

Review

# The Stability of Anthocyanins and Their Derivatives through Clay Minerals: Revising the Current Literature

Robson Cunha <sup>1</sup>, Pollyana Trigueiro <sup>1,2</sup>, María del Mar Orta Cuevas <sup>3</sup>, Santiago Medina-Carrasco <sup>4</sup> , Thiago M. Duarte <sup>1</sup>, Luzia M. de C. Honório <sup>5</sup> , Dihêgo H. L. Damacena <sup>1</sup> , Maria Gardennia Fonseca <sup>6,\*</sup> , Edson C. da Silva-Filho <sup>1</sup>  and Josy A. Osajima <sup>1,\*</sup> 

<sup>1</sup> Interdisciplinary Laboratory for Advanced Materials (LIMAV), UFPI, Teresina 64049-550, PI, Brazil

<sup>2</sup> Materials Science and Engineering Postgraduate Program—PPGCM/CCSST, UFMA, Imperatriz 65900-410, MA, Brazil

<sup>3</sup> Departamento de Química Analítica, Facultad de Farmacia, Universidad de Sevilla, C/Profesor García, González 2, 41012 Sevilla, Spain

<sup>4</sup> Laboratorio de Rayos-X (CITIUS), Universidad de Sevilla, Avenida Reina Mercedes 4B, 41012 Sevilla, Spain

<sup>5</sup> Department of Chemistry and Physics, Center for Agrarian Sciences, UFPB, Areia 58397-000, PB, Brazil

<sup>6</sup> Research and Extension Center-Fuel and Materials Laboratory (NPE-LACOM), Federal University of Paraíba, João Pessoa 58051-970, PB, Brazil

\* Correspondence: mgardennia@quimica.ufpb.br (M.G.F.); josyosajima@ufpi.edu.br (J.A.O.)

**Abstract:** In recent years, anthocyanins, natural dyes, have promoted great scientific and technological interest. Their intrinsic antioxidant properties and health benefits make them ideal representatives of natural dyes as replacements for synthetic dyes. However, their instability can limit their use. A promising strategy to increase the color stability of anthocyanins is their interaction with clay minerals structures. Clay minerals have characteristics favorable to the stabilization of natural dyes, such as adsorption capacity, good surface chemistry, ion exchange capacity, abundance, non-toxicity, and environmental compatibility. This review summarizes relevant works that present different clays or clay minerals as robust inorganic matrices for incorporation, improved stability, and increased resistance against the thermal- and photodegradation of anthocyanins. In addition, several authors propose different applications for the formed anthocyanin-based hybrids.

**Keywords:** clay minerals; natural dyes; bioactive molecules; fading; protection



**Citation:** Cunha, R.; Trigueiro, P.; Orta Cuevas, M.d.M.; Medina-Carrasco, S.; Duarte, T.M.; Honório, L.M.d.C.; Damacena, D.H.L.; Fonseca, M.G.; da Silva-Filho, E.C.; Osajima, J.A. The Stability of Anthocyanins and Their Derivatives through Clay Minerals: Revising the Current Literature. *Minerals* **2023**, *13*, 268. <https://doi.org/10.3390/min13020268>

Academic Editor: Andrey G. Kalinichev

Received: 20 December 2022

Revised: 9 February 2023

Accepted: 10 February 2023

Published: 14 February 2023



**Copyright:** © 2023 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/>).

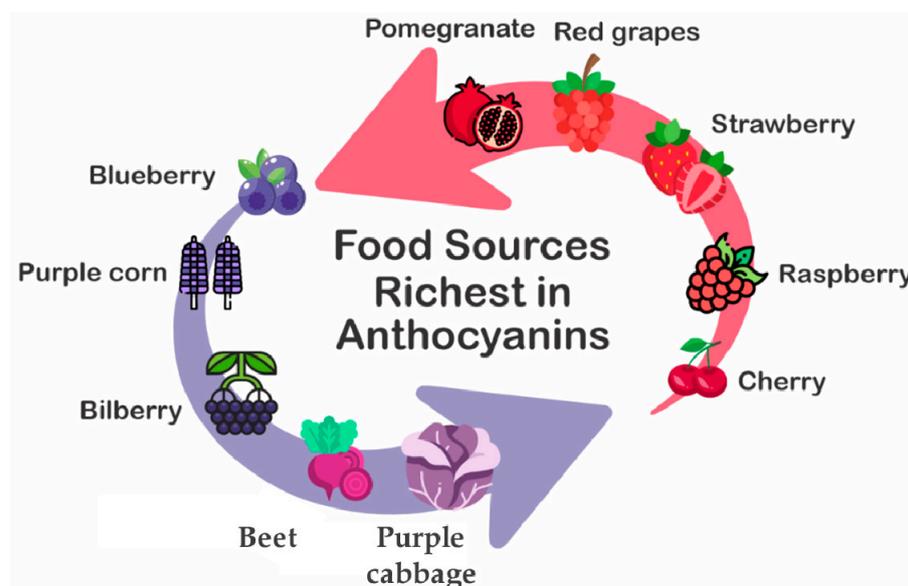
## 1. Introduction

Anthocyanins are natural dyes belonging to the group of flavonoids widely found in fruits and vegetables. They have strong absorption in the visible, ultraviolet region of the electromagnetic spectrum and are determinants in red-blue colors and their derivatives in the plant kingdom. These characteristics place them in second place in importance, immediately after chlorophyll pigments [1]. Anthocyanins play an essential role in seed dispersal, pollination, and the development of plant organs. However, they also adapt to pathogenic attacks, drought, lack of nutrients, and high-intensity light [2]. Due to their chemical structure, with a central core of 2-phenylbenzopyrylium or flavylum cation, anthocyanins can be classified as polyphenols and secondary metabolites [3].

Anthocyanins can carry out interactions with other compounds [4]. A class of compounds comprises more than 700 different species of anthocyanins. Only six are abundant in nature and represent about 90% of all the identified anthocyanins—for example, cyanidin, pelargonidin, delphinidin, peonidin, petunidin, and malvidin [5].

Figure 1 shows some foods that contain anthocyanin. They are complex and have different functions in plants and the human body, mainly due to interactions with several chemical compounds. The hues of these dyes vary between red, blue, and violet colors [6–8]. In addition to providing color in the food industry, anthocyanins also add functionality to

foods. These compounds have therapeutic and medicinal features associated with health maintenance, such as antioxidant, antimicrobial, and anti-inflammatory properties [9–12]. Furthermore, regularly consuming anthocyanins can help prevent cardiovascular, endocrine, immunological, and degenerative diseases and reduce cancer incidence [13]. Due to these properties, anthocyanins are attractive compounds emerging for use in further research and industrial sectors. Molecular modifications can increase the stability of these bioactive compounds to develop new functionalized products which can serve the areas of cosmetics, food, nutraceuticals, molecular biology, and biotechnology [14].

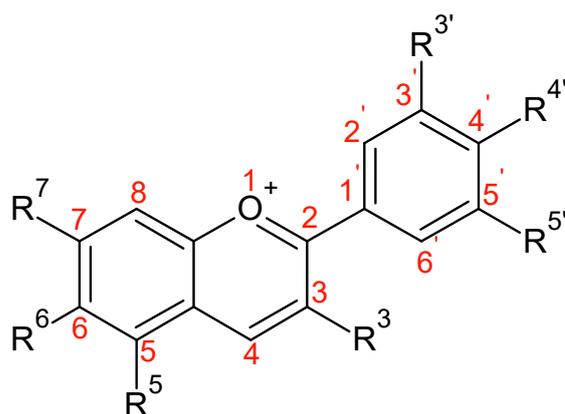


**Figure 1.** Main sources of anthocyanin dyes.

Anthocyanins are natural water-soluble dyes with the most diverse colors and hues: red, blue, and violet. Under acidic conditions, they show red colors due to the presence of the flavylium ion and change to violet and blue as the pH of the medium increases. These dyes have a complex chemical balance, and colored shapes are susceptible to fading by adding water and auto-oxidation reactions [15].

Several studies, mainly *in vitro*, have demonstrated a variety of biological properties of anthocyanins, including antioxidant activities [16], anti-inflammatory [17], antibacterial [18] and anti-carcinogenic effects [19], improved vision [20], and cardioprotective effects [21]. Therefore, these bioactive molecules have essential properties and several health benefits, such as preventing cardiovascular and neurodegenerative diseases, diabetes, cataracts, and cancer; strengthening of the immune and circulatory systems; preventing premature aging and cellular oxidative stress; and assisting in vitamin C absorption by the organism.

Anthocyanins belong to the flavonoid class, a subset of the polyphenol class. They are compounds found in nature as glycosides of polyhydroxy and poly ethoxy derivatives of flavylium or phenyl lbenzopyrilium salts [22]. Although they have a positive charge on the C-ring oxygen atom of the basic flavonoid structure, also called flavylium ion (2-phenyl choro menilyl), they contain a backbone of glycosylated anthocyanidin, which can also be esterified with aliphatic acids and aromatic compounds (Figure 2). The structure of different anthocyanins varies in the number and position of the hydroxyl groups, the degree of methylation of the hydroxyl, the groups attached to the phenolic molecule, and the nature of any aliphatic or aromatic acids attached to the sugar groups [23,24].



**Figure 2.** Anthocyanin structure.

Anthocyanidins are grouped into 3-hydroxy anthocyanidins, 3-deoxyanthocyanidins, and O-methylated anthocyanidins, while anthocyanins are in the glycoside forms of anthocyanidins and acylated anthocyanins. The most common anthocyanidins are cyanidin, delphinidin, pelargonidin, peonidin, malvidin, and petunidin (Table 1). Acylated anthocyanins are also detected in plants, and acylated anthocyanin is further divided into acrylate, co-arylated, caffeoylated, and malonylate [23,25].

**Table 1.** Main types of anthocyanidins.

Name	R <sup>7</sup>	R <sup>6</sup>	R <sup>5</sup>	R <sup>3</sup>	R <sup>5'</sup>	R <sup>4'</sup>	R <sup>3'</sup>
Cyanidin	OH	H	OH	OH	OH	OH	H
Delphinidin	OH	H	OH	OH	OH	OH	OH
Pelargonidin	OH	H	OH	OH	H	OH	H
Peonidin	OH	H	OH	OH	H	OH	OCH <sub>3</sub>
Malvidin	OH	H	OH	OH	OCH <sub>3</sub>	OH	OCH <sub>3</sub>
Petunidin	OH	H	OH	OH	OCH <sub>3</sub>	OH	OH

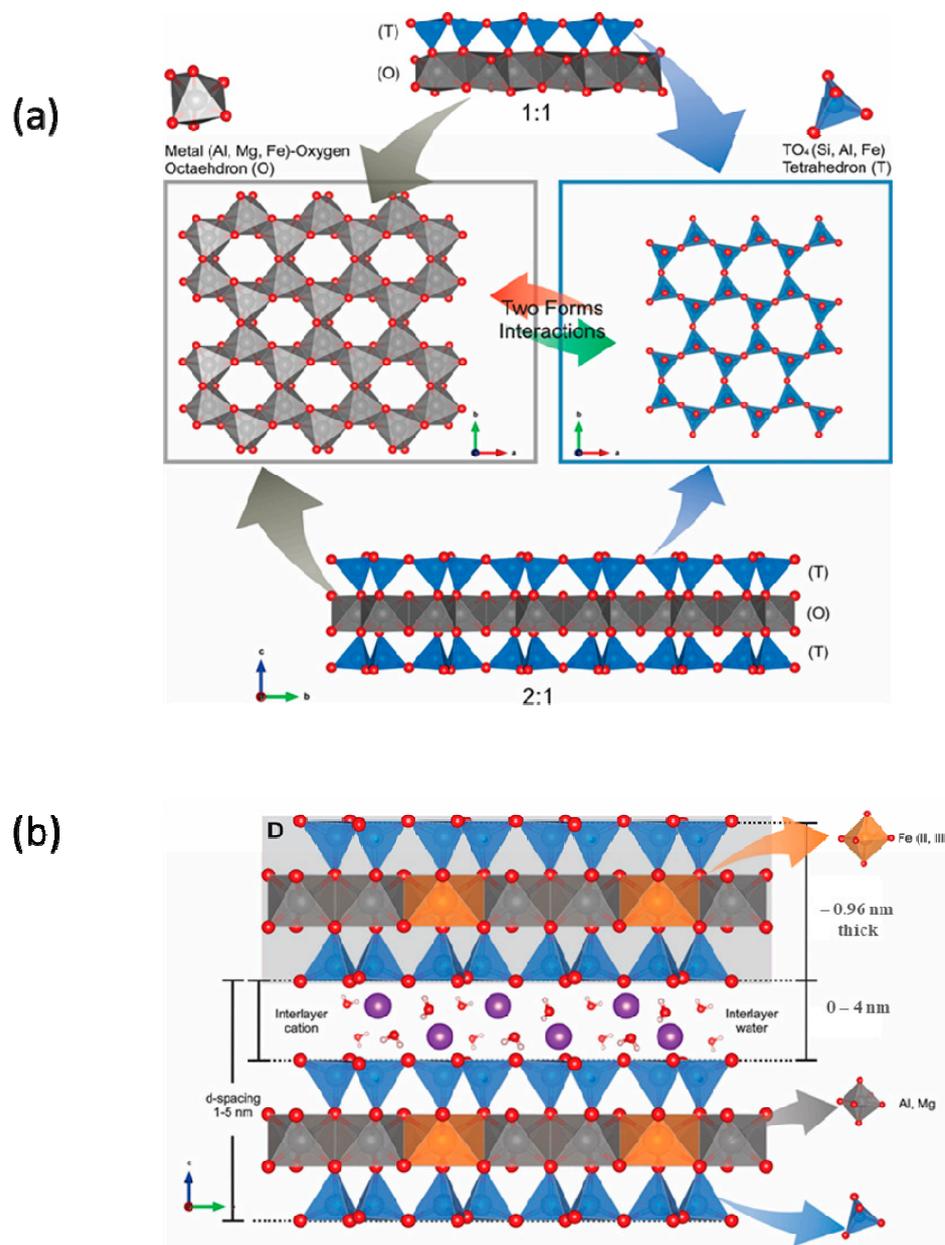
The classification and color diversity of anthocyanins are mainly related to the number and position of the hydroxyl and methoxy groups in their structure and the type and position of sugar groups and acetylating agents [26].

Cyanidin is a reddish-purple dye in fruit berries and reddish colors in vegetables such as red sweet potato and purple corn. Delphinidin has a chemical characteristic similar to most anthocyanidins. It appears as a reddish-blue or purple dye in the plant. The blue hue of flowers is due to the delphinidin dye. Pelargonidin differs from most anthocyanidins in nature; it appears as a red colorant that gives an orange hue to flowers and red to some fruits and berries. Methylated anthocyanidins, such as peonidin, are another type of anthocyanidin found abundantly in plants. They have a visible magenta color, and are widely found in fruits, grapes, and red wines. Malvidin is another O-methylated anthocyanidin, has a visible purple color, is abundant in blue flowers, is the primary red dye in red wine, and appears as a darker "dusty" red. Petunidin is a methylated anthocyanidin present as a dark red or purple dye that is water-soluble and has been detected in blackcurrants and purple flower petals [27–36].

Legal restrictions on synthetic dyes have driven a growing interest in natural dyes. The side effects of synthetic dyes cause people to be concerned about the risks to their health and the environment [37,38]. Moreover, substituting synthetic dyes with natural ones implies some challenges due to problems related to stability, especially in processing and storage conditions, causing loss of color and biological activity in foods and beverages. Among the effective parameters that can reduce the degradation of dyes such as anthocyanins are oxygen, temperature, light, pH, and composition of the food matrix; for example, the presence of vitamins, proteins, acids, and sugars [39–42]. Several studies have

been conducted involving clays and clay minerals as inorganic host materials to improve anthocyanin stability [43–48].

Clays are compounds consisting mostly of fine-grained minerals: the clay minerals. Clay minerals are phyllosilicates characterized by a layered structure with a dimension on the nanometric scale. The layers can be of the 1:1 type (TO), where a tetrahedral sheet is bonded to an octahedral sheet, or of the 2:1 type (TOT), where an octahedral sheet is located between two tetrahedral sheets, as observed in Figure 3a. Each tetrahedron consists of a central cation of  $\text{Si}^{4+}$  or  $\text{Al}^{3+}$ , coordinated to four oxygens and related to the neighboring tetrahedra through the basal oxygens forming a hexagonal symmetry in the continuous tetrahedral sheet. Each octahedron consists of a central cation of  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ , or  $\text{Fe}^{2+}$ , linked to six oxygens. The octahedrons connect to the neighboring octahedra through the edges forming the octahedral sheet and presenting hexagonal symmetry [49–51].



**Figure 3.** (a) Representative models of tetrahedral and octahedral sheets forming the 1:1 (TO) and 2:1 (TOT) layer structures and (b) 2:1 layer with hydrated interlayer cations.

When tetrahedral and octahedral sheets form lamellae, the result can be an electrically neutral lamella or a negatively charged lamella. The negative charge of the lamella is the result of isomorphic substitutions of the tetrahedral ( $\text{Al}^{3+}$  for  $\text{Si}^{4+}$ ) or octahedral (divalent cations for trivalent cations) sites. The excess negative charge is balanced by the presence of different cations in the interlamellar spacings, where  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  are the most found, as observed in Figure 3b. In the case of clay minerals of the 1:1 type, the lamellar charge is generally close to zero, and in the case of clay minerals of the 2:1 type, the charge is calculated based on the chemical formula. It can vary from 0.2 to 2.0 for montmorillonites and brittle micas, respectively. This configuration influences these materials' degree of hydration and cation exchange capacity [52,53]. Porosity arises from intraparticle interactions, the interlamellar region, or channels. It is a characteristic closely related to the water content and adsorption capacity of lamellar and fibrous clay minerals [54].

Clay minerals can currently be classified as planar or non-planar. The planars are subdivided into seven groups according to the layer design and interlayer material, such as kaolinite, smectite, and vermiculite. The non-planar clay minerals are subdivided according to the modulated structures. For example, they include tubular halloysite, sepiolite, and palygorskite. In addition, phyllosilicates have varied particle morphologies, such as plates, laths, discs, or fibers [50].

The interaction of clay minerals with different organic molecules depends on factors such as the pH of the medium, molecular charge, structure, and size of the molecule. For lamellar clay minerals, such as montmorillonites, interactions can occur by intercalation, ion exchange, complexation, or solvation. For fibrous clay minerals, these interactions occur mainly on the external surface. However, penetration into the internal cavities of sepiolite or palygorskite may occur. The interaction with dyes and clay minerals has active sites on the external and internal surfaces that facilitate the incorporation of chromophore groups [55–57]. Moreover, in the case of anionic dyes, electrostatic forces govern the interactions, while in the case of cationic dyes, interactions are possible from changes in clay minerals forming organo-clay minerals.

These properties, combined with features such as abundance, affordable cost, biocompatibility, surface reactivity, and the possibility of structural modifications, make clay minerals promising materials for various applications and mainly for use in the adsorption processes of organic compounds [58–62].

Different clay minerals have different structures and physicochemical properties. Therefore, there are apparent differences in the interaction mechanism, carrying capacity, and environmental stability of natural pigment/clay mineral hybrid materials [63–65].

Montmorillonite, palygorskite, sepiolite, and saponite were highlighted among the clay minerals studied. These minerals have different structures and specific physicochemical properties. Therefore, there are some differences in the interaction mechanism with organic molecules, load capacity, and environmental stability of hybrid materials of natural dyes/clay minerals.

Compared with synthetic substrates, clay minerals have advantages in forming hybrid pigments: low cost, abundance in nature, ecologically correct, chemical stability, large surface area, and significant adsorption capacity [56,57,66,67]. When dispersed in water, clay minerals, such as smectite or vermiculite, can be delaminated or exfoliated, facilitating the intercalation of organic molecules. Adsorption sites are located on clay minerals' outer and inner surfaces. These materials show a strong affinity for the adsorption of cationic and anionic dyes from specific chemical modifications. Consequently, dyes, in general, are rapidly adsorbed by clay minerals, and the different species formed—after adsorption—are easily detected by spectroscopic techniques.

The degradation process under light occurs when a molecule absorbs energy, promoting radical formations. Through this process, photoproducts and loss of color can occur. In addition, in some cases, they are toxic. In photochemical reactions, compounds derived from clay minerals have been successfully reported in the literature [68–71]. Both the functionalized compound and the type of light source used are decisive in the oxida-

tion of a given product and forming reactive intermediates oxidized by reactive oxygen species (ROS) [72,73]. The use of clay minerals to promote photostability is an alternative. One of the photostability mechanisms is the interaction promoted by the substrate and the clay mineral.

Accordingly, to reduce the degradation of natural dyes, further studies are essential in searching for alternatives that enable new sources of stability. Thus, obtaining a final product that is easy to handle, store, and mainly preserve, especially against agents such as light and temperature, assumes great importance in this production context. Due to the growing scientific and technological interest in using natural dyes, the present review aims to investigate the primary sources of degradation and potential mechanisms of chemical/photochemical stabilization of anthocyanin, mainly using clays or clay minerals.

## 2. Methodology

The resulting data for this analysis were obtained from Web of Science, Scopus, and Scielo. The search was done in January of 2023 from 2010. For the systematic search, the following filter topics were used: article title, abstract, keywords, and publication period, and the results are summarized in Table 2. The reference themes used for keywords were anthocyanin, stability, degradation, temperature, pH, protein, light, ascorbic acid, vitamin, oxygen, glucose, clay, and fading. The most diverse combinations with the keywords were made to filter the documents to expand the research field. In addition, this method can lead to a smaller number of specific articles, thus promoting greater relevance on search bases.

**Table 2.** The publications involving the study of anthocyanins.

Keywords	Web of Science	Scopus	Scielo
Anthocyanin	29,667	30,432	345
Anthocyanin AND degradation	2336	1776	33
Anthocyanin AND stability	3835	2634	43
Anthocyanin AND protection	900	1400	4
Anthocyanin AND degradation AND temperature AND fading	13	8	0
Anthocyanin AND degradation AND pH AND fading	14	13	0
Anthocyanin AND degradation AND protein AND fading	11	6	0
Anthocyanin AND degradation AND light AND fading	15	5	0
Anthocyanin AND degradation AND ascorbic acid AND fading	6	7	0
Anthocyanin AND degradation AND vitamin AND fading	4	3	0
Anthocyanin AND degradation AND oxygen AND fading	3	1	0
Anthocyanin AND degradation AND glucose AND fading	1	0	0
Anthocyanin AND clay	65	56	1
Anthocyanin AND clay AND protection	4	1	0
Anthocyanin AND clay AND degradation	3	3	0
Anthocyanin AND degradation AND clay AND fading	0	0	0

The keywords and word combinations used in the search were: anthocyanin, anthocyanin AND degradation, anthocyanin AND stability, anthocyanin AND protection, anthocyanin AND degradation AND temperature AND fading, anthocyanin AND degradation AND pH AND fading, anthocyanin AND degradation AND protein AND fading, anthocyanin AND degradation AND light AND fading, anthocyanin AND degradation AND ascorbic acid AND fading, anthocyanin AND degradation AND vitamin AND fading, anthocyanin AND degradation AND oxygen AND fading, anthocyanin AND degradation AND glucose AND fading, anthocyanin AND clay, anthocyanin AND clay AND protection, anthocyanin AND clay AND degradation, anthocyanin AND degradation AND clay AND fading.

## 3. Results and Discussion

Many articles used only the word “anthocyanin,” and fewer publications were found when only two or three keywords were combined. In contrast, a small number of stud-

ies were obtained by typing combined words in the specific search, including keywords corresponding to the sources of degradation. The keywords “anthocyanin, degradation, protection and fading” were repeated in most combinations. When associated with the keywords “temperature, pH, protein, light, and ascorbic acid,” we obtained a more significant number of publications than when combined with the keywords “vitamin, oxygen, and glucose.” Thus, no published articles were found in specific combinations of the Scopus database and Scielo. By combining the words clay and anthocyanin, 65 and 56 articles were found in the Web of Science and Scopus databases. Among the articles, 26 had in common the study of anthocyanin stabilization using clay or clay mineral. The other articles were not related to the purpose of this review. Instead, their study focused on the effects of soil and climate on growing food, the use of mineral fertilizers, improvements in herbicides, and evaluation of soil and plant behavior after adding natural nutrients, processes, and materials used in winemaking. There was a limited number of works involving clay minerals in studies of degradation, fading, or protection of anthocyanin, signaling that the study of clays or clay minerals as a source of protection or stability mechanism of this compound still needs to be explored. According to the publication dates, it was evident that studies containing anthocyanin degradation mechanisms concerning color fading are relatively recent, as publications between 2010 and 2022 accounted for about 80% of the articles (compared to a survey fast, regardless of the publication time restriction). The papers detailed in the survey were classified by the type of degradation source or stabilization mechanism, described in the keywords: temperature, pH, protein, light, ascorbic acid, vitamin, oxygen, glucose, and clay. The following characteristics were highlighted during the classification of the works found in the research: source of anthocyanin, extracting solvent, purification model, characterization techniques, degradation sources, and stability mechanisms. However, the prospective study and the literature review containing relevant studies on anthocyanin-type dyes mainly involved stabilization strategies and trend applications.

Table 3 shows the studies that investigated the methods for obtaining anthocyanin. The keywords column refers to the sources of degradation used in the combinations used in the systematic search for the papers. The anthocyanin extraction process was described in only some of the publications presented. In some situations, the anthocyanin powder previously obtained was used, which justifies the absence of the extracting solvent and purification in some works [12,74–79].

The most used method for separating and purifying anthocyanins was high-performance liquid chromatography (HPLC). This technique simultaneously separates, identifies, and quantifies anthocyanin dyes without requiring excessive purification of the extracts. Solid-phase extraction in C18 cartridges, presented in only one study, is a widespread technique in laboratories due to the relative ease of eliminating impurities, polar and non-phenolic substances, where first, more polar substances than anthocyanins are eluted, such as sugars, acids, and soluble substances, and afterwards the anthocyanin pigments are eluted [80]. The purple carrot was the source of anthocyanin most used for the experiments. It is preferred for studies of anthocyanin degeneration in beverages [12,74–77].

For extracting solvent, acidic solvents were confirmed, since anthocyanin is dissolved in the cell sap. Its extraction involves using these solvents to break the tissue cell membrane and dissolve the dyes [81]. The extraction method can influence the amount and safety of extracted anthocyanin, antioxidant activity, and biological potential [82].

The combination of keywords with Oxygen (O) or Glucose (G) had a small number of published articles, and the study could be expanded because it is emerging research. On the other hand, temperature (T), Light (L), and pH (pH) were the most used keywords in the articles because of the greater appeal for the food and beverage industry of the search for a stability mechanism that fights the degeneration of anthocyanins during the manufacture and storage of products [12,77]. Table 4 summarizes the main characterization techniques for anthocyanin-type dyes.

**Table 3.** Summary of anthocyanin extraction and purification methods.

Ref.	Keywords	Anthocyanin Source	Extractant Solvent	Separation Method
[74]	T; V; P; pH; AA	Purple carrot	-	-
[75]	pH; L; AA	Purple carrot	-	-
[76]	V; P; AA	Purple carrot extract	-	-
[83]	pH; O; L		-	-
[84]	P; pH	Grape skin	5 mL of 1% formic acid ( <i>v/v</i> ) in methanol and sonicated for 3 min	Liquid Chromatography HPLC
[80]	T; L	Vanda ‘Sansai Blue’ orchid flower petals	Acidified methanol (containing 0.01% HCl) and acidified water (containing 0.01% HCl)	C18 cartridge (Water Sep-Pak)
[77]	V; pH; AA	Black carrots, grape juice, and purple sweet potatoes	-	-
[12]	T; pH	Purple carrot	-	-
[78]	L	Narcissus pseudonarcissus plant	-	-
[81]	pH	Purple sweet potato from Vietnam	Ethanol solution	-
[85]	pH	Purple sweet potato	Methanol containing 0.01% HCl	Liquid Chromatography HPLC
[86]	L	Crabapple flowers ( <i>Malus orientalis</i> )	Phenolic extraction solution Containing 70% methanol and 2% formic acid	Liquid Chromatography HPLC
[79]	L; G	Jujuba fruit ( <i>Ziziphus jujuba</i> Mill.)	-	-
[87]	T; pH; L	Strawberry juice	Citric acid	-
[88]	P; L	‘Red Bartlett’ and ‘Starkrimson’ pears	HCl-methanol solution	-
[89]	P; L	Pear leaves and fruits	1% HCl-methanol solution (5 mL)	-
[36]	T	Chili paprika	Acetic Acid 10% ( <i>v/v</i> )	Liquid Chromatography HPLC

Temperature = T, pH, protein = P, luz = L, ascorbic acid = AA, vitamin = V, oxygen = O, glucose = G.

**Table 4.** Summary of characterization methods and stability mechanisms.

Ref.	Characterization Techniques	Source of Degradation
[74]	UV-visible spectrophotometer; colorimeter; Fluorescence extinction analysis	pH, ascorbic acid, temperature, light
[75]	UV-visible spectrophotometer; colorimeter; Fluorescence measurements	Temperature, pH, light, ascorbic acid
[76]	UV-visible spectrophotometer, colorimetry, visual appearance through digital photography and fluorescence measurements	Ascorbic acid, temperature, pH and light
[83]		pH, oxygen, light
[84]	Fluorescence spectroscopy, Synchronous Fluorescence Measurement (SF), FTIR Spectroscopy Circular dichroism (CD) spectroscopy, thermal stability test, Spectrophotometer for color analysis	pH, Temperature, Light and H <sub>2</sub> O <sub>2</sub>

Table 4. Cont.

Ref.	Characterization Techniques	Source of Degradation
[80]	HPLC	Ethylene, peroxidase enzymes (POD), temperature and light
[77]	UV-visible spectrophotometer	Ascorbic acid, temperature, pH and light
[12]	Instrumental colorimeter; dynamic shear rheometer; UV-visible spectrophotometer; optical and confocal scanning laser microscopy	pH, temperature
[81]	UV-visible spectrophotometer	pH
[85]	UV-visible spectrophotometer, HPLC	pH, temperature
[86]	UV-visible spectrophotometer, HPLC	H <sub>2</sub> O <sub>2</sub>
[79]	Analysis of staining mechanisms using metabolomics and transcriptomics approaches	Light, temperature
[87]	UV-visible spectrophotometer	Temperature, pH and light
[88]	UV-visible spectrophotometer	Light, LAC and POD degrading enzymes
[89]	UV-visible spectrophotometer	Light, COP1 type protein (Photomorphogenic Constituents: PbCOP1.1 and PbCOP1.2)

LAC = Lactase Enzyme; POD = Peroxidase Enzymes; PbCOP1.1 = Protein; PbCOP1.2 = Protein.

UV-Vis spectrophotometry was the most used characterization tool among the papers researched in analyzing anthocyanins, especially when coupled with techniques such as high-performance liquid chromatography (HPLC), a complementary tool for qualitative analysis. However, UV-Vis spectrophotometry is more useful in quantitative analysis [77,81,85,86].

As previously mentioned, anthocyanins have different extraction methods, based mainly on their polar nature, using different solvents such as ethanol, methanol, and water. Therefore, chromatographic techniques are the most used for purification processes. Additionally, the characterization step of anthocyanins and derivatives is essential for stability studies of these substances. Thus, chromatographic and spectroscopic methods are the most commonly used for the structural identification of anthocyanins.

### 3.1. Anthocyanin Degradation Mechanisms

Anthocyanins are highly susceptible to chemical degradation in aqueous solutions, decreasing their color and biological activities. Their chemical stability is compromised by oxygen, temperature, light composition, enzymes, pH, and food matrices; for example, carbohydrates, proteins, acids, salts, sugars, and minerals [90]. Anthocyanin degeneration is also influenced by the B ring in the anthocyanidin structure and the presence of hydroxyl or methoxyl groups [91]. Anthocyanins are sensitive to chemical degradation and color fading in the presence of vitamin C. The potential of three amino acids (L-phenylalanine, L-tyrosine, L-tryptophan) and a polypeptide (e-poly-L-lysine) decreases the degeneration of color in purple carrot anthocyanin extract in beverages. L-ascorbic acid and citric acid with pH 3.0, stored at a high temperature of 40 °C for seven days, were examined. Without amino acids or peptides, anthocyanin degraded at the first-order reaction rate. Adding amino acids or peptides (0.1%) increased the color stability of anthocyanins, with a more significant improvement observed for L-tryptophan [74].

Another study on the effects of ascorbic acid had the presence of flavonoids and sugars in the thermal degradation of anthocyanins in orange juice. Ascorbic acid and sugars significantly accelerated the degradation of anthocyanins, while flavonoids had a protective

effect on anthocyanins. Flavonoids and AA reduce the influence of temperature on the anthocyanin degradation rate [39]. Color fading can be associated with light exposure and the addition of salts and sugars. The color and stability of anthocyanins in tropical fruits, acerola, and açai were evaluated. Under an isotonic soft drink system, sugars and salts harmed stability. In the presence of light, anthocyanin degradation was 1.2 times faster than acerola and 1.6 times faster than açai in isotonic soft drink systems [92]. Color degradation was also observed in blackcurrant and elderberry, concentrated in anthocyanins, common food ingredients for soft drinks, fruit jellies, and salad dressings.

Food-grade organic acids and salts that influence discoloration were found in aqueous media. Color degeneration is decreased with increasing acids and increased with salt concentrations. This can be attributed to characteristic changes in the solvation of aqueous solutions [93]. Temperature is a factor that affects anthocyanins' color and physiological properties. Studies were conducted to evaluate the effect of temperature-induced degradation and biosynthetic inhibition of anthocyanins when exposed to high temperatures [94]. Temperature, light, and pH are common factors that affect the color stability of anthocyanins; an experiment with strawberry juice extracts analyzed all three degradation mechanisms simultaneously. Strawberry juice color was susceptible to heat treatment, pH, and exposure to sunlight. Degradation can be reduced by adjusting the pH to 3.0 and heating to 80 °C or less for 20 min [87]. Knowledge about the degradation mechanisms of anthocyanins can improve the development, preparation, and storage processes of products in the food industry since the color and bioactivity of the components influence the quality of the final product [95].

The instability of anthocyanins is related to structural changes from chemical reactions by external factors such as light, temperature, pH, and oxygen, and by interacting with other substances from pigmentation. The combination of anthocyanin molecules with the structure of clays and clay minerals can improve its stability, as this system protects it from contact with different degradation agents. Increasing the stability of these natural substances from clays and clay minerals is a promising research topic because the developed hybrids can be applied in different sectors, such as food packaging, indicators, and pigments in cosmetics or nutraceuticals.

### 3.2. Strategies for Stability of Anthocyanins Using Clays and Clay Minerals

Clays and clay minerals are presented in this work as the main anthocyanin stabilizing agent for the formation of stable hybrid pigments; several studies show its importance and advantages for the intercalation and encapsulation of natural dyes. In addition, clays and clay minerals are promising inorganic hosts due to their unique chemical and structural characteristics, non-toxicity, excellent surface area and adsorption capacity, and sustainability.

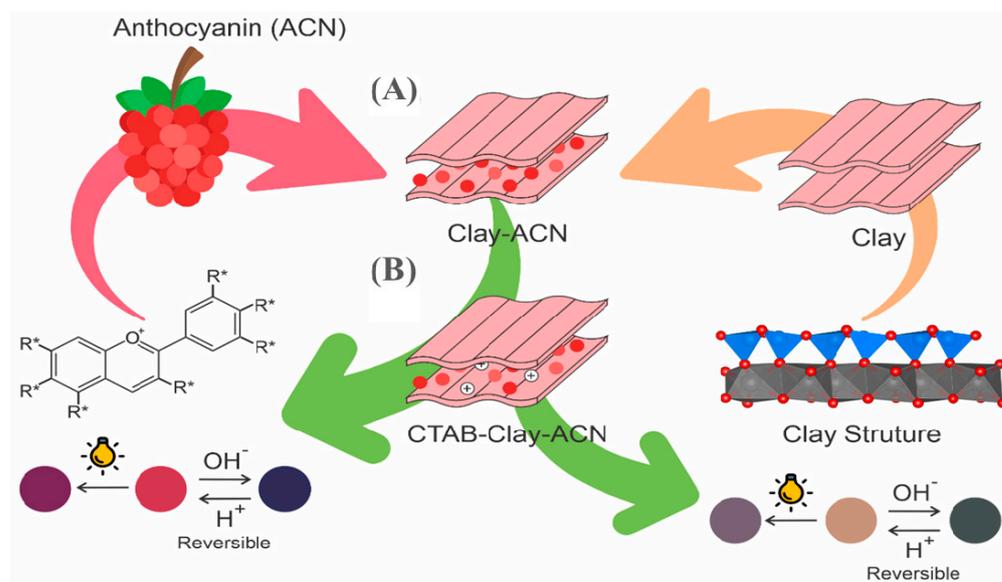
The clays used were natural bentonite and synthetic Laponite. The clay minerals tested were: smectites, halloysite, sepiolite, and palygorskite. Among the smectites in this work are natural or synthetic montmorillonite and saponite. In addition, the kaolinite group was seen in fewer published articles, emphasizing natural halloysite. Finally, with phyllosilicates with strip structure, we can highlight natural sepiolite and palygorskite.

Some reports observed the stabilizing effect of clay minerals combined with anthocyanin; this is a topic to be further explored due to the potentialities of the anthocyanin-clay mineral systems. Flow Chemical provided montmorillonite clay mineral. The presence of montmorillonite with anthocyanin extracted from clarified acerola juice at different concentrations (0%–6% by weight) showed variations in time and pH, and the uncompleted anthocyanin extracts suffered noticeable degradations. With the presence of clay mineral (especially at 4%–6% by weight), the color of the anthocyanin was unchanged, and the color was more stable in the function of time and pH [96]. The photochemical conversion of two 2-hydroxy chalcone derivatives (4'-dimethylamino-2-hydroxy chalcone and 4-methoxy-2-hydroxy chalcone) was carried out in the solid matrix by intercalation in the clay mineral layer, montmorillonite. Montmorillonite, Kunipia was supplied by Kunimine.

The addition of an acidic compound (benzenesulfonic acid) caused the color reaction of the 2-hydroxy chalcone derivatives by conversion to flavylum under UV irradiation between the intermediate layer of montmorillonite [97].

Activated sodium bentonites with different surface charge densities, supplied by Dal Cin Gildo S.P.A., Concorezzo, Italy, can provide different results regarding stabilizing labels composed of anthocyanins in white and red wines. The results demonstrated that  $0.50 \text{ g L}^{-1}$  for each bentonite label provided colloidal stabilization without severely affecting the color. Contrary to what happens in white wines, the less loaded bentonite clay labels were effective in stabilizing the colloidal state of the red wine, partially reducing its protein content [98].

Stable pigments were obtained by combining anthocyanin with different clay minerals [45–47,99–103]. Furthermore, the pigments obtained had reversibility properties under acidic and basic conditions. They improved chemical and thermal stability after interacting with the structure of the phyllosilicates. Hybrid pigments were also obtained by the interaction between saponite, supplied by the LAMS laboratory in France, with cetrimonium bromide (CTAB) and anthocyanin extracted from grape juice. The pigments exhibited different colors depending on the interactions between the components. The blue color of the resulting hybrid indicated the stabilization of the quinoid base form of the dye [104]. Figure 4 shows the organo-clay mineral as a photoprotector for anthocyanin molecules intercalated in the interlayer space.



**Figure 4.** (A) Incorporation of anthocyanin in the surfactant–clay mineral (B) Stability of anthocyanin in the surfactant–clay mineral–anthocyanin hybrid under visible light.

In another study, hybrid pigments [44] based on saponite, cetrimonium bromide (CTAB), and anthocyanin extracted from grape juice and adding  $\beta$ -cyclodextrin ( $\beta$ -CD) were synthesized. Saponite was provided at the LAMS laboratory in France. The study showed the formation of complexes between  $\beta$ -cyclodextrin ( $\beta$ -CD) and cetyltrimethylammonium bromide (CTAB), intercalated in the interlayer spaces of saponite (SAP), with the interaction of anthocyanin Crystal Red Grape (RG), resulting in the compounds: (CTAB\_SAP-RG;  $\beta$ -CD\_SAP-RG and  $\beta$ -CD + CTAB\_SAP-RG). Both studies, analyzing the behavior of anthocyanin in the presence of the inorganic matrix, showed that the hybrids had good stability against visible light irradiation and basic pH conditions. The materials are ecological and can be promising candidates in different fields of application in food engineering.

The clay minerals montmorillonite and saponite, supplied from the Tsukinuno mine, Yamagata, Japan, were also investigated in preparing natural pigments using anthocyanin extracted from purple sweet potato. The resulting biohybrid with the synthetic saponite

exhibited an evident color change between blue and pink after exposure to acidic (HCl) and basic (ammonia) vapors. The color change is similar to the solution's anthocyanin molecule due to the molecular structure change. The response to the color change was reversible within 10 min of exposure to the vapors [105]. Montmorillonite and saponite obtained from the Clay Minerals Society were analyzed as stabilizers in dyes extracted from the açai fruit, which contains mainly anthocyanins of the 3-glycosides class. The presented dye–clay mineral hybrids were incorporated into the organic material in amounts up to 24% by weight. Through spectroscopic data, they showed the presence of flavylium cations intercalated in the inorganic layers. The mass-coupled thermogravimetric analysis data showed a significant gain in the thermostability of the organic material [43].

Another study presented mica-montmorillonite as a stabilizing agent, accompanied by Laponite, in the formation of hybrid pigments produced by adsorption mediated by the exchange of flavylium cations (anthocyanin). Mica-montmorillonite (provided by IQSC-USP, São Carlos, Brazil) and Laponite were supplied from the Source Clays Repository of the Clay Minerals Society. Compared to the anthocyanin/montmorillonite hybrid, the anthocyanin/Laponite pigments exhibited improved thermal stability by color retention and better preferential adsorption of the cationic form at neutral to slightly basic pH (pH 7–8). In addition, they had less susceptibility to color changes at pH 10. Although both synthetic clays adsorbed the cationic form on their external surfaces, Laponite gave more evidence of adsorption in the interlayer regions of the clays [45].

Anthocyanin was extracted from the fresh berries of blueberries. Montmorillonite, halloysite, and sepiolite were used. Montmorillonite was sourced from Jiashan Baishiwei Biotech Co., Jiaxing, China. Halloysite was sourced from Zhengzhou Jinyanguang Ceramics Co., Ltd., Zhengzhou, China. Sepiolite was sourced from Yixian Dazhi Sepiolite Insulation Materials Co., Ltd., Baoding, China. The hybrid pigments showed good thermal stability and resistance to chemical reagents. Reversible gas-sensitive allochromic behavior was seen in HCl or NH<sub>3</sub> gases, especially the anthocyanin/sepiolite pigment. Due to the shielding effect of the sepiolite nanochannels and well-defined grooves. Based on this color change behavior, a plain pH test paper was also prepared with colors at different pH values by coating the filter paper with anthocyanin/sepiolite hybrid pigments [47]. While filtering articles using materials to protect against anthocyanin degradation and fading, many works were found to make or structurally reinforce calorimetric films and intelligent sensors. To develop a protective barrier for colorimetric films incorporated with anthocyanins, an ethylene-vinyl alcohol/montmorillonite copolymer EVOH/Mt multilayer structure was investigated. The exfoliated Mt nanosheets were well-oriented and mounted in an EVOH matrix to form a tightly stacked layer between two EVOH layers of colorimetric films embedded with anthocyanins. Montmorillonite was obtained from Fenghong Clay Chemicals Co., Ltd. Zhejiang, China. The interlayer Mt barrier significantly improved the mechanical properties of the films (below 40 layers) [106]. Acid-activated sepiolite was separated for apple juice clarification. Sepiolite was obtained from Farapooyan Isatis Yazd Co. Yazd, Iran. The sepiolite–gelatin–silica gel treatment was the most active clarifying agent, with a 99.7% reduction in apple juice turbidity [107]. In another study, montmorillonite was added as a color enhancer and stabilizer to gelatin films containing acerola juice. Montmorillonite was supplied by Flow Chemical. The films were produced with different concentrations of montmorillonite (0%–6.5% in gelatin). Increasing clay mineral content resulted in higher tensile strength and modulus, although elongation was decreased. The clay mineral also reduced water vapor permeability by up to 45%. Montmorillonite had two effects on the film's color: first, it changed its color from yellowish to red; second, it stabilized the film color throughout storage, especially when added to 3.9% [96].

It was added to montmorillonite to increase the stability of the anthocyanin extracted from *Lycium ruthenicum*. Montmorillonite was purchased from Jianping Wang-Xing Bentonite Co., Chaoyang, China. The study aimed to form an organic/inorganic hybrid pigment, and then allochromic composite films were synthesized incorporating the hybrid pigment in sodium alginate. The zeta potential demonstrated that the anthocyanin was

adsorbed on the surface and intercalated in the intermediate layer of montmorillonite via host–guest interaction. The hybrid pigments obtained allowed a good reversible acid/base behavior after exposure to HCl and NH<sub>3</sub>. Composite films containing hybrid pigments showed good mechanical properties due to the uniform dispersion of pigments in a sodium alginate substrate and the formation of hydrogen bonds between them. Hybrid pigments prepared in composite films serve as a reinforcing material and an intelligent coloring agent for a polymeric substrate [108].

The formulation of anthocyanin with cation-based clay minerals was observed to produce new natural health products. Clay mineral mixtures were obtained in the Sierra Mountains, USA. The study compared the fact that the total antioxidant capacity of sour cherry extract using the oxygen radical scavenging capacity assay increased almost twice after digestion. There was no significant difference between anthocyanin recovery when they presented the clay mineral formulation about the control. Hence, cationic-based clay mineral is not a factor in reducing anthocyanins' bioaccessibility or increasing the antioxidant capacity [109].

Anthocyanins stabilized by clays or clay minerals have provided an efficient alternative in the manufacture of intelligent, active packaging, some to prolong the shelf life of the food, others improving properties or inhibiting microorganisms [110–115]. One of these works studied the structural, morphological, thermal, optical, hygroscopic, mechanical properties, and pH sensitivity of films based on anthocyanin molecules from red cabbage and sepiolite as functional additives [110].

Another study presents anthocyanin (ACY) functionalized layer double hydroxides (HDLs@ACY-Cu). The milk spoilage test indicated that active multilayer films could inhibit rapid bacterial reproduction in pasteurized milk and extend the shelf life of the milk. Therefore, active multilayer films show good potential for applications in active food packaging [111]. Anthocyanins extracted from Jamaican flowers (*Hibiscus sabdariffa*) and montmorillonite (Mt) as active and pH-sensitive nanofillers for use in intelligent packaging have also been investigated. The montmorillonites were supplied by Laviosa Chimica Mineraria S.P.A. Livorno, Italy [112,113]. Organo-modified montmorillonite is an efficient antioxidant nano-packaging system compared to natural montmorillonite packages and polymeric anthocyanins. However, due to their toxicity, these nano-packaging systems based on organo-modified Mt and polymeric anthocyanin stabilizers are limited for food applications [112]. The thermal and mechanical properties of the obtained bio-nanocomposite films were improved due to the addition of modified clay mineral nanofillers and the nano-packing of anthocyanins between the montmorillonite clay mineral layers [113].

Chitosan/PVA films containing black carrot anthocyanins as a natural pH indicator and bentonite as a nanofiller show better thermal stability, inhibition of bacterial growth, and improved mechanical properties. Bentonite clay was purchased from the eastern mines in Iran [114]. Edible films and nanocomposites were developed using pure blueberry extract (BE) and modified montmorillonites (Mt). Materials containing nanofillers with a higher degree of interlamellar spacing showed higher thermal resistance and Young's modulus but lower stress values at rupture. However, none of the formulated films were sensitive to pH. The Montmorillonites were supplied by Laviosa Chimica Mineraria S.P.A. Livorno, Italy [115].

Available alternatives for stabilizing natural pigments are research targets, and their stabilization mechanisms are discussed in the literature. Among the numerous strategies included are the addition of co-pigment compounds, formation of supramolecular complexes, encapsulation systems, shielding protection of nanocarriers, intercalation, and/or adsorption on solid surfaces and/or in confined spaces [38,45].

Constantino et al. [43] reported interactions between the adsorption of dyes on clay minerals when evaluating the increase in anthocyanin stability from immobilization on different clay minerals; for example, smectites, montmorillonite, and saponite. According to the nature of the dye charges and basal spacing of the clay minerals, the dyes can adopt different arrangements, either in the parallel or perpendicular position favored by  $\pi$ - $\pi$  inter-

actions between adjacent species [43]. The XRD data confirm the possibilities of orientation concerning the layers. This shows the relevance of the intercalation through the change of the interlamellar spacing. The swelling of the clay minerals, the nature of the interlamellar cations, and the surface area of the hybrid samples must be respected to evaluate the main determining points in the kinetic process. Electron paramagnetic resonance (EPR) analyses show that radicals must combine anthocyanins between clay minerals layers for the reaction to occur. However, the materials retain the radical scavenging activity of the extract, with the anthocyanins being accessible by radicals even if they are immobilized between clay mineral layers.

Quina et al. [45] present the properties of hybrid pigments produced from substituted flavilium cations and two distinct lamellar materials: a Laponite (Laponite RD, SYnL-1) and a mica-montmorillonite (Barasym SSM-100, SYn-1). Clays showed stability adsorbing in the cationic form on their external surfaces, with SYnL-1 being more evident in the adsorption in the intermediate regions of the clays. In comparative terms with the FL/SYn-1 hybrids, the FL/SYnL-1 pigments showed stability through observations of properties, such as color retention, preferential adsorption in the cationic form of FL1 at neutral to slightly basic pH (pH 7–8), and less sensitivity to color changes at basic pH (pH 10). The adsorption between layers and the influence of pH contributed to the best properties of the FL/SYnL-1 hybrids. Laponite is a promising inorganic class for producing new hybrid pigments with vibrant colors that are thermally more stable. Silva et al. [102] evaluated hybrid pigments based on flavilium cations adsorbed on palygorskite, which had photochemical stability in the cationic form improved by adsorption on clay mineral.

Therefore, considering intercalation research in clay minerals layers, one of the main advantages of its application is the shielding of sensitive molecules against degradation [43]. By intercalation, saponite–anthocyanin hybrids were synthesized by Brandão et al. [44] and Ogawa et al. [105]. They possessed stability against visible light and essential pH conditions after adding synthetic saponite [38]. Castro Silva et al. [116] published a study on the stability of hectorite-based materials modified by cetyltrimethylammonium and pectin to produce organo-hectorites. Similarly Guillermin et al. [57] developed organo-montmorillonites-based hybrid pigments. The main reason for the stability of the dyes is explained by mechanisms of interactions favored by electrostatic forces, van der Waals forces, and/or hydrogen bonds.

Currently, the interest in techniques that increase the stability and bioavailability of anthocyanins continues to grow [14,38,90,108,117,118], as the consumer population has been more demanding in terms of the consumption of food and cosmetic products enriched with vitamins, minerals, and antioxidants.

### 3.3. The Importance of the Increase in Stability

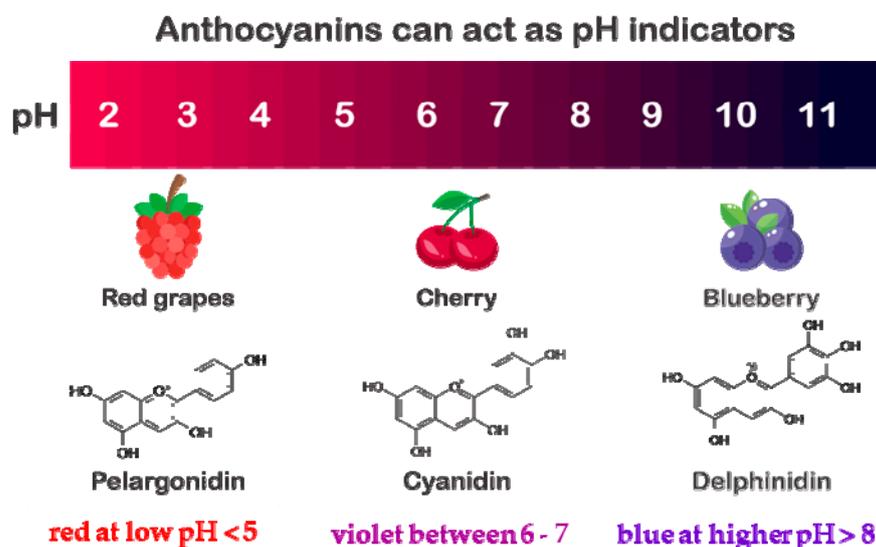
The increased consumption of natural colorants in place of synthetic and mineral dyes, mainly by the food and cosmetic industry, has increased due to their health benefits. In addition, the trend of biological applications of natural compounds has aroused great interest due to their therapeutic effects.

The colors obtained under different pH conditions favor these compounds in food engineering [119]. Figure 5 shows the change in colors and molecular structure of anthocyanins as a function of the pH of the medium.

Several medical and biological applications can be attributed to the properties of anthocyanins [120]. First, the absorption capacity in the UV region is responsible for the photoprotection effect on retinal cells.

The antioxidant, cytoprotective, and antiangiogenic effects of anthocyanins were investigated for these dyes' potential biotechnological and pharmaceutical applications [121]. The different tests showed an excellent nutraceutical potential of these compounds with an active role in health benefits. In addition, inhibitory potential against cancer cells was investigated for anthocyanin, anthocyanidin, and proanthocyanidin. In their studies [122], from the cell viability and morphological analysis results, the authors observed anticancer

activity and DNA fragmentation in HeLa cells, showing the great potential for biological and medical applications of anthocyanins and their derivatives.



**Figure 5.** Impact on the coloration of anthocyanins derivatives at different pH.

Clay minerals have increasingly attracted attention for the loading and incorporation of natural dyes. Clay minerals are abundant on earth and have been recognized as promising inorganic carriers for improving the stability of many natural dyes due to unique structures, low cost, non-toxicity, high specific surface area, surface chemistry, and excellent adsorption properties. Different clay minerals showed different morphologies, structures, chemical compositions, and properties depending on the arrangement of silica-oxygen tetrahedra and metal-oxygen octahedra [47,123,124], which resulted in different encapsulation effects for cationic and anionic dyes. Furthermore, they can be modified and reshaped by physical and chemical techniques to change their charge and surface properties to improve the loading capacity of target dyes [50,125,126]. Therefore, clay minerals can be highlighted as promising inorganic supports for forming stable pigments that can be applied—replacing artificial dyes—in the coloring of a range of products. Effectively, developing biocompatible materials for stabilizing natural dyes is of growing interest for clinical and technological applications. In addition, in-depth research on the structure and function of dye/clay mineral hybrids is needed to ensure safety for in vivo use of these materials in cosmetic or pharmaceutical products [127].

#### 4. Final Considerations

Systematic research has indicated the growing interest in anthocyanins stabilized by clays and clay minerals, mainly due to the development of products based on natural compounds and their beneficial health effects. In the works presented, it is possible to observe satisfactory results with the interaction of anthocyanin and several types of clays or clay minerals, which provides more excellent options of compounds for the formation of hybrid dyes. Furthermore, in the food industry, the stability of anthocyanins has been studied for improvement during the processing and storage of the product. In the cosmetic industry, there are concerns regarding the exposure of the applied products to temperature and light. However, it can be observed that several parameters are essential for understanding the degradation mechanisms of these natural dyes. Thus, developing materials and techniques to increase the stability of anthocyanin systems becomes challenging, where clays and clay minerals are attractive to improve the thermal and photostability of these dyes. In addition, anthocyanins have interesting properties as bioactive agents in biological and biotechnological processes, expanding the perspective of innovation in research and application.

**Author Contributions:** R.C.: methodology and writing—original draft; P.T.: conceptualization, writing—review and editing; T.M.D. methodology; L.M.d.C.H.: methodology; D.H.L.D.: writing—review; M.G.F.: supervision; S.M.-C.: writing—review; M.d.M.O.C.: writing—review; E.C.d.S.-F.: writing—review; J.A.O.: supervision, project administration, and writing—review and editing. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by CAPES and CNPq Fellowship.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The authors thank UFPI and IFPI.

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

## References

1. Sinopoli, A.; Calogero, G.; Bartolotta, A. Computational Aspects of Anthocyanidins and Anthocyanins: A Review. *Food Chem.* **2019**, *297*, 124898. [[CrossRef](#)] [[PubMed](#)]
2. Šamec, D.; Karalija, E.; Šola, I.; Vujčić Bok, V.; Salopek-Sondi, B. The Role of Polyphenols in Abiotic Stress Response: The Influence of Molecular Structure. *Plants* **2021**, *10*, 118. [[CrossRef](#)] [[PubMed](#)]
3. Brooks, M.S.-L.; Celli, G.B. (Eds.) *Anthocyanins from Natural Sources: Exploiting Targeted Delivery for Improved Health*; Royal Society of Chemistry: London, UK, 2019.
4. Fernandes, A.; Brás, N.F.; Mateus, N.; De Freitas, V. A Study of Anthocyanin Self-Association by NMR Spectroscopy. *New J. Chem.* **2015**, *39*, 2602–2611. [[CrossRef](#)]
5. Wallace, T.C.; Giusti, M.M. Anthocyanins—Nature’s Bold, Beautiful, and Health-Promoting Colors. *Foods* **2019**, *8*, 550. [[CrossRef](#)] [[PubMed](#)]
6. Perez, M.B.; Da Peña Hamparsomian, M.J.; Gonzalez, R.E.; Denoya, G.I.; Dominguez, D.L.E.; Barboza, K.; Iorizzo, M.; Simon, P.W.; Vaudagna, S.R.; Cavagnaro, P.F. Physicochemical Properties, Degradation Kinetics, and Antioxidant Capacity of Aqueous Anthocyanin-Based Extracts from Purple Carrots Compared to Synthetic and Natural Food Colorants. *Food Chem.* **2022**, *387*, 132893. [[CrossRef](#)] [[PubMed](#)]
7. Kong, J.-M.; Chia, L.-S.; Goh, N.-K.; Chia, T.-F.; Brouillard, R. Analysis and Biological Activities of Anthocyanins. *Phytochemistry* **2003**, *64*, 923–933. [[CrossRef](#)] [[PubMed](#)]
8. De Araújo, F.F.; de Paulo Farias, D.; Neri-Numa, I.A.; Pastore, G.M. Polyphenols and Their Applications: An Approach in Food Chemistry and Innovation Potential. *Food Chem.* **2021**, *338*, 127535. [[CrossRef](#)] [[PubMed](#)]
9. Basu, A.; Rhone, M.; Lyons, T.J. Berries: Emerging Impact on Cardiovascular Health. *Nutr. Rev.* **2010**, *68*, 168–177. [[CrossRef](#)] [[PubMed](#)]
10. Dohadwala, M.M.; Holbrook, M.; Hamburg, N.M.; Shenouda, S.M.; Chung, W.B.; Titas, M.; Kluge, M.A.; Wang, N.; Palmisano, J.; Milbury, P.E.; et al. Effects of Cranberry Juice Consumption on Vascular Function in Patients with Coronary Artery Disease. *Am. J. Clin. Nutr.* **2011**, *93*, 934–940. [[CrossRef](#)] [[PubMed](#)]
11. Agregán, R.; Munekata, P.E.S.; Feng, X.; Astray, G.; Gullón, B.; Lorenzo, J.M. Recent Advances in the Extraction of Polyphenols from Eggplant and Their Application in Foods. *LWT* **2021**, *146*, 111381. [[CrossRef](#)]
12. Liu, J.; Tan, Y.; Zhou, H.; Muriel Mundo, J.L.; McClements, D.J. Protection of Anthocyanin-Rich Extract from PH-Induced Color Changes Using Water-in-Oil-in-Water Emulsions. *J. Food Eng.* **2019**, *254*, 1–9. [[CrossRef](#)]
13. Liu, J.; Zhou, H.; Song, L.; Yang, Z.; Qiu, M.; Wang, J.; Shi, S. Anthocyanins: Promising Natural Products with Diverse Pharmacological Activities. *Molecules* **2021**, *26*, 3807. [[CrossRef](#)] [[PubMed](#)]
14. Alappat, B.; Alappat, J. Anthocyanin Pigments: Beyond Aesthetics. *Molecules* **2020**, *25*, 5500. [[CrossRef](#)]
15. Denish, P.R.; Fenger, J.A.; Powers, R.; Sigurdson, G.T.; Grisanti, L.; Guggenheim, K.G.; Laporte, S.; Li, J.; Kondo, T.; Magistrato, A.; et al. Discovery of a Natural Cyan Blue: A Unique Food-Sourced Anthocyanin Could Replace Synthetic Brilliant Blue. *Sci. Adv.* **2021**, *7*, eabe7871. [[CrossRef](#)] [[PubMed](#)]
16. Torres Vargas, O.L.; Galeano Loaiza, Y.V.; González, M.L. Effect of Incorporating Extracts from Natural Pigments in Alginate/Starch Films. *J. Mater. Res. Technol.* **2021**, *13*, 2239–2250. [[CrossRef](#)]
17. Zhu, Y.; Ling, W.; Guo, H.; Song, F.; Ye, Q.; Zou, T.; Li, D.; Zhang, Y.; Li, G.; Xiao, Y.; et al. Anti-Inflammatory Effect of Purified Dietary Anthocyanin in Adults with Hypercholesterolemia: A Randomized Controlled Trial. *Nutr. Metab. Cardiovasc. Dis.* **2013**, *23*, 843–849. [[CrossRef](#)] [[PubMed](#)]
18. Sun, X.; Zhou, T.; Wei, C.; Lan, W.; Zhao, Y.; Pan, Y.; Wu, V.C.H. Antibacterial Effect and Mechanism of Anthocyanin Rich Chinese Wild Blueberry Extract on Various Foodborne Pathogens. *Food Control* **2018**, *94*, 155–161. [[CrossRef](#)]
19. Hui, C.; Bin, Y.; Xiaoping, Y.; Long, Y.; Chunye, C.; Mantian, M.; Wenhua, L. Anticancer Activities of an Anthocyanin-Rich Extract from Black Rice against Breast Cancer Cells in Vitro and in Vivo. *Nutr. Cancer* **2010**, *62*, 1128–1136. [[CrossRef](#)] [[PubMed](#)]
20. Nomi, Y.; Iwasaki-Kurashige, K.; Matsumoto, H. Therapeutic Effects of Anthocyanins for Vision and Eye Health. *Molecules* **2019**, *24*, 3311. [[CrossRef](#)]
21. Cassidy, A. Berry Anthocyanin Intake and Cardiovascular Health. *Mol. Asp. Med.* **2018**, *61*, 76–82. [[CrossRef](#)] [[PubMed](#)]

22. Welch, C.R.; Wu, Q.; Simon, J.E. Recent Advances in Anthocyanin Analysis and Characterization. *Curr. Anal. Chem.* **2008**, *4*, 75–101. [[CrossRef](#)] [[PubMed](#)]
23. Mazza, G.; Kay, C.D. *Bioactivity, Absorption and Metabolism of Anthocyanins*; Daayf, F., Lattanzio, V., Eds.; John Wiley: Blackwell, UK, 2009; ISBN 1444302418.
24. de Pascual-Teresa, S.; Moreno, D.A.; García-Viguera, C. Flavanols and Anthocyanins in Cardiovascular Health: A Review of Current Evidence. *Int. J. Mol. Sci.* **2010**, *11*, 1679–1703. [[CrossRef](#)] [[PubMed](#)]
25. Seeram, N.P.; Momin, R.A.; Nair, M.G.; Bourquin, L.D. Cyclooxygenase Inhibitory and Antioxidant Cyanidin Glycosides in Cherries and Berries. *Phytomedicine* **2001**, *8*, 362–369. [[CrossRef](#)] [[PubMed](#)]
26. Miguel, M.G. Anthocyanins: Antioxidant and/or Anti-Inflammatory Activities. *J. Appl. Pharm. Sci.* **2011**, *1*, 7–15.
27. Bakowska-Barczak, A. Acylated Anthocyanins as Stable, Natural Food Colorants : A Review. *Polish J. Food Nutr. Sci.* **2005**, *14*, 107–116.
28. Barnard, H.; Dooley, A.N.; Areshian, G.; Gasparyan, B.; Faull, K.F. Chemical Evidence for Wine Production around 4000 BCE in the Late Chalcolithic Near Eastern Highlands. *J. Archaeol. Sci.* **2011**, *38*, 977–984. [[CrossRef](#)]
29. Cevallos-Casals, B.A.; Cisneros-Zevallos, L. Stoichiometric and Kinetic Studies of Phenolic Antioxidants from Andean Purple Corn and Red-Fleshed Sweetpotato. *J. Agric. Food Chem.* **2003**, *51*, 3313–3319. [[CrossRef](#)]
30. Robinson, G.M.; Robinson, R. A Survey of Anthocyanins. II. *Biochem. J.* **1932**, *26*, 1647–1664. [[CrossRef](#)]
31. Jaakola, L. New Insights into the Regulation of Anthocyanin Biosynthesis in Fruits. *Trends Plant Sci.* **2013**, *18*, 477–483. [[CrossRef](#)]
32. Katsumoto, Y.; Fukuchi-Mizutani, M.; Fukui, Y.; Brugliera, F.; Holton, T.A.; Karan, M.; Nakamura, N.; Yonekura-Sakakibara, K.; Togami, J.; Pigeaire, A.; et al. Engineering of the Rose Flavonoid Biosynthetic Pathway Successfully Generated Blue-Hued Flowers Accumulating Delphinidin. *Plant Cell Physiol.* **2007**, *48*, 1589–1600. [[CrossRef](#)]
33. Mazza, G. Anthocyanins in Grapes and Grape Products. *Crit. Rev. Food Sci. Nutr.* **1995**, *35*, 341–371. [[CrossRef](#)]
34. Slimestad, R.; Solheim, H. Anthocyanins from Black Currants (*Ribes nigrum* L.). *J. Agric. Food Chem.* **2002**, *50*, 3228–3231. [[CrossRef](#)] [[PubMed](#)]
35. Tanaka, Y.; Tsuda, S.; Kusumi, T. Metabolic Engineering to Modify Flower Color. *Plant Cell Physiol.* **1998**, *39*, 1119–1126. [[CrossRef](#)]
36. Yabuya, T.; Nakamura, M.; Iwashina, T.; Yamaguchi, M.; Takehara, T. Anthocyanin-Flavone Copigmentation in Bluish Purple Flowers of Japanese Garden Iris (*Iris ensata* Thunb.). *Euphytica* **1997**, *98*, 163–167. [[CrossRef](#)]
37. Kiumarsi, A.; Parvinzadeh Gashti, M.; Salehi, P.; Dayeni, M. Extraction of Dyes from Delphinium Zalil Flowers and Dyeing Silk Yarns. *J. Text. Inst.* **2017**, *108*, 66–70. [[CrossRef](#)]
38. Li, S.; Mu, B.; Wang, X.; Wang, A. Recent Researches on Natural Pigments Stabilized by Clay Minerals: A Review. *Dyes Pigments* **2021**, *190*, 109322. [[CrossRef](#)]
39. Cao, S.; Liu, L.; Lu, Q.; Xu, Y.; Pan, S.; Wang, K. Integrated Effects of Ascorbic Acid, Flavonoids and Sugars on Thermal Degradation of Anthocyanins in Blood Orange Juice. *Eur. Food Res. Technol.* **2009**, *228*, 975–983. [[CrossRef](#)]
40. Hubbermann, E.M.; Heins, A.; Stöckmann, H.; Schwarz, K. Influence of Acids, Salt, Sugars and Hydrocolloids on the Colour Stability of Anthocyanin Rich Black Currant and Elderberry Concentrates. *Eur. Food Res. Technol.* **2006**, *223*, 83–90. [[CrossRef](#)]
41. Buchweitz, M.; Speth, M.; Kammerer, D.R.; Carle, R. Stabilisation of Strawberry (*Fragaria × Ananassa* Duch.) Anthocyanins by Different Pectins. *Food Chem.* **2013**, *141*, 2998–3006. [[CrossRef](#)]
42. Buchweitz, M.; Speth, M.; Kammerer, D.R.; Carle, R. Impact of Pectin Type on the Storage Stability of Black Currant (*Ribes nigrum* L.) Anthocyanins in Pectic Model Solutions. *Food Chem.* **2013**, *139*, 1168–1178. [[CrossRef](#)]
43. Teixeira-Neto, Â.A.; Izumi, C.M.S.; Temperini, M.L.A.; Ferreira, A.M.D.C.; Constantino, V.R.L. Hybrid Materials Based on Smectite Clays and Nutraceutical Anthocyanins from the Açai Fruit. *Eur. J. Inorg. Chem.* **2012**, *32*, 5411–5420. [[CrossRef](#)]
44. Brandão Lima, L.C.; Castro-Silva, F.; Silva-Filho, E.C.; Fonseca, M.G.; Jaber, M. Saponite-Anthocyanin Pigments: Slipping between the Sheets. *Microporous Mesoporous Mater.* **2020**, *300*, 110148. [[CrossRef](#)]
45. Silva, G.T.M.; Silva, K.M.; Silva, C.P.; Gonçalves, J.M.; Quina, F.H. Hybrid Pigments from Anthocyanin Analogues and Synthetic Clay Minerals. *ACS Omega* **2020**, *5*, 26592–26600. [[CrossRef](#)]
46. Silva, G.T.M.T.M.; Da Silva, K.M.M.; Silva, C.P.P.; Rodrigues, A.C.B.C.B.; Oake, J.; Gehlen, M.H.H.; Bohne, C.; Quina, F.H.H. Highly Fluorescent Hybrid Pigments from Anthocyanin- and Red Wine Pyranoanthocyanin-Analogs Adsorbed on Sepiolite Clay. *Photochem. Photobiol. Sci.* **2019**, *18*, 1750–1760. [[CrossRef](#)]
47. Li, S.; Mu, B.; Wang, X.; Kang, Y.; Wang, A. A Comparative Study on Color Stability of Anthocyanin Hybrid Pigments Derived from 1D and 2D Clay Minerals. *Materials* **2019**, *12*, 3287. [[CrossRef](#)]
48. Kohno, Y.; Kinoshita, R.; Ikoma, S.; Yoda, K.; Shibata, M.; Matsushima, R.; Tomita, Y.; Maeda, Y.; Kobayashi, K. Stabilization of Natural Anthocyanin by Intercalation into Montmorillonite. *Appl. Clay Sci.* **2009**, *42*, 519–523. [[CrossRef](#)]
49. Bergaya, F.; Jaber, M.; Lambert, J. Clays and Clay Minerals. In *Rubber-Clay Nanocomposites*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2011; pp. 1–44.
50. Bergaya, F.; Lagaly, G. *General Introduction: Clays, Clay Minerals, and Clay Science*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 2013; Volume 5, ISBN 9780080982588.
51. Tournassat, C.; Bourg, I.C.; Steefel, C.I.; Bergaya, F. Surface Properties of Clay Minerals. In *Developments in Clay Science*; Elsevier: Amsterdam, The Netherlands, 2015; Volume 6, pp. 5–31, ISBN 9780081000274.
52. Brigatti, M.F.; Galán, E.; Theng, B.K.G. Structure and Mineralogy of Clay Minerals. In *Developments in Clay Science*; Elsevier: Amsterdam, The Netherlands, 2013; Volume 5, pp. 21–81, ISBN 9780080982588.

53. Schoonheydt, R.A.; Johnston, C.T.; Bergaya, F. Clay Minerals and Their Surfaces. In *Developments in Clay Science*; Elsevier: Amsterdam, The Netherlands, 2018; Volume 9, pp. 1–21, ISBN 9780081024324.
54. Lagaly, G.; Ogawa, M.; Dékány, I. Clay Mineral–Organic Interactions. In *Developments in Clay Science*; Elsevier: Amsterdam, The Netherlands, 2013; Volume 5, ISBN 9780080982588.
55. Cavalcanti, G.R.S.; Souprayan, C.; Guillermin, D.; Rodrigues, F.; Fonseca, M.G.; Jaber, M. Designing Photochromatic Pigments Based on Clay Minerals and Spiropyran. *Dyes Pigments* **2022**, *204*, 110358. [[CrossRef](#)]
56. Fournier, F.; de Viguierie, L.; Balme, S.; Janot, J.M.; Walter, P.; Jaber, M. Physico-Chemical Characterization of Lake Pigments Based on Montmorillonite and Carminic Acid. *Appl. Clay Sci.* **2016**, *130*, 12–17. [[CrossRef](#)]
57. Guillermin, D.; Debroise, T.; Trigueiro, P.; de Viguierie, L.; Rigaud, B.; Morlet-Savary, F.; Balme, S.; Janot, J.-M.; Tielens, F.; Michot, L.; et al. New Pigments Based on Carminic Acid and Smectites: A Molecular Investigation. *Dyes Pigments* **2019**, *160*, 971–982. [[CrossRef](#)]
58. Alcântara, A.C.S.; Darder, M.; Aranda, P.; Ruiz-Hitzky, E. Effective Intercalation of Zein into Na-Montmorillonite: Role of the Protein Components and Use of the Developed Biointerfaces. *Beilstein J. Nanotechnol.* **2016**, *7*, 1772–1782. [[CrossRef](#)]
59. Kohno, Y.; Kato, Y.; Shibata, M.; Fukuhara, C.; Maeda, Y.; Tomita, Y.; Kobayashi, K. Fixation and Stability Enhancement of Beta-Carotene by Organo-Modified Mesoporous Silica. *Microporous Mesoporous Mater.* **2016**, *220*, 1–6. [[CrossRef](#)]
60. Santos, S.S.G.; França, D.B.; Castellano, L.R.C.; Trigueiro, P.; Silva Filho, E.C.; Santos, I.M.G.; Fonseca, M.G. Novel Modified Bentonites Applied to the Removal of an Anionic Azo-Dye from Aqueous Solution. *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, *585*, 124152. [[CrossRef](#)]
61. da Silva, J.C.S.S.; França, D.B.; Rodrigues, F.; Oliveira, D.M.; Trigueiro, P.; Silva Filho, E.C.; Fonseca, M.G. What Happens When Chitosan Meets Bentonite under Microwave-Assisted Conditions? Clay-Based Hybrid Nanocomposites for Dye Adsorption. *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, *609*, 125584. [[CrossRef](#)]
62. da Rocha, M.C.; Galdino, T.; Trigueiro, P.; Honorio, L.M.C.; de Melo Barbosa, R.; Carrasco, S.M.; Silva-Filho, E.C.; Osajima, J.A.; Viseras, C. Clays as Vehicles for Drug Photostability. *Pharmaceutics* **2022**, *14*, 796. [[CrossRef](#)] [[PubMed](#)]
63. Lu, Y.; Dong, W.; Wang, W.; Wang, Q.; Hui, A.; Wang, A. A Comparative Study of Different Natural Palygorskite Clays for Fabricating Cost-Efficient and Eco-Friendly Iron Red Composite Pigments. *Appl. Clay Sci.* **2019**, *167*, 50–59. [[CrossRef](#)]
64. Ghadiri, M.; Chrzanowski, W.; Rohanzadeh, R. Biomedical Applications of Cationic Clay Minerals. *RSC Adv.* **2015**, *5*, 29467–29481. [[CrossRef](#)]
65. Rautureau, M.; Figueiredo Gomes, C.D.S.; Liewig, N.; Katouzian-Safadi, M.; Rautureau, M.; Figueiredo Gomes, C.D.S.; Liewig, N.; Katouzian-Safadi, M. Clay Reactivity Depending Upon the Crystallochemical Properties of Clay Minerals. *Clays Health Prop. Ther. Uses* **2017**, *2017*, 63–94.
66. Trigueiro, P.; Rodrigues, F.; Rigaud, B.; Balme, S.; Janot, J.-M.; dos Santos, I.M.G.; Fonseca, M.G.; Osajima, J.; Walter, P.; Jaber, M.; et al. When Anthraquinone Dyes Meet Pillared Montmorillonite: Stability or Fading upon Exposure to Light? *Dyes Pigments* **2018**, *159*, 384–394. [[CrossRef](#)]
67. Cavalcanti, G.R.S.; Rodrigues, F.; Zhuang, G.; Balme, S.; Janot, J.-M.; Fonseca, M.G.; Jaber, M. Inorganic–Organic Hybrid Pigments Based on Carminic Acid and Clay Minerals. *Dyes Pigments* **2021**, *190*, 109306. [[CrossRef](#)]
68. Chuaicham, C.; Sekar, K.; Balakumar, V.; Uchida, J.; Katsurao, T.; Sakabe, H.; Ohtani, B.; Sasaki, K. Efficient Photocatalytic Degradation of Emerging Ciprofloxacin under Visible Light Irradiation Using BiOBr/Carbon Quantum Dot/Saponite Composite. *Environ. Res.* **2022**, *212*, 113635. [[CrossRef](#)]
69. Fatimah, I.; Nurillahi, R.; Sahroni, I.; Muraza, O. TiO<sub>2</sub>-Pillared Saponite and Photosensitization Using a Ruthenium Complex for Photocatalytic Enhancement of the Photodegradation of Bromophenol Blue. *Appl. Clay Sci.* **2019**, *183*, 105302. [[CrossRef](#)]
70. Dlamini, M.C.; Maubane-Nkadimeng, M.S.; Moma, J.A. The Use of TiO<sub>2</sub>/Clay Heterostructures in the Photocatalytic Remediation of Water Containing Organic Pollutants: A Review. *J. Environ. Chem. Eng.* **2021**, *9*, 106546. [[CrossRef](#)]
71. Heidari, A.; Shahbazi, A.; Aminabhavi, T.M.; Barceló, D.; Rtimi, S. A Systematic Review of Clay-Based Photocatalysts for Emergent Micropollutants Removal and Microbial Inactivation from Aqueous Media: Status and Limitations. *J. Environ. Chem. Eng.* **2022**, *10*, 108813. [[CrossRef](#)]
72. Lalevée, J.; Morlet-Savary, F.; Dietlin, C.; Graff, B.; Fouassier, J.P. Photochemistry and Radical Chemistry under Low Intensity Visible Light Sources: Application to Photopolymerization Reactions. *Molecules* **2014**, *19*, 15026–15041. [[CrossRef](#)] [[PubMed](#)]
73. Zyoud, A.H.; Asaad, S.; Zyoud, S.H.; Zyoud, S.H.; Helal, M.H.; Qamhieh, N.; Hajamohideen, A.; Hilal, H.S. Raw Clay Supported ZnO Nanoparticles in Photodegradation of 2-Chlorophenol under Direct Solar Radiations. *J. Environ. Chem. Eng.* **2020**, *8*, 104227. [[CrossRef](#)]
74. Chung, C.; Rojanasasithara, T.; Mutilangi, W.; McClements, D.J. Stability Improvement of Natural Food Colors: Impact of Amino Acid and Peptide Addition on Anthocyanin Stability in Model Beverages. *Food Chem.* **2017**, *218*, 277–284. [[CrossRef](#)] [[PubMed](#)]
75. Chung, C.; Rojanasasithara, T.; Mutilangi, W.; McClements, D.J. Stabilization of Natural Colors and Nutraceuticals: Inhibition of Anthocyanin Degradation in Model Beverages Using Polyphenols. *Food Chem.* **2016**, *212*, 596–603. [[CrossRef](#)] [[PubMed](#)]
76. Chung, C.; Rojanasasithara, T.; Mutilangi, W.; McClements, D.J. Enhanced Stability of Anthocyanin-Based Color in Model Beverage Systems through Whey Protein Isolate Complexation. *Food Res. Int.* **2015**, *76*, 761–768. [[CrossRef](#)] [[PubMed](#)]
77. Gérard, V.; Ay, E.; Graff, B.; Morlet-Savary, F.; Galopin, C.; Mutilangi, W.; Lalevée, J. Ascorbic Acid Derivatives as Potential Substitutes for Ascorbic Acid to Reduce Color Degradation of Drinks Containing Ascorbic Acid and Anthocyanins from Natural Extracts. *J. Agric. Food Chem.* **2019**, *67*, 12061–12071. [[CrossRef](#)]

78. Li, X.; Tang, D.; Du, H.; Shi, Y. Transcriptome Sequencing and Biochemical Analysis of Perianths and Coronas Reveal Flower Color Formation in *Narcissus Pseudonarcissus*. *Int. J. Mol. Sci.* **2018**, *19*, 4006. [[CrossRef](#)]
79. Zhang, Q.; Wang, L.; Liu, Z.; Zhao, Z.; Zhao, J.; Wang, Z.; Zhou, G.; Liu, P.; Liu, M. Transcriptome and Metabolome Profiling Unveil the Mechanisms of *Ziziphus jujuba* Mill. Peel Coloration. *Food Chem.* **2020**, *312*, 125903. [[CrossRef](#)] [[PubMed](#)]
80. Khunmuang, S.; Kanlayanarat, S.; Wongs-Aree, C.; Meir, S.; Philosoph-Hadas, S.; Oren-Shamir, M.; Ovadia, R.; Buanong, M. Ethylene Induces a Rapid Degradation of Petal Anthocyanins in Cut Vanda ‘Sansai Blue’ Orchid Flowers. *Front. Plant Sci.* **2019**, *10*, 1004. [[CrossRef](#)] [[PubMed](#)]
81. Nhut Pham, T.; Quoc Toan, T.; Duc Lam, T.; Vu-Quang, H.; Vo, D.V.N.; Anh Vy, T.; Bui, L.M. Anthocyanins Extraction from Purple Sweet Potato (*Ipomoea batatas* (L.) Lam): The Effect of PH Values on Natural Color. *IOP Conf. Ser. Mater. Sci. Eng.* **2019**, *542*, 012031. [[CrossRef](#)]
82. Coelho, M.; Silva, S.; Costa, E.; Pereira, R.N.; Rodrigues, A.S.; Teixeira, J.A.; Pintado, M. Anthocyanin Recovery from Grape By-Products by Combining Ohmic Heating with Food-Grade Solvents: Phenolic Composition, Antioxidant, and Antimicrobial Properties. *Molecules* **2021**, *26*, 3838. [[CrossRef](#)]
83. Esteves, L.C.; Pinheiro, A.C.; Pioli, R.M.; Penna, T.C.; Baader, W.J.; Correra, T.C.; Bastos, E.L. Revisiting the Mechanism of Hydrolysis of Betanin. *Photochem. Photobiol.* **2018**, *94*, 853–864. [[CrossRef](#)] [[PubMed](#)]
84. He, Z.; Zhu, H.; Xu, M.; Zeng, M.; Qin, F.; Chen, J. Complexation of Bovine  $\beta$ -Lactoglobulin with Malvidin-3-O-Glucoside and Its Effect on the Stability of Grape Skin Anthocyanin Extracts. *Food Chem.* **2016**, *209*, 234–240. [[CrossRef](#)]
85. Qian, B.-J.; Liu, J.-H.; Zhao, S.-J.; Cai, J.-X.; Jing, P. The Effects of Gallic/Ferulic/Caffeic Acids on Colour Intensification and Anthocyanin Stability. *Food Chem.* **2017**, *228*, 526–532. [[CrossRef](#)]
86. Rehman, R.N.U.; You, Y.; Yang, C.; Khan, A.R.; Li, P.; Ma, F. Characterization of Phenolic Compounds and Active Anthocyanin Degradation in Crabapple (*Malus orientalis*) Flowers. *Hortic. Environ. Biotechnol.* **2017**, *58*, 324–333. [[CrossRef](#)]
87. Wang, Z.; Zhang, M.; Wu, Q. Effects of Temperature, PH, and Sunlight Exposure on the Color Stability of Strawberry Juice during Processing and Storage. *LWT-Food Sci. Technol.* **2015**, *60*, 1174–1178. [[CrossRef](#)]
88. Wang, Z.; Du, H.; Zhai, R.; Song, L.; Ma, F.; Xu, L. Transcriptome Analysis Reveals Candidate Genes Related to Color Fading of ‘Red Bartlett’ (*Pyrus communis* L.). *Front. Plant Sci.* **2017**, *8*, 455. [[CrossRef](#)]
89. Wu, M.; Si, M.; Li, X.; Song, L.; Liu, J.; Zhai, R.; Cong, L.; Yue, R.; Yang, C.; Ma, F.; et al. PbCOP1.1 Contributes to the Negative Regulation of Anthocyanin Biosynthesis in Pear. *Plants* **2019**, *8*, 39. [[CrossRef](#)] [[PubMed](#)]
90. Fang, J.-L.; Luo, Y.; Yuan, K.; Guo, Y.; Jin, S.-H. Preparation and Evaluation of an Encapsulated Anthocyanin Complex for Enhancing the Stability of Anthocyanin. *LWT* **2020**, *117*, 108543. [[CrossRef](#)]
91. Castañeda-Ovando, A.; de Pacheco-Hernández, M.L.; Páez-Hernández, M.E.; Rodríguez, J.A.; Galán-Vidal, C.A. Chemical Studies of Anthocyanins: A Review. *Food Chem.* **2009**, *113*, 859–871. [[CrossRef](#)]
92. de Rosso, V.V.; Mercadante, A.Z. Evaluation of Colour and Stability of Anthocyanins from Tropical Fruits in an Isotonic Soft Drink System. *Innov. Food Sci. Emerg. Technol.* **2007**, *8*, 347–352. [[CrossRef](#)]
93. Idaka, E.; Ohashi, Y.; Ogawa, T.; Kondo, T.; Goto, O. Structure of Zebrinin, a Novel Acylated Anthocyanin Isolated from Zebrina Pendula. *Tetrahedron Lett.* **1987**, *28*, 1901–1904. [[CrossRef](#)]
94. Rehman, R.N.U.; You, Y.; Zhang, L.; Goudia, B.D.; Khan, A.R.; Li, P.; Ma, F. High Temperature Induced Anthocyanin Inhibition and Active Degradation in Malus Profusion. *Front. Plant Sci.* **2017**, *8*, 1401. [[CrossRef](#)]
95. Sun, Y.; Zhang, Y.; Xu, W.; Zheng, X. Analysis of the Anthocyanin Degradation in Blue Honeysuckle Berry under Microwave Assisted Foam-Mat Drying. *Foods* **2020**, *9*, 397. [[CrossRef](#)]
96. Ribeiro, H.L.; de Oliveira, A.V.; de Brito, E.S.; Ribeiro, P.R.; Azeredo, H.M. Stabilizing Effect of Montmorillonite on Acerola Juice Anthocyanins. *Food Chem.* **2018**, *245*, 966–973. [[CrossRef](#)]
97. Kohno, Y.; Ito, M.; Kurata, M.; Ikoma, S.; Shibata, M.; Matsushima, R.; Tomita, Y.; Maeda, Y.; Kobayashi, K. Photo-Induced Coloration of 2-Hydroxychalcone in the Clay Interlayer. *J. Photochem. Photobiol. A Chem.* **2011**, *218*, 87–92. [[CrossRef](#)]
98. Dordoni, R.; Galasi, R.; Colangelo, D.; De Faveri, D.M.; Lambri, M. Effects of Fining with Different Bentonite Labels and Doses on Colloidal Stability and Colour of a Valpolicella Red Wine. *Int. J. Food Sci. Technol.* **2015**, *50*, 2246–2254. [[CrossRef](#)]
99. Li, S.; Mu, B.; Wang, X.; Kang, Y.; Wang, A. Fabrication of Eco-Friendly Betanin Hybrid Materials Based on Palygorskite and Halloysite. *Materials* **2020**, *13*, 4649. [[CrossRef](#)] [[PubMed](#)]
100. Lopes, T.J.; Yaginuma, S.R.; Quadri, M.G.N.; Quadri, M.B. Evaluation of Red Cabbage Anthocyanins after Partial Purification on Clay. *Brazilian Arch. Biol. Technol.* **2011**, *54*, 1349–1356. [[CrossRef](#)]
101. Tulun, Ş.; Şimşek, İ.; Bahadır, T.; Çelebi, H. Investigation of Removal of Anthocyanin in Turnip Juice Wastewater by Using Different Adsorbents. *SN Appl. Sci.* **2019**, *1*, 967. [[CrossRef](#)]
102. Silva, G.T.M.; Silva, C.P.; Gehlen, M.H.; Oake, J.; Bohne, C.; Quina, F.H. Organic/Inorganic Hybrid Pigments from Flavylum Cations and Palygorskite. *Appl. Clay Sci.* **2018**, *162*, 478–486. [[CrossRef](#)]
103. Capello, C.; Leandro, G.C.; Maduro Campos, C.E.; Hotza, D.; Mattar Carciofi, B.A.; Valencia, G.A. Adsorption and Desorption of Eggplant Peel Anthocyanins on a Synthetic Layered Silicate. *J. Food Eng.* **2019**, *262*, 162–169. [[CrossRef](#)]
104. Lima, L.C.B.; Silva, F.C.; Silva-Filho, E.C.; Fonseca, M.G.; Zhuang, G.; Jaber, M. Saponite-Anthocyanin Derivatives: The Role of Organoclays in Pigment Photostability. *Appl. Clay Sci.* **2020**, *191*, 105604. [[CrossRef](#)]
105. Ogawa, M.; Takee, R.; Okabe, Y.; Seki, Y. Bio-Geo Hybrid Pigment; Clay-Anthocyanin Complex Which Changes Color Depending on the Atmosphere. *Dyes Pigments* **2017**, *139*, 561–565. [[CrossRef](#)]

106. Kang, S.; Wang, H.; Guo, M.; Zhang, L.; Chen, M.; Jiang, S.; Li, X.; Jiang, S. Ethylene-Vinyl Alcohol Copolymer–Montmorillonite Multilayer Barrier Film Coated with Mulberry Anthocyanin for Freshness Monitoring. *J. Agric. Food Chem.* **2018**, *66*, 13268–13276. [[CrossRef](#)]
107. Mirzaaghaei, M.; Goli, S.A.H.; Fathi, M. Clarification of Apple Juice Using Activated Sepiolite as a New Fining Clay. *Clay Miner.* **2017**, *52*, 497–508. [[CrossRef](#)]
108. Li, S.E.; Mu, B.; Ding, J.J.; Zhang, H.; Wang, X.W.; Wang, A.Q. Fabrication of Anthocyanin/Montmorillonite Hybrid Pigments To Enhance Their Environmental Stability and Application in Allochromic Composite Films. *Clays Clay Miner.* **2021**, *69*, 142–151. [[CrossRef](#)]
109. Singh, A.; Kitts, D.D. In Vitro Bioaccessibility of Tart Cherry Anthocyanins in a Health Supplement Mix Containing Mineral Clay. *J. Food Sci.* **2019**, *84*, 475–480. [[CrossRef](#)]
110. Raji, M.; El Foujji, L.; Mekhroum, M.E.M.; El Achaby, M.; Essabir, H.; Bouhfid, R.; Qaiss, A.E.K. PH-Indicative Films Based on Chitosan–PVA/Sepiolite and Anthocyanin from Red Cabbage: Application in Milk Packaging. *J. Bionic Eng.* **2022**, *19*, 837–851. [[CrossRef](#)]
111. Mao, L.; Wang, C.; Yao, J.; Lin, Y.; Liao, X.; Lu, J. Design and Fabrication of Anthocyanin Functionalized Layered Clay/Poly(Vinyl Alcohol) Coatings on Poly(Lactic Acid) Film for Active Food Packaging. *Food Packag. Shelf Life* **2023**, *35*, 101007. [[CrossRef](#)]
112. Gutiérrez, T.J.; León, I.E.; Ponce, A.G.; Alvarez, V.A. Active and PH-Sensitive Nanopackaging Based on Polymeric Anthocyanin/Natural or Organo-Modified Montmorillonite Blends: Characterization and Assessment of Cytotoxicity. *Polymers* **2022**, *14*, 4881. [[CrossRef](#)]
113. Toro-Márquez, L.A.; Merino, D.; Gutiérrez, T.J. Bionanocomposite Films Prepared from Corn Starch With and Without Nanopackaged Jamaica (*Hibiscus sabdariffa*) Flower Extract. *Food Bioprocess Technol.* **2018**, *11*, 1955–1973. [[CrossRef](#)]
114. Koosha, M.; Hamedi, S. Intelligent Chitosan/PVA Nanocomposite Films Containing Black Carrot Anthocyanin and Bentonite Nanoclays with Improved Mechanical, Thermal and Antibacterial Properties. *Prog. Org. Coat.* **2019**, *127*, 338–347. [[CrossRef](#)]
115. Gutiérrez, T.J.; Alvarez, V.A. Bionanocomposite Films Developed from Corn Starch and Natural and Modified Nano-Clays with or without Added Blueberry Extract. *Food Hydrocoll.* **2018**, *77*, 407–420. [[CrossRef](#)]
116. De Castro Silva, F.; Brandão Lima, L.C.; Silva-Filho, E.C.; Fonseca, M.G.; Jaber, M. Through Alizarin-Hectorite Pigments: Influence of Organofunctionalization on Fading. *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, *587*, 124323. [[CrossRef](#)]
117. Wu, Y.; Xu, L.; Liu, X.; Hasan, K.M.F.; Li, H.; Zhou, S.; Zhang, Q.; Zhou, Y. Effect of Thermosonication Treatment on Blueberry Juice Quality: Total Phenolics, Flavonoids, Anthocyanin, and Antioxidant Activity. *LWT* **2021**, *150*, 112021. [[CrossRef](#)]
118. Ji, Y. Synthesis of Porous Starch Microgels for the Encapsulation, Delivery and Stabilization of Anthocyanins. *J. Food Eng.* **2021**, *302*, 110552. [[CrossRef](#)]
119. Laleh, G.H.; Frydoonfar, H.; Heidary, R.; Jameei, R.; Zare, S. The Effect of Light, Temperature, PH and Species on Stability of Anthocyanin Pigments in Four Berberis Species. *Pakistan J. Nutr.* **2006**, *5*, 90–92. [[CrossRef](#)]
120. Oliveira, H.; Correia, P.; Pereira, A.R.; Araújo, P.; Mateus, N.; de Freitas, V.; Oliveira, J.; Fernandes, I. Exploring the Applications of the Photoprotective Properties of Anthocyanins in Biological Systems. *Int. J. Mol. Sci.* **2020**, *21*, 7464. [[CrossRef](#)] [[PubMed](#)]
121. Laganà, G.; Barreca, D.; Smeriglio, A.; Germanò, M.P.; D’angelo, V.; Calderaro, A.; Bellocco, E.; Trombetta, D. Evaluation of Anthocyanin Profile, Antioxidant, Cytoprotective, and Anti-Angiogenic Properties of Callistemon Citrinus Flowers. *Plants* **2020**, *9*, 1045. [[CrossRef](#)]
122. Pan, F.; Liu, Y.; Liu, J.; Wang, E. Stability of Blueberry Anthocyanin, Anthocyanidin and Pyranoanthocyanidin Pigments and Their Inhibitory Effects and Mechanisms in Human Cervical Cancer HeLa Cells. *RSC Adv.* **2019**, *9*, 10842–10853. [[CrossRef](#)] [[PubMed](#)]
123. Mu, B.; Wang, A. Adsorption of Dyes onto Palygorskite and Its Composites: A Review. *J. Environ. Chem. Eng.* **2016**, *4*, 1274–1294. [[CrossRef](#)]
124. Tangaraj, V.; Janot, J.; Jaber, M.; Bechelany, M.; Balme, S. Adsorption and Photophysical Properties of Fluorescent Dyes over Montmorillonite and Saponite Modified by Surfactant. *Chemosphere* **2017**, *184*, 1355–1361. [[CrossRef](#)]
125. Grassi, G.; Michels, L.; Rozynek, Z.; Altoé, M.A.S.; dos Santos, E.C.; da Fonseca, C.L.S.; Droppa, R.; Gholamipour-Shirazi, A.; Fossum, J.O.; da Silva, G.J. Cation Exchange Dynamics Confined in a Synthetic Clay Mineral. *Eur. Phys. J. Spec. Top.* **2014**, *223*, 1883–1893. [[CrossRef](#)]
126. Zhang, D.; Zhou, C.-H.; Lin, C.-X.; Tong, D.-S.; Yu, W.-H. Synthesis of Clay Minerals. *Appl. Clay Sci.* **2010**, *50*, 1–11. [[CrossRef](#)]
127. Cao, L.; Xie, W.; Cui, H.; Xiong, Z.; Tang, Y.; Zhang, X.; Feng, Y. Fibrous Clays in Dermopharmaceutical and Cosmetic Applications: Traditional and Emerging Perspectives. *Int. J. Pharm.* **2022**, *625*, 122097. [[CrossRef](#)]

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.