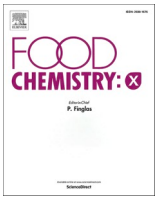
Food Chemistry: X 24 (2024) 101883

Contents lists available at ScienceDirect

Food Chemistry: X

journal homepage: www.sciencedirect.com/journal/food-chemistry-x



Factors affecting the stability of anthocyanins and strategies for improving their stability: A review

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ARTICLE INFO

Keywords:
Anthocyanins
Stability
Factor
Strategy

ABSTRACT

Anthocyanins, as the most common and widely distributed flavonoid compounds, are widely present in fruits and vegetables. Anthocyanins show various biological activities including antioxidant, anticancer, anti-inflammatory, antibacterial, and immunomodulatory activities. Hence, anthocyanins are widely used in the fields of food and pharmaceuticals. However, anthocyanins are susceptible to environmental and processing factors due to their structural characteristics, which leads to poor storage and processing stability. Numerous studies have indicated that structural modification, co-pigmentation, and delivery systems could improve the stability and bioavailability of anthocyanins in the external environment. This article reviews the main factors affecting the stability of anthocyanins. Moreover, this review comprehensively introduces methods to improve the stability of anthocyanins. Finally, the current problems and future research advances of anthocyanins are also introduced. The findings can provide important references for deeper research on the stability, biological activities, and bioavailability of anthocyanins.

1. Introduction

Anthocyanins, as a water-soluble natural pigment, are formed by the glycosidic bond between anthocyanidin and sugars. Anthocyanins are widely present in fruits, vegetables, and grains, which can give them an attractive color (Yuan et al., 2022). In recent years, the harm brought by synthetic pigments has become increasingly prominent with the increasing emphasis on health. Natural anthocyanins have attracted increasing attention due to their safe and non-toxic. Numerous studies have confirmed that anthocyanins exhibited various biological activities including antioxidant, anti-inflammatory, anti-tumor, hypoglycemic, and other activities (Yang et al., 2021). Hence, anthocyanins have been widely used in food, cosmetics, and medicine fields. However, anthocyanins are prone to degradation during the preparation process due to the presence of a large number of unstable phenolic hydroxyl groups in their structure. Numerous studies have indicated that various factors including pH, temperature, light, oxygen, enzymes, solvents, metal ions, and proteins could affect the stability of anthocyanins (Liu, Tong, Tong, Xu, & Wang, 2023). Meanwhile, previous report has found that the absorption of anthocyanins into plasma accounted for only 1 % of the total intake (Liu, Ou, Zhou, & Hu, 2017). Anthocyanins are difficult to fully and extensively enter the intestine and exert their biological activities, which limits their application in food processing and health product preparation (Fraisse, Bred, Felgines, & Senejoux, 2020). Therefore, how to stabilize the structure of anthocyanins, reduce the degradation rate of anthocyanins in the gastrointestinal tract, and improve the absorption rate of cells has become an urgent problem for the further application of anthocyanins in the fields of food, medicine, and health products.

In recent years, the research on improving the stability and bioavailability of anthocyanins has received widespread attention. Fig. 1 shows the different strategies for improving the stability of anthocyanins. Structural modification of anthocyanins is one of the most commonly used methods to improve the stability of anthocyanins. The

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https://doi.org/10.1016/j.fochx.2024.101883
Received 26 August 2024; Received in revised form 3 October 2024; Accepted 4 October 2024
Available online 5 October 2024

structural modification of anthocyanins mainly involves grafting new functional groups onto the anthocyanin structure through various chemical reactions, which maintains the structure of the precursor anthocyanin unchanged and improves their structural stability. Currently, growing studies focus on chemical methods (acylation and pyranization) to modify the structure of anthocyanins and improve their stability and biological activities (Wang, Sun, Zhou, Qiu, & Cui, 2020; Zeng et al., 2022). In addition, co-pigmentation is often considered a critical method that can effectively resist high temperature, light, and oxygen to stabilize anthocyanins (Zhao et al., 2020). Co-pigmentation technology refers to the formation of complexes between the colored forms of anthocyanins (flavylium cations and quinonoid bases) and colorless organic molecules through non covalent interaction, which is beneficial for enhancing the stability of anthocyanins. Intramolecular and intermolecular co-pigmentation, metal complexation, and self-association are effective co-pigmentation methods for improving the stability of anthocyanins (Jiang, Qin, Chen, & He, 2019). Additionally, microencapsulation is also an important method to improve the stability of anthocyanins. Microencapsulation of anthocyanins refers to the encapsulation of anthocyanins through microcapsule technology, which can form a small capsule structure to enhance their stability and protect them from external environmental influences (Zhang et al., 2020). Gelatin and Arabic gum can form nanoscale microcapsules that effectively encapsulate anthocyanins, which can improve the retention and release of anthocyanins in the gastrointestinal environment (Kanha, Regenstein, Surawang, Pitchakarn, & Laokuldilok, 2021). Currently, mounting studies have found that delivery systems are an effective method for improving the stability and bioavailability of anthocyanins (Zhang et al., 2020). The delivery systems utilize the physicochemical properties and selective distribution of the carrier to adsorb, embed, or interact with anthocyanins, which can effectively solve the problems of poor stability and limited absorption of anthocyanins during the delivery process. Currently, the common anthocyanins delivery systems include the 5 types: 1) protein-anthocyanin delivery system; 2) polysaccharide-anthocyanin delivery system; 3) liposome-anthocyanin delivery system; 4) multiple emulsion delivery system; 5) composite delivery system (Ma, Bai, Chen, & Sun, 2022). In addition, the delivery systems can also increase the dissolution rate and absorption rate of anthocyanins, and improve their bioavailability. In recent years, previous report has found that microcapsules, nanoparticles, lotion, and liposomes were used as delivery carriers of anthocyanins, which had excellent biocompatibility, safety, non-toxic, and other advantages (Steiert, Radi, Fach, & Wich, 2018). The above-mentioned carriers are of great significance in improving the stability and enhancing the bioavailability of anthocyanins.

At present, there are limited reviews on factors affecting anthocyanins stability and strategies for improving anthocyanin stability. To improve the development and application prospects of anthocyanins, it is particularly important to systematically review the characteristics of anthocyanins and elucidate the stability of anthocyanins. Thus, this article systematically reviews the characteristics of anthocyanins, analyzes the main factors affecting the anthocyanin's stability, and elucidates strategies to improve their stability. Moreover, this review analyzes the current problems of anthocyanins and looks forward to future development directions. The findings can provide a theoretical basis for the further development and utilization of anthocyanins as functional factors in food and medicine.

2. Source and structural characteristics of anthocyanins

Anthocyanin is a flavonoid compound composed of anthocyanidin and sugars connected by glycosidic bonds (Attaribo et al., 2020). According to statistics, tens of thousands of plant species (27 families and 73 genera) contain anthocyanins. Anthocyanins mainly exist in the cell sap of plants, resulting in different colors (blue, magenta, and red) in roots, stems, flowers, leaves, and fruits (Zeng et al., 2022). The parent nucleus of anthocyanins is a 2-phenylbenzopyran cation, which is bonded from an aromatic ring (A) to an oxygen-containing heterocycle (C), and then connected to a third aromatic ring (B) through a C—C bond to form a highly conjugated C6-C3-C6 skeleton structure (Junior, Martins, Pereira, Chiste, & Pena, 2023). Anthocyanins exhibit maximum absorption in the visible light range (510–530 nm) and ultraviolet light range (270–280 nm). At present, more than 700 natural anthocyanins have been isolated from plants, which mainly included six anthocyanins monomers (cyanidin, delphinidin, malvidin, pelargonidin, peonidin, and petunidin) (Ai et al., 2023), and Fig. 2 shows their structure (Zang et al., 2022).

3. Factors affecting the stability of anthocyanins

Increasing studies have indicated that pH, temperature, light, antioxidants, metal ions, and other factors could affect the stability of

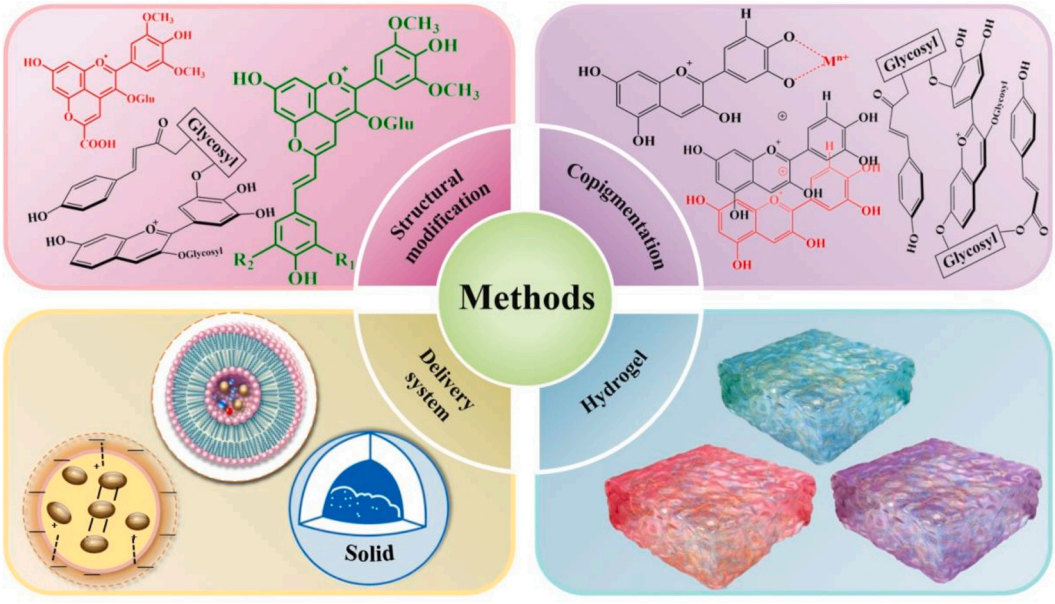

Fig. 1. Methods to improve the stability of anthocyanins.

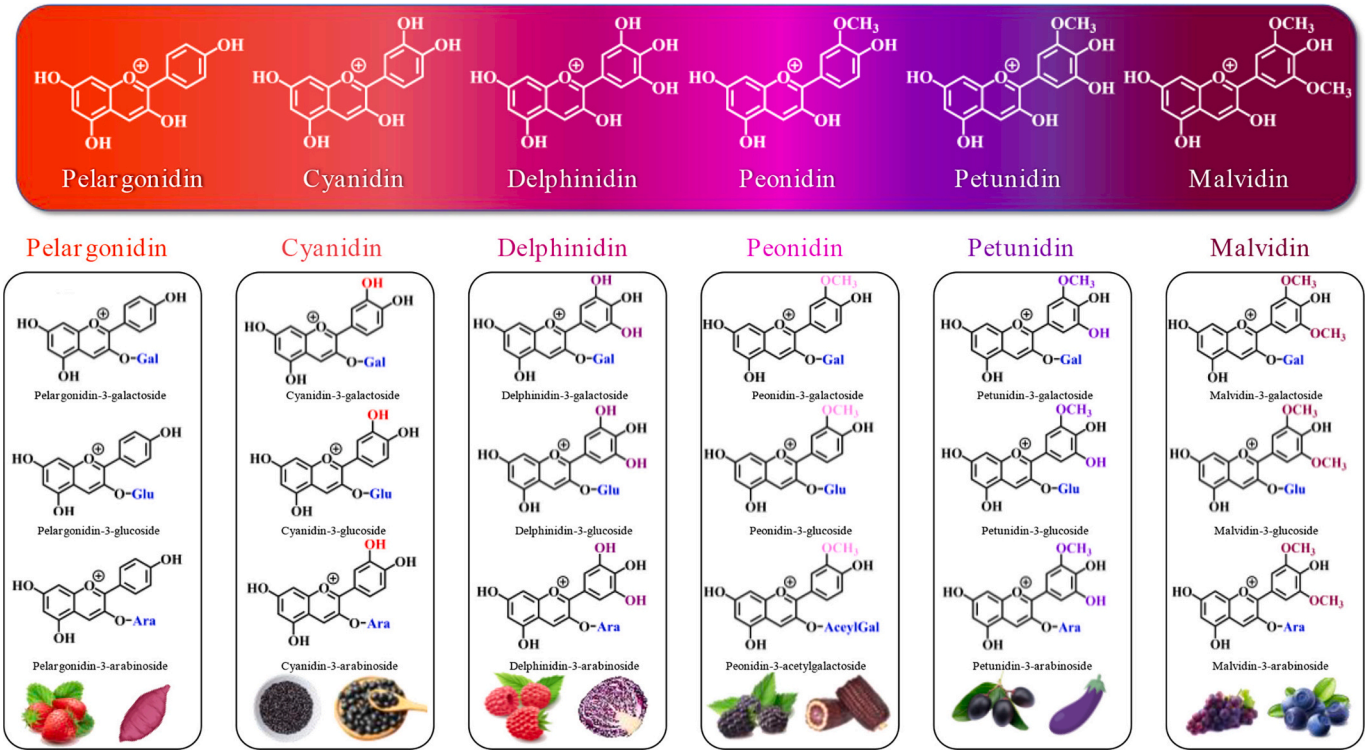

Fig. 2. Six common anthocyanidin aglycones and chemical structures of their glycosides (Zang et al., 2022).

anthocyanins (Fig. 3). Hence, this article systematically introduces the influence of the above factors on anthocyanins stability.

3.1. pH

The anthocyanins color is easily affected by pH due to the ionic properties of their molecular structure. Anthocyanins exist in five forms in aqueous solution, which mainly depends on pH of the solution. Anthocyanins mainly exist in the flavylium cationic forms when pH of the aqueous solution is below 2. Anthocyanins exist in the form of colorless methanol off base or hemiacetal when pH is within the range of 3–6, and then heterocycles in methanol off base or hemiacetal may break and form yellow chalcone. Anthocyanins deprotonate and form purple neutral quinonoid bases with the increase of pH. Anthocyanins form blue ionized quinonoid bases when pH is within the range of 8–10. Fig. 3A exhibits the structural changes of anthocyanins at different pH levels (Zhao, Zhang, Chen, Zhang, & He, 2019). The color change of anthocyanins is generally red–pink–colorless–blue under different pH. Growing studies have confirmed that anthocyanins had strong stability at pH 2–3, and the stability of anthocyanins was relatively poor under neutral and alkaline conditions (Jiang et al., 2019; Liu et al., 2018; Zhao et al., 2019). Moreover, the structure of anthocyanins changes and presents different colors at different pH levels, which can develop anthocyanins into safer and more reliable pH test strips.

3.2. Temperature

Temperature is a key parameter in the food industry. Heating treatment is one of the most commonly used methods for preserving and extending the shelf life of food, as well as ensuring food safety in food manufacturing. Previous report has indicated that the degradation process of anthocyanins was endothermic and easily influenced by temperature (Sendri, Singh, Sharma, Purohit, & Bhandari, 2023). The degradation rate constant of anthocyanins improved with the increase of temperature, while the half-life of anthocyanins decreased (Liu et al., 2023). Previous study has found that the thermal degradation kinetics of anthocyanins followed a first-order reaction kinetics model (Sendri et al., 2023). At present, anthocyanins mainly include two thermal degradation pathways as follows: (1) Water molecules have strong aggressiveness, leading to the deglycosylation of anthocyanins into anthocyanidin glycosides at high temperatures, and anthocyanidin are then sequentially converted into methanol, chalcone, diketone, and even benzoic acid and aldehyde derivatives (Stintzing & Carle, 2004); (2) High temperature promotes the ring opening and conversion of anthocyanins into chalcones, which are further converted into coumarin glycoside derivatives (Stintzing & Carle, 2004). Compared to high temperature, low temperature is more conducive to maintaining the structural stability of anthocyanins. Increasing studies have indicated that anthocyanins had strong stability in the temperature range of 2–4 °C (Liu et al., 2023; Stoica et al., 2023). Moreover, temperature can directly affect relevant factors in plants, thereby regulating the accumulation of anthocyanins. High temperature can induce an increase in the content of negative transcription factors, thereby binding to promoters and inhibiting the expression of anthocyanins genes (Zhou et al., 2021). Low temperature induces demethylation gene expression, reduces the methylation expression levels of anthocyanin-related genes, and better promotes the accumulation of anthocyanins (Yu et al., 2022).

3.3. Light

Light plays a crucial role in the growth process of plants. Moreover, light can induce and regulate the expression levels of anthocyanin-related genes. Therefore, light plays an indispensable role in the biosynthesis of anthocyanins. The effect of light on anthocyanins has a dual effect. Previous report has found that blue light could better induce the expression levels of anthocyanins biosynthesis genes in plants and increase the accumulation of anthocyanins (Wei et al., 2023). However, anthocyanins are significantly degraded and their half-life is shortened when anthocyanins are exposed to ultraviolet radiation (Junior et al., 2023). UV light can accelerate anthocyanin degradation and produce an intermediate product from the C4 hydroxyl group, which hydrolyzes at the C2 position to open the ring and finally produce a chalcone (Yang

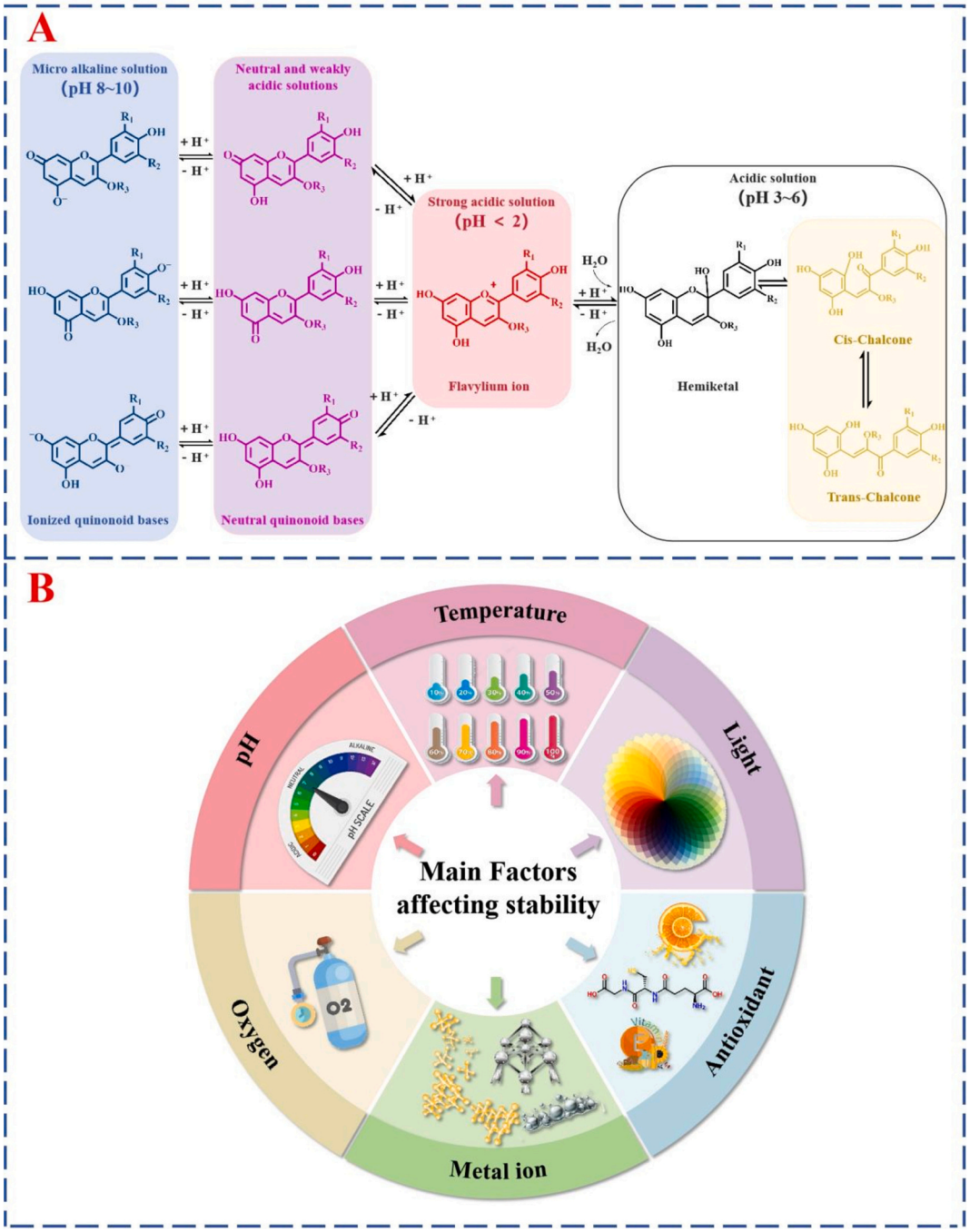

Fig. 3. Conformations of anthocyanins in aqueous solution under different pH conditions (A) and factors affecting the stability of anthocyanins (B).

et al., 2024). Then, the produced chalcone rapidly degrades into small molecular products including benzoic acid and 2,4,6-trihydroxybenzaldehyde (Zhang et al., 2022). In addition, light intensity is also one of the important factors affecting anthocyanins content. Previous study has found that the accumulation of anthocyanins in plants was the highest under sufficient light (An et al., 2023). Hence, anthocyanins can avoid light treatment and reduce their degradation caused by light.

3.4. Antioxidant

Ascorbic acid, as an antioxidant, is widely present in various fruits and vegetables, and it plays a very important regulatory role in normal physiological functions of the human body. Notably, previous report has confirmed that ascorbic acid could accelerate the degradation of anthocyanins and change their color (Enaru, Dretcanu, Pop, Stanila, & Diaconeasa, 2021). However, the degradation mechanisms of anthocyanins by ascorbic acid have not been fully elucidated. At present, it is mainly believed that ascorbic acid disrupts their stability by directly condensing with anthocyanins (Enaru et al., 2021; Farr & Giusti, 2018). Ascorbic acid undergoes self-oxidation reaction to generate hydrogen peroxide, which opens the nucleus of anthocyanins to form chalcone, thereby reducing their stability (Levy, Okun, & Shpigelman, 2019). In addition to ascorbic acid, epicatechin gallate could inhibit peroxidase, which could protect anthocyanins from enzymatic degradation (Luo et al., 2017). Glutathione forms complexes with other unstable factors, which can reduce their influence on anthocyanins and thus improve their stability (Stebbins, Howard, Prior, Brownmiller, & Mauromoustakos, 2017). α-Tocopherol, as an antioxidant, has a dual effect on

anthocyanins. α-Tocopherol acts as protectant to protect anthocyanins (Tavano, Muzzalupo, Picci, & de Cindio, 2014). However, α-tocopherol can promote the oxidation of anthocyanins, thereby reducing their stability (Do Carmo, Teixeira, e Souza, Figueiredo, Fernandes, Botrel, & Borges, 2021).

3.5. Metal ion

Anthocyanins can chelate metal ions, further altering their color and stability, which is related to the type, concentration, and structure of metal ions. Compared with Al^{3+} and Ca^{2+}, Sn^{2+} and Fe^{3+} had a greater impact on the stability of anthocyanins from red cabbage (Ratanapoompinyo, Nguyen, Devkota, & Shrestha, 2017). Fe^{2+} has a dual effect on the anthocyanins from red cabbage. Fe^{2+} can stabilize the color by forming stable complexes, preventing the oxidation of anions and hydrolysis of acyl groups. In addition, Fe^{2+} can promote the irreversible degradation of non acylated and monoacylated pigments (Fenger, Moloney, Robbins, Collins, & Dangles, 2019). The concentration of metal ions is also one of the critical factors affecting the stability of anthocyanins. Luo, Liu, and Chen (2019) found that Zn^{2+} and Ca^{2+} with high concentrations could enhance the stability of anthocyanins. Besides, metal ions could promote acylation or self-association of anthocyanins with catechol groups, thereby improving the stability of anthocyanins. The degree of self-association enhanced with the increase of pH (Sigurdson, Robbins, Collins, & Giusti, 2016).

3.6. Oxygen

The easy reaction of anthocyanins with molecular oxygen is attributed to the presence of unsaturated bonds in their structure. Therefore, oxygen is another important factor affecting the stability of anthocyanins, which plays a role in anthocyanins degradation. The presence of oxygen can accelerate the degradation process of anthocyanins either by direct oxidative mechanisms or by the action of oxidases (Patras, Brunton, Odonnell, & Tiwari, 2010). Compared with storage in an oxygen-containing environment, anthocyanins are more stable when stored under vacuum, nitrogen, and argon. Previous reports have found that the degradation of anthocyanins in wine was accelerated under high oxygen conditions (Gambuti et al., 2017; Remini et al., 2018). Zhou et al. (2017) found that the degradation rate of blueberry anthocyanins under aerobic conditions was six times faster than under anaerobic conditions. Previous report has found that if food was stored in an environment enriched with 60 %–100 % oxygen and at a low temperature, during the onset (0–7 days) of cold storage, the retention rate of anthocyanins increased (Patras et al., 2010). Therefore, we should pay attention to the oxygen content of anthocyanins during storage and packaging to avoid anthocyanins degradation in the future.

3.7. Other factors

In addition to the above factors, other factors can also have a certain impact on the stability of anthocyanins, which is due to the unsaturated structure of anthocyanins. Humidity could also have a certain impact on the stability of anthocyanins. High humidity could promote the oxidation reaction between oxygen and anthocyanins and reduce the stability of anthocyanins (Moratalla-Lopez, Lorenzo, Chaouqi, Sanchez, & Alonso, 2019). Additionally, some impurities, enzymes, unstable functional groups, and microorganisms can also reduce the stability and even destroy the structure of anthocyanins, ultimately leading to a decrease in their biological activities (Zia, Riaz, & Saad, 2016).

4. Methods to improve the stability of anthocyanins

Currently, structural modification (glycosylation, acylation, pyranization, and other methods), co-pigmentation (intermolecular, intramolecular, and self-associations, and metal complexation), and delivery system (microcapsulation, protein, polysaccharides, liposome, multiple emulsion, and composite delivery systems) can improve the stability of anthocyanins to a certain extent. Next, we systematically review the above methods to improve anthocyanins stability.

4.1. Structural modification

Pigments have a wide range of applications in the food industry. However, natural pigments are receiving increasing attention due to the threat of synthetic pigments to human health. Anthocyanins, as a naturally soluble pigment, can meet the needs of the food industry. However, the structure of anthocyanins is unstable and easily affected by factors including temperature, pH, light, metal ions, and redox agents, ultimately leading to color changes (Liu et al., 2023). Moreover, anthocyanins have low lipid solubility and are not easily able to penetrate the phospholipid bilayer biofilm, which ultimately leads to their low utilization rate (Zhang et al., 2024). Research has confirmed that modifying the structure of anthocyanins through different methods was beneficial for increasing their lipid solubility, stability, and bioavailability (Marathe, Shah, Bajaj, & Singhal, 2021). Currently, the structural modification methods of anthocyanins mainly include glycosylation, acylation, and pyranization. These methods can improve the stability of anthocyanins and enhance their biological activities to a certain extent.

4.1.1. Glycosylation

Glycosylation refers to the chemical reaction between one or more hydroxyl groups in anthocyanin molecules and sugar molecules to form glycosidic bonds. Sugar molecules can be linked to hydroxyl groups at positions C3, C5, C7, C3', and C5'. Monosaccharides are more commonly glycosylated at the C3 position, and bisaccharides are generally glycosylated at the C3 and C5 positions (Liu, Cheng, Ma, Liang, & Jing, 2022). Previous report has found that glycosylation could form hydrogen bond networks, promote self-assembly, reduce hydrolysis rates, and alter fading activation energy, which could provide effective protection for the color stability of anthocyanins (Kim et al., 2011). Chen et al. (2024) found that glycosylation improved the stability of anthocyanins and expanded their commercial value. Monoglycosylated anthocyanins had better stability than disaccharide anthocyanins. Monoglycosylated cyanidin-3-O-glucoside could alter the interaction between anthocyanins and lipid bilayers, which was beneficial for improving their lipid solubility and stability (Cyboran-Mikolajczyk, Jurkiewicz, Hof, & Kleszczynska, 2018). Besides, the type of sugar molecules is also one of the important factors affecting the stability of anthocyanins. Glucose, rhamnose, galactose, xylose, arabinose, and other sugars bind more frequently to anthocyanins. These sugar molecules enhance the stability of anthocyanins by increasing non covalent interaction between molecules (Liu, Cheng, et al., 2022). However, the complex glycosylation reduces the number of hydroxyl groups in anthocyanins and their antioxidant capacity (Overall et al., 2017). Thus, the glycosylation modification of anthocyanins needs to be set according to the actual situation.

4.1.2. Acylation

Acylation modification of anthocyanins usually refers to the esterification of hydroxyl groups in the anthocyanin structure by fatty acids or aromatic acids. The changes in the type, quantity, and connection position of acyl groups greatly increase the type of anthocyanins and affect their stability and biological activities (Wang et al., 2020). Zhang et al. (2022) found that acylated anthocyanins significantly increased the stability and antioxidant capacity of anthocyanin. The acyl groups could prevent anthocyanins from being nucleophilic attacked by water, which further inhibited the transformation of anthocyanins into colorless chalcones or blue quinones, maintaining the original color of the solution. Aromatic acyl groups could cause steric hindrance and π-π conjugation to anthocyanins, resulting in intramolecular co-pigmentation effects. Additionally, aromatic acyl groups could reduce the steric

hindrance of anthocyanin loss in solution, which contributed to significant improvement in the stability of anthocyanins (Dangles, Saito, & Brouillard, 1993). Monoacyl groups could only protect one side of the benzopyridine ring of anthocyanins, while the other side was easily attacked by water molecules, resulting in limited stability improvement. However, both sides of the benzopyridine ring of anthocyanins with diacylation or polyacylation were simultaneously protected from nucleophilic attack, which could further improve the stability of anthocyanins (Mendoza et al., 2018). *p*-coumaric acid and caffeic acid were grafted on blueberry anthocyanins through enzyme catalysis method to improve their color stability and antioxidant activity. *p*-coumaric acylated anthocyanins and caffeic acid anthocyanins showed stronger antioxidant activity in DPPH assay and β-carotene bleaching assay and higher color stability during storage at 25 °C, 40 °C and 60 °C than native blueberry anthocyanins (Liu et al., 2020). Chemical acylation and enzymatic acylation are the most commonly used acylation modification methods for anthocyanins. Chemical modification is mainly based on organic synthesis, selecting appropriate acyl donors, catalysts, and reaction conditions. However, the chemical acylation process has certain limitations including lack of good directionality and selectivity, low conversion rate, and easy generation by-products. In addition, the chemical acylation process also easily introduces more solvents, which is not conducive to the separation and purification of the target product in the later stage. Furthermore, the chemical modification cannot perform acylation reactions on specific hydroxyl groups, which can easily bind or shield the main active phenolic hydroxyl groups of anthocyanins, thus reducing their antioxidant capacity (Cai et al., 2022). Enzymes have good specificity and selectivity for catalyzing substrates, mild reaction conditions, and high catalytic efficiency. Enzymatic acylation can target hydroxyl groups in certain parts of anthocyanins for acylation reactions, which can effectively compensate for the shortcomings of chemical acylation (Nishizaki et al., 2013; Sasaki, Nishizaki, Ozeki, & Miyahara, 2014).

4.1.3. Pyranization

Pyranization modification is the most common method for modifying the structure of anthocyanins. Pyranoanthocyanins is an additional pyran D-ring compound formed between the hydroxyl groups at the C4 and C5 positions of anthocyanins (Quaglieri, Jourdes, Waffo-Teguo, & Teissedre, 2017). Pyranoanthocyanins were first discovered in the study of red wine. Anthocyanins in red wine have been discovered for a long time. However, there is little research on the reasons for color changes during the aging process of red wine. Researchers first proposed that the color change of red wine during the process from new production to aging may be due to the synthesis of new pigments (pyranoanthocyanins) during the aging process until 1996. In addition to wine, the presence of pyranoanthocyanins has also been detected in blood orange, black currant, onion, and black carrot juices. The discovery of the pyranoanthocyanins family greatly expands the potential application of anthocyanins. Currently, there are four main types of pyranoanthocyanins including methyl, vitisins, portisins, and flavanol types (Zeng et al., 2022). Fig. 4A displays the formation process of four main types of pyranoanthocyanins. Methyl pyranoanthocyanins and vitisin-type pyranoanthocyanins are similar, and their maximum absorption wavelengths have undergone a blue shift compared to the original anthocyanins (Guzman-Figueroa, Ortega-Regules, Bautista-Ortin, Gomez-Plaza, & Anaya-Berrios, 2016). The stability of pyranized anthocyanins was stronger than that of unpyranized anthocyanins (Rakic & Poklar Ulrih, 2021). Sun et al. (2020) found that pyranized anthocyanins were more stable under different pH, SO_2, and temperature than that of unpyranized anthocyanins. Farr and Giusti (2018) found that the half-life of vitisins type pyranoanthocyanins was 8–13 times longer than that of unpyranized anthocyanins. In addition, vitisins-type pyranoanthocyanins had a good resistance to the bleaching effect of ascorbic acid. Portisins type pyranoanthocyanins had two types including Portisin A and Portisin B (Zeng et al., 2022). Portisin A-type anthocyanins are formed by the combination of Vitisin A and vinyl flavanols. Portisin B-type anthocyanins are obtained by nucleophilic attack of the C═C double bond of hydroxycinnamic acid on the C10 site of Viticin A, followed by removal of formic acid and oxidation. Both types of portisin-type anthocyanins undergo a red shift compared to the prototype anthocyanins (Zeng et al., 2022). Flavonol-type pyranoanthocyanins exhibited high stability and attractive color under moderate to strong acidic conditions (He, Carvalho, Mateus, & De Freitas, 2010). Moreover, flavonol-type pyranoanthocyanins could produce strong intramolecular co-pigmentation, inhibit the ability of hydrate formation, and maintain the color stability of anthocyanins (Zeng et al., 2022). The conversion rate of anthocyanins is relatively high in the production process of anthocyanins. Pyranoanthocyanins, as a natural plant pigment, have advantages in environmental protection, safety, and health benefits that cannot be compared to other artificially synthesized pigments. Therefore, pyranoanthocyanins are more suitable for application in related fields such as food, cosmetics, and health products. Based on the above analysis, it was found that compared with the prototype anthocyanins, pyranoanthocyanins were more stable and had better biological activity. However, further in-depth research is needed on the structure-activity relationship and absorption metabolism of pyranoanthocyanins in the future.

4.1.4. Other modification methods

The structure of anthocyanins contains a large number of hydroxyl groups, which are highly polar and easily soluble in water, whereas anthocyanins are insoluble in lipophilic solvents. Thus, esterification modification of anthocyanin structure is of great significance. The esterification and acylation of anthocyanins have a similar mechanism. However, the substrates for esterification reactions are mainly hydrophobic compounds such as succinic anhydride or fatty acids. After esterification modification, the hydrophilicity of anthocyanins decreased, whereas their lipophilicity increased, further indicating that the esterified anthocyanins are easily soluble in organic solvents and effectively enhance the antioxidant activity and stability of anthocyanins (Marathe et al., 2021). Sulfonation modification is also an important method for modifying the structure of anthocyanins. Sulfonation modification refers to the introduction of sulfonic acid groups into anthocyanins to improve their stability. The introduction of sulfonic acid groups enhanced the stability of anthocyanins under high temperature and weak alkaline conditions, which was beneficial for anthocyanins to exert their biological activities (Strabmann, Passon, & Schieber, 2021). Besides, methylation modification is also an effective method to improve the anthocyanins stability. Methylation modification can alter the spatial structure and electron density distribution of anthocyanins, cause wavelength blue shift, increase bond energy, and improve the stability of anthocyanins (Brar et al., 2018). However, the steric hindrance of methyl groups and the interaction with solvent molecules can increase the hydrophobicity of anthocyanins and reduce their water solubility, which limits the commercial-scale application and promotion of anthocyanins (Cheng et al., 2014). Hydroxyl groups are important functional groups in anthocyanins. Hydroxyl groups can determine the reaction site and participate in numerous reactions such as substitution and esterification of anthocyanins. Moreover, hydroxyl groups play an important role in the antioxidant, anti-inflammatory, anticancer, and antibacterial activities of anthocyanins.

4.2. Co-pigmentation

Co-pigmentation is often considered an important method for stabilizing anthocyanins by effectively resisting high temperatures, light, and oxygen (Zhao et al., 2020). Co-pigmentation technology refers to the formation of complexes between the colored form of anthocyanins (flavylium cations and quinonoid) and colorless organic molecules through non covalent interaction to stabilize their structure. Intramolecular and intermolecular co-pigmentation, metal complexation,

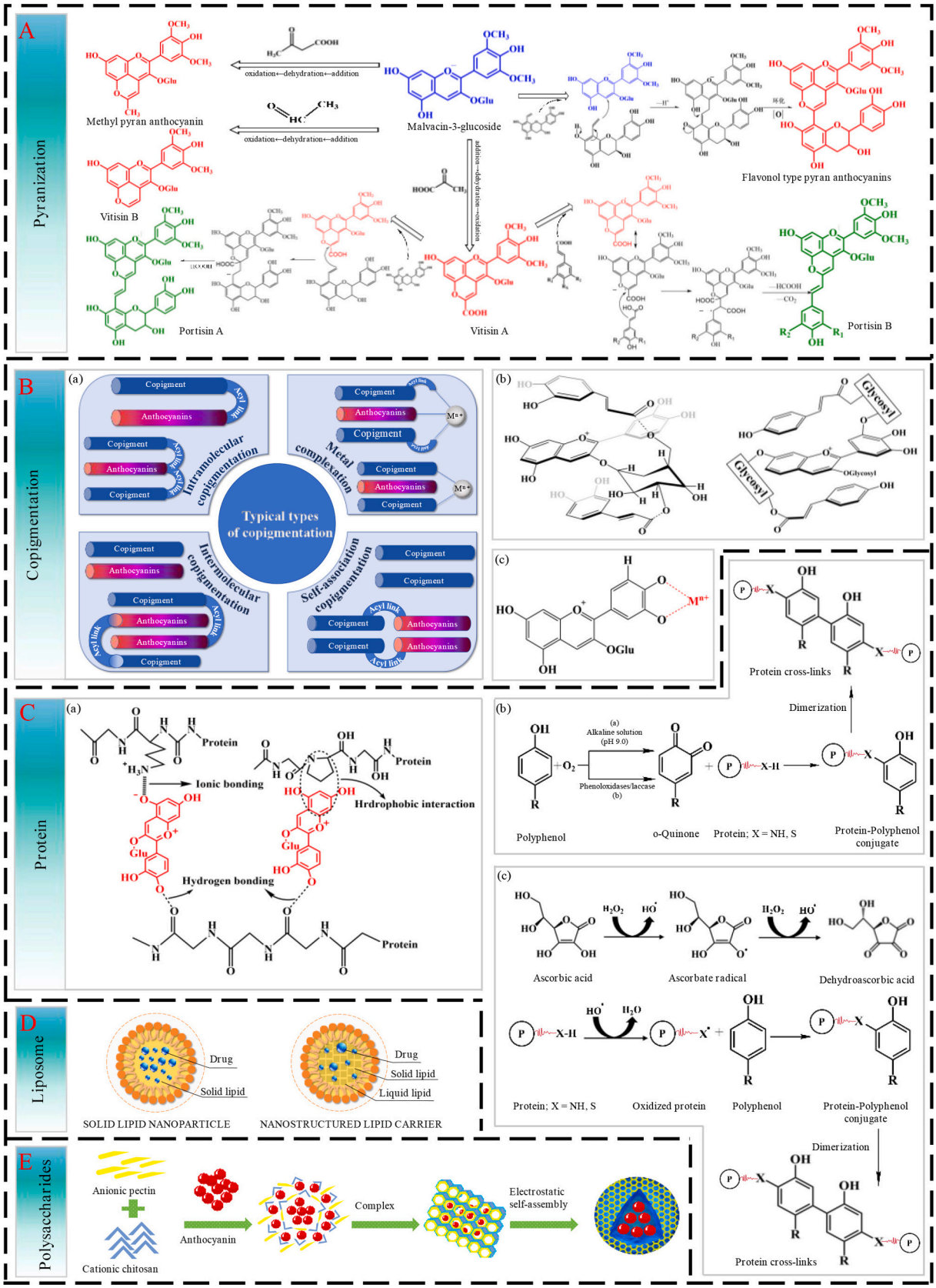

Fig. 4. The formation process and structure of common pyran-anthocyanins (A); improving the stability of anthocyanins through different copigmentation techniques (B); The intrinsic mechanisms by which anthocyanins bind to proteins in different forms (C); Structural diagram of SLN and NLC (D); Schematic diagram of pectin-chitosan nanoparticles loaded with anthocyanins (E).

and self-association are effective co-pigmentation methods to increase the stability of anthocyanins (Fig. 4 B-a) (Jiang, Qin, et al., 2019).

4.2.1. Intermolecular co-pigmentation

Intermolecular co-pigmentation refers to the non covalent binding of anthocyanins with non anthocyanin co-colorants through π-π interaction, hydrogen bonding, hydrophobic interaction van der Waals forces, and ion interaction. Among them, co-pigments have electron-rich π conjugated systems. Co-pigments form the π-π stacking state with anthocyanin molecules in space, protecting anthocyanins from water attack, which can produce the hyperchromic effect of solution and improve the stability of anthocyanins (Trouillas et al., 2016). Additionally, co-pigments can also serve as hydrogen bond donors or acceptors, thus enhancing the stability of anthocyanins. The strength of intermolecular co-pigmentation mainly depends on the structure of anthocyanins and co-colorants, concentration, pH, and temperature. Flavanols are an important class of co-colorants in red wine (Garcia-Marino, Escudero-Gilete, Heredia, Escribano-Bailon, & Rivas-Gonzalo, 2023). Flavanols, as the class of colorless polyphenols, have a typical catechol structure and contain a large number of phenolic hydroxyl groups. Both monomers and oligomers of flavanols can form intermolecular complexes with anthocyanins, which plays a color-stabilizing role in anthocyanins (Canuti et al., 2012; Ghasemifar & Saeidian, 2014). The non planar spatial structure of flavanols hinders the approach of anthocyanins molecules. Hence, the synergistic effect of flavanols is significantly weaker than that of hydroxycinnamic acid and flavonols (Gonzalez-Manzano, Duenas, Rivas-Gonzalo, Escribano-Bailon, & Santos-Buelga, 2009). Gras, Bogner, Carle, and Schweiggert (2016) found that co-pigments could enhance the color expression and thermal stability of anthocyanins when the concentration of co-pigments was 9.4 times that of anthocyanins. Gras, Bause, Leptihn, Carle, and Schweiggert (2018) added chlorogenic acid to non acylated anthocyanins at pH 3.6 and 4.6. The results show that its absorbance increased by 97.9 % and 122.9 %, respectively, further indicating that pH can affect the formation of anthocyanins co-pigment complexes. Temperature is an important factor affecting the co-pigmentation. High temperature can disrupt the non covalent interaction between anthocyanins co-pigment complexes, thereby disrupting the co-pigmentation (Sendri et al., 2023). Besides, previous study has found that the steric hindrance of co-pigments could reduce the non covalent interactions between anthocyanins and co-pigments, which was unfavorable for intermolecular co-pigmentation interactions (Gonzalez-Manzano et al., 2009). In addition to phenols, amino acids, organic acids, and polysaccharides can also serve as co-pigments to participate in co-pigmentation and further improve the stability of anthocyanins (Sendri et al., 2023).

4.2.2. Intramolecular co-pigmentation

Intramolecular co-pigmentation refers to the color change caused by the interaction of functional groups within anthocyanins molecules, and the main sites of action include acylation, methylation, and glycosylation structures. Anthocyanins themselves act as co-pigments and protect themselves through special conformations (Moloney et al., 2018). The planar polarizable nucleus of colored anthocyanins binds to other aromatic residues of the same or similar anthocyanins through hydrophobic interaction (π - π stacking). The accumulation of anthocyanins molecules in the co-pigments complex creates a sandwich structure (Fig. 4 B-b), which can prevent nucleophilic attack from water molecules (Wang et al., 2023). Otherwise, it will lead to the formation of colorless hydrated forms (*i.e.* hemiketal or chalcone), thereby improving the color stability of anthocyanins (Trouillas et al., 2016). Previous report have found that the intramolecular co-pigmentation effect of acylated anthocyanins was superior to the intermolecular co-pigmentation effect, and the acylated anthocyanins competitively hindered the intermolecular co-pigmentation effect (Escribano-Bailon & Santos-Buelga, 2012). Overall, the co-pigmentation effect can improve the color problem of anthocyanins. However, the co-pigmentation effect is unstable due to the poor stability and easy dissociation of the co-pigments themselves.

4.2.3. Self-association co-pigmentation

Self-association is a special type of intermolecular co-pigmentation. The molecules of anthocyanins mainly undergo hydrophobic interaction and vertically polymerize in a left-handed spiral manner, which can protect them from the nucleophilic attack of water, enhance the color expression of anthocyanins, and improve their stability (Trouillas et al., 2016). The concentration of anthocyanins has become one of the important factors affecting self-association due to the special intermolecular interaction of self-association. Previous study has confirmed that the concentration of anthocyanins solution needed to be greater than 1 mmol/L to undergo a self-association phenomenon (Gonzalez-Manzano, Santos-Buelga, Duenas, Rivas-Gonzalo, & Escribano-Bailon, 2008). Self-association plays a stabilizing role in the early wine-making process, reducing the loss of anthocyanins due to other factors, which have a significant impact on the final color of the wine. Therefore, the color change of self-association during the brewing process plays an undeniable role.

4.2.4. Metal complexation

The principle of metal complexation is that anthocyanin molecules combine with metal ions to form anthocyanin metal complexes, which further reacts with compounds (aglycones, sugars, and other co-colorants) to improve the stability of anthocyanins (Fenger, Robbins, Collins, & Dangles, 2020) (Fig. 4 B-c). These metal ions (Fe^{2+}, Fe^{3+}, Cu^{2+}, Mg^{2+}, K^{+}, Na^{+}, Ca^{2+}, and $A1^{3+}$) could form complexes with anthocyanins, which could improve the stability of anthocyanins (Fenger et al., 2020; Ratanapoompinyo et al., 2017; Sigurdson, Robbins, Collins, & Giusti, 2017). Anthocyanins initially cooperated with metal ions as connecting points and then interacted with other co-pigments to enhance their stability. In addition, the metal complexation-assisted color process required anthocyanins with a catechol or pyrogallol structure, which limited the metal complexation method to improve the stability of anthocyanins (Sigurdson et al., 2016).

4.3. Delivery system

Stabilizing the structure of anthocyanins, reducing their degradation rate in the gastrointestinal tract, and improving their cellular absorption rate have become urgent issues for the further application of anthocyanins in food, medicine, and other fields (Fraisse et al., 2020). Currently, delivery systems are an important method for effectively improving the stability and bioavailability of anthocyanins. Delivery systems are a type of targeted, localized, and controlled release drug delivery carrier system with broad application prospects. Delivery systems are the process of adsorbing, embedding, or directly connecting functional substances to a carrier. The problems of low solubility, poor stability, and limited absorption during drug delivery can be addressed by utilizing the physicochemical properties of the carrier and its selective distribution characteristics (Ma, Cheng, Jiao, & Jing, 2022). In addition, delivery systems can also increase the dissolution and absorption rates of drugs, thus improving their bioavailability. Overall, delivery systems have many advantages in drug delivery as follows (Jiang et al., 2023): 1) control drug release and prolong action time; 2) target drug delivery; 3) reduce medication dosage and alleviate or avoid adverse reactions while ensuring drug efficacy; 4) improve the stability and bioavailability of drugs. The delivery system provides an ideal delivery method for improving drug stability.

Microencapsulation is one of the effective strategies for improving the stability and bioavailability of anthocyanins, which plays an important role in anthocyanins delivery systems (Zhang et al., 2020). Microencapsulation refers to the encapsulation of bioactive substances in small sealed capsules in solid, liquid, or gas form, which maximizes their bioactivity, performance, and structure without being affected by

external environmental factors. In practical applications, microencapsulation have the advantages of improving drug stability, sustained-release or controlled release of drugs, masking drug odor, and focusing drugs on the target area (Ahmad, Ashraf, Gani, & Gani, 2018; Zhang et al., 2020). In microcapsule systems, bioactive compounds are referred to as core materials, while the materials surrounding the core materials are referred to as wall materials (Rocha et al., 2019).

In recent years, increasing studies have found that proteins, polysaccharides, and lipids are used as delivery carriers to prepare microcapsules, nanoparticles, lotion, and liposomes (Ko, Lee, Sop Nam, & Gyu Lee, 2017; Ma, Cheng, et al., 2022). These delivery carriers have excellent biocompatibility, safety, non-toxic, and other advantages. Hence, the above-mentioned delivery carriers can be used for the delivery of food functional factors, which have significant practical value in improving the stability of functional active substances. Currently, common anthocyanins delivery systems include (Ma, Cheng, et al., 2022) (Fig. 5): 1) protein-anthocyanin delivery system; 2) polysaccharide-anthocyanin delivery system; 3) liposome-anthocyanin delivery system; 4) composite delivery system. The sustained release of anthocyanins is crucial for the potential biological activities and bioavailability of the loaded substances (Okawa et al., 2021). Table 1 summarizes the advantages and disadvantages of different delivery systems.

Table 1
Advantages and disadvantages of different delivery systems.

Delivery systems	Advantage	Disadvantage
Protein delivery system	Enhance stability Enhance bioavailability Target delivery	Complicated process High cost Latent immune response
Polysaccharides delivery system	Enhance stability Excellent biocompatibility Sustained release Target delivery	Complicated process Solubility issue High technical requirements
Liposome delivery system	Enhance stability Enhance bioavailability Target delivery	Complicated process Poor storage stability High cost
Multiple emulsion delivery system	Enhance stability Sustained release Strong carrying capacity	Complicated process High technical requirements Poor storage stability Complicated process
Hydrogel delivery system	Enhance stability Sustained release High biocompatibility	High technical requirements Effect of water absorption

4.3.1. *Protein delivery system*

Common protein carrier materials include animal-derived proteins (whey protein, casein, and gelatin) and plant-derived proteins (soy protein and zein). Animal-derived proteins have good film-forming properties and good biocompatibility. In addition, animal-derived proteins can quickly disperse to form stable emulsions. Plant-derived proteins have abundant sources, low processing costs, good film-forming properties, and certain antioxidant properties. The interaction between anthocyanins and proteins mainly occurs through two methods, namely, non covalent binding and covalent binding. Non covalent interaction includes hydrogen bonding, van der Waals forces, hydrophobic interaction, and ionic interaction (Fig. 4 C-a). The non covalent binding between anthocyanins and proteins is mostly reversible, and this interaction is weaker than covalent binding (Liu, Ma, Gao, & McClements, 2017). Rose anthocyanin extract interacted with whey protein, and its main forces were hydrogen bonding and van der Waals forces (Wang, Zhang, & Zhang, 2022). Mulberry anthocyanins and soy protein isolate could form complexes through hydrophobic interaction, which contributed to the improvement the stability and biological activities of anthocyanins (Ma et al., 2022b). Rose anthocyanins were bound to plant proteins through hydrophobic interaction and ionic bonds, which could significantly improve the digestibility of plant proteins by gastric proteases and the thermal stability of anthocyanins (Wang et al., 2023a). The covalent binding between anthocyanins and proteins is generally irreversible, and covalent binding has high stability and strong interaction (Liu, Ou, et al., 2017). Notably, proteins and anthocyanins conjugates can be covalently formed through enzymatic or non enzymatic (alkaline reaction (Fig. 4 C-b) or free radical grafting (Fig. 4 C-c) methods. Enzymatically synthesized proteins and anthocyanin conjugates exhibited strong free radical scavenging activity and a more stable structure (Gu et al., 2017). The free radical grafting reaction is the formation of covalent bonds between redox hydroxyl radicals through oxidation and protein side chain amino acids. Anthocyanins and

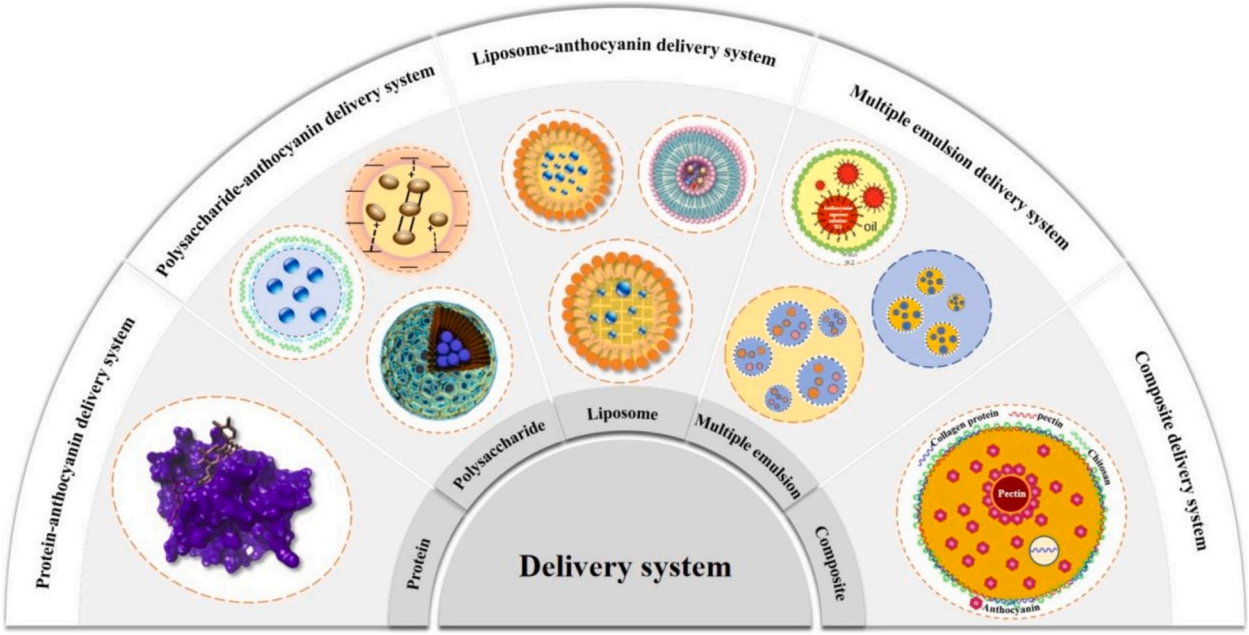

Fig. 5. Common 5 types of anthocyanin delivery systems.

proteins generated conjugate through free radical grafting reaction, which was beneficial for improving the stability and antioxidant activity of anthocyanins (Quan, Benjakul, Sae-leaw, Balange, & Maqsood, 2019). Black bean protein isolate bound to anthocyanins through hydrophobic interaction, which could increase the α-helix and β-folding content of protein, reduce the β-corner content, and improve the thermal and structural stability of anthocyanins (Wang & Xie, 2019). Liu, Lin, Cheng, Liu, and Han (2022) found that the secondary structure (decreasing α-helix content and increasing β-folding content) of zein changed after the binding of zein and anthocyanins and improved the stability of anthocyanins. A complex formed by the combination of natural purple potato protein and anthocyanins. The complex could protect the structure of anthocyanins from external factors and enhance their anti-inflammatory and antioxidant activities (Jiang et al., 2020). Zang et al. (2021) interacted blueberry anthocyanins with whey protein/bovine serum protein, which could improve the stability of anthocyanins under light, high temperature, and ascorbic acid to some extent. In addition, this interaction simultaneously increased the solubility, foaming, and emulsifying properties of proteins and reduced their surface hydrophobicity and Zeta potential. The combination of silkworm pupa protein and cyanidin-3-glucoside (C3G) could improve the thermal and oxidative stability of C3G (Attaribo et al., 2020). β-lactoglobulin bound non covalently to C3G, which could significantly improve the ability of C3G to scavenge DPPH and ABTS radicals (Meng et al., 2021). Based on the above analysis, it was found that the interaction between proteins and anthocyanins not only enhances the stability and biological activities of anthocyanins, but also changes the structure and properties of proteins, improves emulsifying and foaming properties, and reduces surface hydrophobicity. Moreover, anthocyanins also can change the secondary and tertiary structures of proteins by coupling with plant proteins, which contributes to increasing the stability and digestibility of protein.

Whey protein and casein, as the main components of natural milk protein, are often used as wall materials to protect bioactive substances. Whey protein is a dense spherical protein with high hydrophilicity, while casein contains a large number of hydrophilic and hydrophobic groups. Casein often exists in the form of spherical micelles. Liao et al. (2022) used casein and whey protein to combine with anthocyanins to prepare anthocyanins loaded particles by spray drying technology. The results indicate that anthocyanins bound to C, N, and O in the peptide chain of proteins through hydrogen bonding. The embedding rates of casein and whey protein particles for anthocyanins were 49.73 % ± 0.68 % and 59.99 % ± 0.49 %, respectively. Moreover, the non covalent binding of anthocyanins and proteins altered the tertiary structure of proteins, which contributed to enhancing the hydrophilicity of endogenous hydrophobic amino acids. Casein and whey proteins loaded with anthocyanins exhibited stable protein structures in gastric juice through *in vitro* gastrointestinal digestion simulation, which was beneficial for maintaining the structure of particles and preserving anthocyanins. Oancea et al. (2017) prepared microcapsules of whey protein and anthocyanins by enzymatic cross-linking method. The encapsulation efficiency of microcapsules for anthocyanins was 64.69 % ± 0.24 %. More than 80 % of anthocyanins are retained in microcapsules during gastric digestion. In the intestine, the release of anthocyanins ranged from 55 % to 60 %, indicating that anthocyanins exhibit more stable release and absorption.

After encapsulating anthocyanins in microcapsules, the bioavailability of anthocyanins further improved. Wu, Hui, Mu, Brennan, and Brennan (2021) prepared microcapsules of whey protein and anthocyanins by spray drying and freeze drying, respectively. The encapsulation efficiency of anthocyanins in microcapsules prepared by spray-drying method was 99.64 % ± 0.16 % higher than that of the freeze-drying method 95.43 % ± 0.14 %. Moreover, both microcapsules could effectively control the release of anthocyanins and inhibit α-amylase activity, further indicating that anthocyanins bind tightly to proteins and effectively control their release in the stomach.

4.3.2. Polysaccharides delivery system

Polysaccharides are a type of natural polymer formed by multiple monosaccharides connected by glycosidic bonds. Polysaccharides have some merits including low prices, strong biological activities, and stable structure. Moreover, polysaccharides also have good biodegradability. Therefore, polysaccharides are widely used in microcarrier drug delivery systems. The molecular structure and functionality of polysaccharides such as agar, alginate, carrageenan, chitosan, cellulose, guar gum, pectin, starch, and xanthan gum largely depend on their biological sources, extraction method, and subsequent processing method. The interaction between anthocyanins and polysaccharides mainly occurs through two methods including non covalent binding and covalent binding. Fu et al. (2023) found that purple potato anthocyanins with pectin, inulin, starch, and cellulose were compounded through electrostatic interaction, which could significantly improve the stability and antioxidant activity of anthocyanins. Arabic gum and anthocyanins bound through hydrogen bonds to enhance the stability of anthocyanins under the action of ascorbic acid (Chung, Rojanasasithara, Mutilangi, & McClements, 2016). Berry anthocyanins and fucoidan formed the complex through π-π stacking and electrostatic interactions. The complex showed higher cell permeability and plasma chemical stability than free anthocyanins. Moreover, the complex could inhibit inflammation and cancer production. The bioavailability of the complex was 3.24 times higher than that of free anthocyanins (Lee et al., 2020). Tan, Selig, and Abbaspourrad (2018) prepared a complex by complexing chitosan with chondroitin sulfate and then combined it with anthocyanins. The results show that the embedding rate of the complex for anthocyanins was 88 %. Additionally, the complex could improve the stability of anthocyanins under high temperature and ascorbic acid conditions. Zou et al. (2021) combined anthocyanins with alginate through electrostatic interaction and hydrogen bonding to form microcapsules. The encapsulation efficiency of microcapsules for anthocyanins was 84.2 %. Besides, microcapsules could improve the stability of anthocyanins. Zhao, Zhang, et al. (2020) prepared nanoparticles by mixing chitosan, pectin, and anthocyanins in different proportions (Fig. 4E). The particle size of the nanoparticles ranged from 100 nm to 300 nm. The embedding rate of nanoparticles for anthocyanins was 66.68 %. The embedded anthocyanins had controlled release ability in the gastrointestinal tract. Besides, the encapsulated anthocyanins could accelerate the apoptosis of tumor cells. Mehran, Masoum, and Memarzadeh (2020) prepared microcapsules by using corn starch, maltodextrin, and anthocyanins. Microcapsules could enhance the antioxidant activity and stability of anthocyanins. Moreover, the dissociation of acetyl groups in modified corn starch generated intermolecular repulsion, which further disrupted the microcapsule structure and accelerated the release of anthocyanins in the intestine. Overall, nanoparticles and microcapsules loaded with anthocyanins can effectively enhance the biological activities and color stability of anthocyanins at high temperature. At present, research is no longer focused on a single polysaccharide nano encapsulated anthocyanins. However, current research mainly focuses on utilizing the structural characteristics of anthocyanins and cleverly introducing a combination of *co*-pigmentation and polysaccharides delivery, which can achieve a dual improvement in the stability and biological activities of anthocyanins.

4.3.3. Liposome delivery system

Liposome delivery systems with good bioavailability and therapeutic effects have been recognized as a method to improve the limitations of drug delivery *in vivo*. Liposomes are bilayer microsphere-shaped vesicles composed of phospholipids or synthesized amphiphilic compounds, which have hydrophobic and hydrophilic regions (Sun et al., 2021). The liposome delivery system is formed by hydrophobic interaction as the main driving force and other intermolecular forces, which can be used to deliver various hydrophilic and hydrophobic substances. Liposomes are non-toxic, non immunogenic, biocompatible, biodegradable, and amphiphilic. Therefore, liposomes have broad application prospects in

delivering drugs and food. Chi et al. (2019) optimized the preparation process of anthocyanin nanoliposomes by using response surface methodology. The results show that the optimal process for preparing anthocyanin nanoliposomes was obtained as follows: the temperature of 25 °C and average liposome particle size of 53.01 nm, and the retention rate of anthocyanins was 85.60 % under the above conditions. Zhao et al. (2017) prepared liposome capsules loaded with anthocyanins by using an improved supercritical carbon dioxide (SC-CO_2) method. The results show that the encapsulation efficiency and particle size of liposome capsules were 50.6 % and 159 nm ± 0.2 nm, respectively. Sun et al. (2021) prepared nanoliposome capsules loaded with anthocyanins by using a combination of ethanol injection and ultrasound methods. The results show that the capsule embedding rate was 91.1 % ± 1.7 %, and the particle size of nanoliposome capsules was smaller than that of the unloaded liposomes, which was more conducive to the intestinal release of anthocyanins. Mounting studies have confirmed that liposomes had good development prospects for the delivery of anthocyanins, which could improve the stability of anthocyanins, retain their original biological activities, and fully release them at the main absorption sites (Chi et al., 2019; Sun et al., 2021). Compared with liposomes, solid lipid nanoparticles (SLN) had better drug stability and longer release time. Based on the original SLN, adding liquid lipids to SLN could form nanostructured lipid carriers (NLC). NLC could improve the stability and loading capacity of drugs. In addition, NLC could control the release rate of drugs at specific locations and improve the bioavailability of drugs. The difference between NLC and SLN lay in the composition of the solid matrix (Viegas et al., 2023) (Fig. 4D). Ravanfar, Tamaddon, Niakousari, and Moein (2016) prepared anthocyanins-SLN by using palmitic acid, pluronic F127, lecithin, and span 85. The results show that the embedding rate and average particle size of SLN were 89.2 % ± 0.3 % and 455 nm ± 2 nm, respectively. Pimentel-Moral et al. (2019) loaded wood hibiscus anthocyanins into NLC. The results show that the average particle size and embedding rate of anthocyanin-NLC were 344 nm ± 12 nm and 84 % ± 4 %, respectively. Transmission electron microscopy and Fourier transform infrared analysis indicate that the interaction between lipids and polyphenols improved the physical and chemical stability of NLC particles. All in all, both SLN and NLC have high value in the delivery of anthocyanins. Further in-depth research is needed on the utilization of SLN and NLC-loaded anthocyanin delivery systems in simulating gastrointestinal digestion in the future.

4.3.4. Multiple emulsion delivery system

Double emulsion, also known as secondary emulsion, is a composite system with a double-layer or multi-layer emulsification structure formed by further emulsification based on a single emulsion. The single emulsion is wrapped in another continuous phase, which can be simply divided into oil in water single layer emulsion dispersed in the oil phase (O/W/O), water in oil single layer emulsion dispersed in the water phase (W/O/W), solid dispersed in the oil phase and then dispersed in the continuous water phase (S/O/W). Double emulsion, as a carrier, can protect the internal aqueous or oil phase substances from external influences. In addition, double emulsion has some advantages including sustained release, targeted release, and reduced use of certain food ingredients (Aditya, Espinosa, & Norton, 2017). Although the double emulsion system has enormous potential for application, its inherent thermodynamic and kinetic instability limits its application in food (Kanha, Surawang, Pitchakarn, & Laokuldilok, 2020). Therefore, it is necessary to study a new type of compound milk system to improve its stability. Aniya et al. (2022) used xanthan gum (1 %) and pea protein to form a double emulsion. Compared with pure pea protein emulsion, double emulsion exhibited the smaller particle size, lower emulsification index, higher Zeta potential absolute value and encapsulation efficiency, and higher thermal stability. Kanha et al. (2021) used gelatin and Arabic gum B as double emulsions. The results indicate that the double emulsion could slow down the release of free fatty acids and prolong the protection of anthocyanins. In addition, the release of spray-dried microcapsules in simulated gastric juice was mainly a diffusion mechanism. The release of freeze-dried microcapsules in simulated gastric and intestinal fluids was mainly achieved through erosion and destruction of the wall material to release anthocyanins. Kanha et al. (2020) prepared four types of composite coagulation double emulsion microcapsules by combining the co-pigmentation effect and carrier delivery system. The results show that all four types of microcapsules could enhance the antioxidant capacity, stability, and encapsulation efficiency of anthocyanins. The stability of double emulsions is decided by the primary emulsion and the secondary emulsion and is also affected by the emulsification mechanism. Pickering particles have been commonly used as stabilizers to improve the stability of emulsion systems. The emulsion system uses solid particles instead of surfactants to inhibit droplet coalescence (Jiang, Sun, & Zhang, 2024; Yang, Wang, Lan, Sun, & Li, 2009). Moreover, the stable emulsion of the system is achieved by utilizing the adsorption of particles on the surface of oil droplets. The stability of emulsions is mainly achieved by increasing steric hindrance and changing the interfacial properties or rheological properties of continuous phases (Muiz, Klojdova, & Stathopoulos, 2023). The inner phase encapsulates sensitive active substances to improve stability and control their release in the gastrointestinal tract. Compared with the traditional W/O lotion, Pickering lotion has lower fat and salt content, which is in line with the trend of the modern human diet.

4.3.5. Composite delivery system

The stability of anthocyanins can be improved through the interaction between a single wall material and anthocyanins to a certain extent. A single wall material cannot possess all the necessary characteristics. Hence, mounting studies are improving the embedding effect of active ingredients by compounding the proportions between different wall materials. Righi da Rosa et al. (2021) prepared anthocyanin capsules with various composite wall materials. The results indicate that the composite wall materials have higher encapsulation efficiency. The embedding rate of anthocyanins in all three composite wall materials was higher than 60 %. In addition, the composite wall material showed the ability to control the release of anthocyanins in simulated gastric juice. Dumitrascu et al. (2021) used soybean protein and maltodextrin for spray drying to embed anthocyanins. The results display that the surface of anthocyanins appeared as a thin film sphere and was retained in the form of droplets after embedding, which significantly improved the stability and bioavailability of anthocyanins. Wang et al. (2021) utilized chitosan hydrochloride, carboxymethyl chitosan, and whey protein isolate as carriers to embed anthocyanins in nanocomposites. The nanocomposites exhibited the ideal particle size (332.20 nm), zeta potential (23.65 mV), and high encapsulation efficiency (60.70 %). The antioxidant capacity of embedded anthocyanins was stronger than that of non embedded anthocyanins. A double-layer coating formed by cross-linking whey protein and chitosan derivatives during simulated *in vitro* digestion. The combination of double-layer coating and anthocyanins improved the stability of anthocyanins in a high pH environment and prevented their degradation during intestinal digestion. In addition to microcarrier delivery systems, some researchers have combined co-pigmentation with microcarrier delivery systems to improve the stability of anthocyanins. Tan et al. (2019) developed a stable, efficient, and multifunctional core-shell nanostructure for delivering anthocyanins by using bovine serum albumin and chondroitin sulfate. The formation of double nanoshell water core nanocapsules was driven by covalent bonds and electrostatic interaction. Chondroitin sulfate and bovine serum albumin formed strong cross-linking through disulfide and amide bonds between proteins, enhancing the encapsulation of anthocyanins by the cross-linked shell. The combination of co-pigmentation effect and embedding could improve the stability of the entire system. The embedding rate of anthocyanins by co-pigmentation effect 54.6 % ± 1.4 % was higher than that by the individual embedding effect 47.4 % ± 1.6 %. Pan et al. (2022) used 4 % soy protein isolate and 2 % high methyl pectin to prepare microcapsules by spray drying, and then embedded

blueberry anthocyanins. The results indicate that microcapsules exhibited superior controlled release, sustained release, and stable antioxidant properties of anthocyanins. The half-life of the embedded anthocyanins was the longest and the degradation rate was the lowest at 25 °C and 35 °C. In addition, compared with the traditional microcapsule delivery, hydrogels have better biocompatibility and regulatory properties. Hydrogels are a kind of hydrophilic three-dimensional network structure gels due to their cross-linking network. Hydrogels can swell and retain a lot of water, and the amount of water absorption is closely related to the degree of cross-linking (Li et al., 2023). Compared with the low cross-linking degree, gel with the high cross-linking degree showed lower water absorption. Water-soluble polymers form hydrogels through chemical or physical cross-linking. Hydrogels can be divided into two categories according to the source as follows: 1) natural high molecular weight polymers, including sugars and peptides; 2) synthetic high molecular weight polymers. However, synthetic hydrogels have disadvantages including low strength, poor toughness, and slow absorption of water, which cannot meet the application requirements. Composite hydrogel is a kind of functional material with high water content, which is a three-dimensional network structure formed by physical or chemical cross-linking of two or more different types of polymer materials. Composite hydrogels combine some advantages such as excellent mechanical properties, biocompatibility, stimulation responsiveness, and drug loading capacity. Li et al. (2023) utilized the chemical cross-linking method to prepare anthocyanin/chitosan salicylaldehyde hydrogel with salicylaldehyde as a cross-linking agent. The results show that the hydrogel not only improved the thermal stability of anthocyanins, but also showed good pH responsiveness. Wu, Jia, Fu, and Xia (2020) prepared a multiple lotion hydrogel ball with chitosan hydrogel as the raw material. The encapsulation efficiency of proanthocyanidins was 78.47 %, and the ball had good stability when stored in the dark at 25 °C. Zhang et al. (2020) adopted a new emulsification/internal gel combined with spray/freeze drying technology, which was conducive to gel showing high encapsulation efficiency and small particle size. In simulating the stomach and intestinal digestive tract, the retention rates were above 70 % and 15 %, respectively. Chen, Zhang, Tang, and Li (2020) found that the encapsulation efficiency of calcium-induced sodium alginate-pectin composite gel for purple potato anthocyanins was 1.10 mg/mL. Moreover, the encapsulation effect of gel effectively alleviated the degradation of purple potato anthocyanins by gastric juice. In summary, a single wall material often has certain defects and cannot achieve the ideal embedding effect. The composite wall materials can effectively improve the embedding effect, enhance the stability of anthocyanins, and regulate the controlled release and sustained release of anthocyanins in the intestine. However, the composite wall materials pose certain obstacles to the biological activities of anthocyanins. Therefore, the type, proportion, and interaction between wall materials and anthocyanins need to be fully considered to maximize the bioavailability of anthocyanins.

5. Conclusions and prospects

In recent years, significant progress has been made in the potential molecular mechanisms of anthocyanins in antioxidant, anti-inflammatory, anti-tumor, and immune regulation activities. However, anthocyanins have poor stability and are easily affected by external factors. These unstable factors (temperature, light, pH, *etc.*) can cause significant degradation of anthocyanins. Some advanced techniques for structural modification of anthocyanins have been proposed to improve the stability of anthocyanins. Currently, acylation and pyranization modifications are the most important ways to modify the structure of anthocyanins. Acylated anthocyanins have been extensively studied in artificial reactions, among which acylated anthocyanins have high stability and strong antioxidant properties. Besides, acylated anthocyanins can better maintain the color of the solution. However, acylated anthocyanins generally suffer from low conversion rates. Most studies have not determined the structure of acylated anthocyanins, and there is also little research on their physicochemical properties. Pyran-modified anthocyanins have advantages in bioavailability and biological activities, while maintaining their original water solubility. The artificial synthesis time required for pyranization modification is relatively long. In addition, the structures of esterification and acylation compounds of anthocyanins are not clear, and there is relatively little research on their physiological activities. Effectively solving the problem of structural modification of anthocyanins is the most important aspect of anthocyanins as new antioxidants and natural pigments. The co-pigmentation effect also improves the stability of anthocyanins to a certain extent. However, there are also certain tests of the structural stability of the co-pigments themselves, and further in-depth research and evaluation are needed on the safety of wall materials. Moreover, microencapsulation can improve the stability of anthocyanins to a certain extent, and microencapsulation also can target the delivery of anthocyanins and reduce their degradation in the gastrointestinal tract. Furthermore, the development of nanotechnology has also provided new strategies for the study of anthocyanin delivery. Notably, there is currently limited research on the structure-activity relationship between delivery systems composed of different wall materials and anthocyanins, as well as the binding sites between anthocyanins and wall materials. The evaluation of anthocyanins delivery systems is currently mainly based on *in vitro* gastrointestinal simulation systems. In the future, further animal and human experiments are needed to study the pharmacokinetics of embedded anthocyanins *in vivo* and clarify the absorption rates and bioavailability of various delivery systems. The findings can provide basic data for the development of anthocyanin products. In the future, the anthocyanin delivery system will develop towards intelligence, precision, multifunctionality, and green environmental protection in the future. Firstly, the intelligent delivery systems will respond to multiple stimuli such as pH, temperature, and light, thus achieving precise release of anthocyanins and enhancing drug efficacy. Secondly, precision will be combined with targeted molecules to improve the delivery efficiency of anthocyanins in target tissues or cells and promote personalized and precision medicine. Nanotechnology will enhance the penetration and stability of delivery systems, and improve the bioavailability of anthocyanins. At the same time, the multifunctional delivery systems will achieve collaborative delivery and integrated diagnosis and treatment, improving the comprehensive treatment effect. Finally, more green and environmentally friendly materials and preparation technologies will be adopted to ensure the biodegradability and safety of the system, meeting the needs of sustainable development. With the help of digital and artificial intelligence technology, the design and optimization of conveyor systems will be more efficient, which can effectively promote their widespread application in fields such as medicine, food, and cosmetics.

Funding

The authors gratefully thank the financial support provided by China Postdoctoral Science Foundation (2023M733795), Medical Science Foundation of Hebei University (2022B12 and 2023B11), Hebei Provincial Natural Science Youth Fund (C2023201015 and C2024201007), and Hebei Province Higher Education Science and Technology Research Project (QN2023227), and Shijiazhuang Basic Research Program General Project (241791447A).

CRediT authorship contribution statement

Hongkun Xue: Writing – original draft, Investigation, Formal analysis. **Jianduo Zhao:** Writing – original draft, Investigation, Formal analysis. **Yu Wang:** Formal analysis, Investigation, Writing – original draft. **Zhangmeng Shi:** Investigation, Formal analysis. **Kaifang Xie:** Investigation, Formal analysis. **Xiaojun Liao:** Writing – review & editing, Project administration, Funding acquisition. **Jiaqi Tan:** Writing –

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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