioana Popa, **Diana-Ioana Buliga**, Aurelian Cristian Boscornea, *Bioactive compounds extraction from blackthorn fruits.*

4. Conference **PRIOCHEM XVIII 2022**, Bucharest, Romania - **D.-I. Buliga**, I. Popa, C.A. Boscornea, A.M. Draghici-Popa, *Recovery of Natural Pigments with Potential Applications in Cosmetics and Food through Conventional and Unconventional Methods* (BBB PP-47), Book of Abstracts, 82

5. Conference **PRIOCHEM XIX-2023**, Bucharest, Romania - **Diana-Ioana BULIGA**, Monica RADULY, Valentin RĂDIȚOIU, Cristian Aurelian BOSCORNEA, *Optical and tinctorial properties of some natural dyes embedded in hybrid silica coatings*.

6. Conference **PRIOCHEM XIX-2023**, Bucharest, Romania - Ana-Maria DRAGHICI-POPA, **Diana-Ioana BULIGA**, Ioana POPA, Stefan TOMAS, Aurelian Cristian BOSCORNEA, 2023, *Photoprotective cosmetic products with polyphenolic extract from grape marc*.

7. Conference **SICHEM 2024**, Bucharest, Romania - **Diana-Ioana Buliga**, Alexandra Mocanu, Edina Rusen, Aurel Diacon, Gabriela Toader, Oana Brincoveanu, Ioan Calinescu, Aurelian Cristian Boscornea, *Phycocyanin loaded alginate-based hydrogels with potential medical applications.*

8. Conference **RICCCE 2024**, Constanta, Romania - **Diana-Ioana Buliga**, Ioana Popa, Aurel Diacon, Cristian Aurelian Boscornea, *Optimization of a green method for extracting bioactive compounds from plant materials and techniques for stabilization improvement.*

9. Conference **RICCCE 2024**, Constanta, Romania - Ioana Popa, Ana-Maria Drăghici-Popa, Adina Ionuța Gavrilă, **Diana-Ioana Buliga**, Cristian Aurelian Boscornea, *A promising solvent, fatty acid ethyl esters, for ultrasound-assisted extraction of liposoluble bioactive compounds.*

References

1. Singh, H.B. and Bharati, K.A., *History of natural dyes*, in *Handbook of natural dyes and pigments*. 2014, Woodhead Publishing India PVT LTD.
2. Abel, A., *24 - the history of dyes and pigments: From natural dyes to high performance pigments*, in *Colour design (second edition)*, Best, J., Editor. 2012, Woodhead Publishing. p. 557-587.
3. Braudel, F., De Ayala, R., Braudel, P., et al., *Fire, art and magic*, in *The mediterranean in the ancient world*, Lane, A., Editor. 2001. p. 52-63.
4. Melo, M.J., *History of natural dyes in the ancient mediterranean world*, in *Handbook of natural colorants*. 2009. p. 3-20.
5. Broadbent, A.D., *An introduction to dyes and dyeing*, in *Basic principal of textile coloration*. 2001. p. 174-197.
6. Yusuf, M., Shabbir, M., and Mohammad, F., *Natural colorants: Historical, processing and sustainable prospects*. Natural products and bioprospecting, 2017. **7**(1): p. 123-145.
7. Clottes, J., *Cave art*, in *Britannica*. 2018: UK.
8. Hübner, J., *The analysis of some ancient egyptian fabrics*. Journal of the Society of Dyers and Colourists, 1909. **25**(8): p. 223-227.
9. Lucas, A., *Ancient egyptian materials and industries*. 1989, London.
10. Crowfoot, G.M. and Davies, N.D.G., *The tunic of tut'ankhamūn*. The Journal of Egyptian Archaeology, 1941. **27**(1): p. 113-130.
11. Fostiridou, A., Karapanagiotis, I., Vivdenko, S., et al., *Identification of pigments in hellenistic and roman funeral figurines*. Archaeometry, 2016. **58**(3): p. 453-464.
12. Dapson, R. and Bain, C., *Brazilwood, sappanwood, brazilin and the red dye brazilein: From textile dyeing and folk medicine to biological staining and musical instruments*. Biotechnic & Histochemistry, 2015. **90**(6): p. 401-423.
13. Purinton, N. and Watters, M., *A study of the materials used by medieval persian painters*. Journal of the American Institute for Conservation, 1991. **30**(2): p. 125.
14. Bowersox, G.W. and Chamberin, B.E., *Gemstones of afghanistan*. 1995: Geoscience Press.
15. Mansour, R. and Yusuf, M., *Natural dyes and pigments: Extraction and applications*. Handbook of Renewable Materials for Coloration and Finishing, 2018: p. 75-102.
16. Zhang, Q.-W., Lin, L.-G., and Ye, W.-C., *Techniques for extraction and isolation of natural products: A comprehensive review*. Chinese Medicine, 2018. **13**(1): p. 20.
17. Li, P., Xu, G., Li, S.P., et al., *Optimizing ultraperformance liquid chromatographic analysis of 10 diterpenoid compounds in salvia miltiorrhiza using central composite design*. Journal of Agricultural and Food Chemistry, 2008. **56**(4): p. 1164-71.
18. Ćujić, N., Šavikin, K., Janković, T., et al., *Optimization of polyphenols extraction from dried chokeberry using maceration as traditional technique*. Food Chemistry, 2016. **194**: p. 135-42.