Hybrid Pigments Based on Anthocyanins and Clay Minerals: A Mini Review

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Abstract: The synthesis of hybrid pigments has been studied as these provide a safer alternative to modern synthetic pigments that are stable but are unsafe. This paper provides a systematic review of previous research on hybrid pigments composed of anthocyanins combined with different mineral clays, particularly saponite, montmorillonite, halloysite, palygorskite, and sepiolite. The research was carried out by summarizing the related literature cited and comparing each paper to another by the processes that were used and interactions that occurred in creating the hybrid pigment. The findings showed that the literature cited used adsorption as the method of combining the anthocyanin dye and the mineral clays used; the interactions that occurred were the intercalation of the dye and stabilizer used. Additionally, it was shown that the hybrid pigments exhibited improvement with respect to their stability in different areas, particularly pH, chemical, thermal, color, and light stability. Overall, the paper has shown the development and improvement in hybrid pigment research, particularly with anthocyanin hybrid pigments.

Key Words: hybrid pigments; anthocyanins; clay minerals

1. INTRODUCTION

Pigments have played an important role in multiple industries, particularly the food, automotive, plastic, and paint industries (Bruni et al., 2019). Natural pigments are organic pigments derived from organic sources such as plants, animals, and fungi (Dufosśe, 2014). These plant-based natural dyes and pigments are useful but are unstable, meaning they are susceptible to fading and possess poor colorfastness (Kasiri & Safapour, 2013). Synthetic inorganic pigments are used in different applications across different industries for their incredible stability, although their disadvantage is their toxicity (Venil & Lakshmanaperumalsamy, 2009). With these in mind, the synthesis of hybrid pigments has been studied as hybrid pigments are a combination of the qualities of both organic and inorganic materials.

In order for a hybrid pigment to be produced, a natural pigment source will have its dye extracted through different methods. After the dye is extracted, another set of processes is done to combine the dye and the inorganic material, such as a binder or a stabilizer. It is incorporated into the composition of the pigment to improve the quality of the colorant, making a hybrid pigment in the process (Li et al., 2019). Current research papers have shown different results depending on the materials used and the processes involved in creating the hybrid pigment.

The information produced by each paper contributes to the existing body of knowledge regarding hybrid pigments, although papers which summarize these research papers for convenience are not common. The research gap presents itself, as there is a need for organized information and knowledge regarding hybrid pigments. This paper aims to summarize past research regarding the production of hybrid pigments and discuss the processes, chemical interactions, and results of the cited literature.

As discussed, organic pigments are environmentally friendly and safe to use compared to inorganic pigments that are more stable but harmful. Hybrid pigments are created to combine the stability and safety of both, although there is a lack of organized information regarding hybrid pigments. The objective of this research is to address the following research statements:

a) Identify past research that discusses hybrid pigments created with anthocyanins and different stabilizers.
b) Determine the processes and chemical interactions brought about by the experimentation.
c) Compare the pigments produced based on the processes, safety, and stability given the information gathered from past research.

The paper discusses different research done in the past regarding hybrid pigments, which will involve the combination of a dye or colorant, specifically anthocyanin, stabilizers including saponite, montmorillonite, halloysite, palygorskite, and sepiolite. The paper will only cover descriptions of the materials, processes involved in creating hybrid pigments, interactions between the anthocyanin and the stabilizer, and results from each of the experiments performed. The research will be done to help gather the existing knowledge into one paper which would serve as a review of literature for the research papers used and cited. This would help add convenience to future researchers, as the summary paper will help provide the necessary information needed by the researchers to gain a better understanding of hybrid pigments, particularly those made using anthocyanin as the dye material and stabilizers previously mentioned.

2. COMPARISON RESEARCH

The research was carried out by gathering and summarizing multiple research papers regarding hybrid pigments specifically made with anthocyanin dyes and clay minerals such as saponite, montmorillonite, halloysite, palygorskite, and sepiolite. The papers were sourced from different articles and journals from websites such as Google Scholar, ResearchGate, and ScienceDirect.

Anthocyanins were chosen due to their versatility in a variety of applications as well as their abundance in the environment. These compounds exhibit the potential as better industrial colorants, health supplements, and as a component in the development of solar-based, renewable energies (Silva et al., 2017). Singh et al. (2018) cite that anthocyanins are extracted from numerous sources, including flowers, fruits, vegetables, and leaves, thus being a renewable resource.

The clay minerals used were chosen based on the availability of papers that used anthocyanin dyes in creating the hybrid pigment. According to Trigueiro et al. (2018), clay minerals have layered structures and are capable of ion exchange, thus being useful as stabilizing agents for anthocyanins. The ion exchange capacity contributes to the intercalation process with the help of intermolecular forces. The research studies cited were compared to each other by determining the process used in combining the dye and stabilizer, the interactions that occurred, as well as the characteristics of the pigment produced and its applications.

Table 1. *Summary of Cited Research based on Processes Used and Interactions*

Hybrid Pigment	Stabilizer (Reagents Used)	Processes Used	Interactions	Researchers
(1) anthocyanin-saponite	modified saponite (saponite + cetyltrimethylammonium bromide (CTAB))	Adsorption	Intercalation	Lima, Castro-Silva, Silva-Filho, Fonseca, & Jaber (2020)
(2) anthocyanin-saponite	modified saponite (deionized water + hydrofluoric acid + sodium acetate + magnesium acetate tetrahydrate + basic aluminum acetate + silica)	Adsorption	Intercalation	Lima, Silva, Silva-Filho, Fonseca, Zhuang, & Jaber (2020)
(3) anthocyanin-saponite	synthetic saponite (methanol + hydrochloric acid)	Adsorption	Intercalation	Ogawa, Takee, Okabe, & Seki (2017)
(4) anthocyanin-montmorillonite, anthocyanin-halloysite	montmorillonite and halloysite	Adsorption	Intercalation	Li, Mu, Wang, Kang, & Wang (2019)
(5) anthocyanin-montmorillonite	montmorillonite	Adsorption	Intercalation	Ribeiro, Oliveira, Brito, Ribeiro, Souza, Filho, & Azeredo (2018)
(6) anthocyanin-palygorskite	palygorskite	Adsorption	Intercalation	Li, Ding, Mu, Wang, Kang, & Wang (2019)
(7) anthocyanin-sepiolite	sepiolite	Adsorption	Intercalation	Silva et al. (2019)

Table 1 shows a summary of the different research papers cited in this paper. It is noted that several reagents mentioned in the table are modified versions of existing clay minerals to improve the quality of the hybrid pigment further. Adsorption, a process in which a dye and stabilizer solution is centrifuged and left out to dry for the dye to adhere to the stabilizer's surface, is the method commonly used in the cited studies to combine the anthocyanin pigment with the stabilizers (Britannica, 2013). This was the chosen method as clays have high adsorption capacity and are capable of ion-exchange (Trigueiro et al., 2018). The adsorption process, despite being done with different clay minerals, exhibited the same interaction throughout. As explained in a paper by Lagaly, Ogawa, and Dékány (2012), intercalation occurs when molecules from a compound penetrate another compound's layers. In this case, the anthocyanin dyes intercalated into the mineral clays' layers in each of the respective research to form hybrid pigments. Dipole forces attract both the dye and clay together, causing deformation in the interlayers by slowly widening the space between two clay layers. Once the space is large enough, the rest of the dye molecules enter the interspace, combining with the clay and forming a hybrid pigment.

Table 2. *Summary of Cited Research based on Characteristics, Color, Stability, and Application of Pigments*

Hybrid Pigment	Characteristics of Pigment	Pigment Color	Stability	Applications
(1) anthocyanin-saponite	Pigment is able to change color by manipulating pH level of the environment	pink/blue	Exhibited good stability against visible light and basic pH conditions	Atmospheric acidity sensor
(2) anthocyanin-saponite	Pigment is able to change color by manipulating pH level of the environment; pigment is observed to be environmentally friendly	pink/blue	Exhibited good stability against visible light and basic pH conditions	Atmospheric acidity sensor
(3) anthocyanin-saponite	Pigment is able to change color by manipulating pH level of the environment	light pink/light blue	Exhibited good pH stability	Color-changing advanced pigment
(4) anthocyanin-montmorillonite, anthocyanin-halloysite	Pigment is able to change color by manipulating pH level of the environment	dark brown/ light brown and pale red/light yellow, respectively.	Exhibited good thermal and chemical stability	pH indicators
(5) anthocyanin-montmorillonite	Higher concentrations of montmorillonite contribute to more stability.	red/dark red	Improved pH and color stability	Anthocyanin-based colorants
(6) anthocyanin-palygorskite	Pigment exhibited excellent acid/base allochronic behavior	bright pink/steel gray	Exhibited thermal and chemical corrosion resistance	Intelligent film that can detect the freshness of food
(7) anthocyanin-sepiolite	Hue, color, and stability of pigments are pH dependent	peach, orange, green, light purple, and yellow	Improved color and thermal stability	Fluorescent hybrid pigments

Table 2 shows a summary of the cited research, specifically on the characteristics of and stability of the pigments produced. It was observed that most of the pigments produced are affected by the pH level. The research cited showed that a color change occurs when the pH level is manipulated wherein the process was carried out by exposing the hybrid pigment in an acidic atmosphere using hydrochloric acid (HCl) and then exposing it in a basic atmosphere using either ammonium hydroxide (NH4OH) or ammonia (NH3) for at least 6 to 10 minutes per exposure in a desiccator. Li et al. (2019) used slow oscillation at 70 revolutions per minute (rpm) for 24 hours at room temperature after applying the pigment into 10mL of hydrochloric acid and 10mL ammonium hydroxide, respectively. Silva et al. (2019) used sodium borate buffer solutions with a pH level of 10 and sodium acetate buffer solutions with pH levels of 4, 5, and 6 that were mixed with a sample of the pigments made and was stirred for 24 hours and was centrifuged and dried. This characteristic contributes to the overall stability of the pigment, particularly the chemical and pH stability of the produced pigment. It was also observed in the research done by Lima et al. (2020) that the pigments were environmentally friendly, making them a potentially useful pigment in terms of sustainability and safety. This is due to hybrid pigments possessing the carbon-based structures of natural pigments which are considered to be environmentally friendly as these do not generally include heavy metals or similar chemicals that are toxic and can cause damage to the environment but at the same time, possessing the stability and durability of inorganic materials (Bruni et al, 2019; Ebrahimi & Gashti, 2015; Li et al 2019). Ribeiro et al. (2020) mentioned that higher concentrations of montmorillonite contribute to more stability, which was observed throughout the experimentation.

The colors exhibited by the hybrid pigments made in each of the research varied across the research cited. It was observed in anthocyanin-saponite hybrid pigments produced in the research done by Lima et al. (2020a), Lima et al. (2020b), and Ogawa et al. (2017) that the colors exhibited by the hybrid pigment were pink or blue, although the pigment exhibited by Ogawa et al. (2017) was shown to exhibit lighter variants of the colors mentioned. The colors of the pigments are capable of changing from pink to blue depending on the pH level, wherein the hybrid pigment becomes pink when exposed to an acidic environment or blue when exposed to a basic environment. This principle also applies to the pigments produced by Li et al. (2019a) which exhibited dark brown or light brown colors for the anthocyanin-montmorillonite hybrid pigment and pale red or light-yellow colors for the anthocyanin-halloysite hybrid pigment; Ribeiro et al. (2018) which exhibited red or dark red colors for the anthocyanin-montmorillonite hybrid pigment and Li et al. (2019b) which exhibited bright pink or steel gray colors for the anthocyanin-palygorskite hybrid pigment. Lastly, the pigment produced by Silva et al. (2019) showed a variety of colors which included peach, orange, green, light purple, and yellow, as the pigments produced in this research were aimed to be bright and fluorescent, hence the large variety of colors. The differences in colors were mainly due to the different sources of anthocyanins used in each of the respective research cited.

All pigments have exhibited better stability in different aspects. The anthocyanin-saponite hybrid pigments by Lima et al. (2020a), Lima et al. (2020b), and Ogawa et al. (2017) have shown to be resistant to degradation due to pH changes in the environment as well as light. The anthocyanin-montmorillonite hybrid pigments by Li et al. (2019a) and Ribeiro et al. (2018) have shown improvements with thermal, chemical, light, pH, and color stability based on the cited research. The anthocyanin-halloysite hybrid pigment by Li et al. (2019a) has shown improved pH and color stability. The anthocyanin-palygorskite hybrid pigment by Li et al. (2019b) has shown stability against heat and chemical erosion. Lastly, the anthocyanin-sepiolite hybrid pigment by Silva et al. (2019) exhibited improved color and thermal stability. Each of the different improvements in stability was observed from the testing carried out in each of the research. The improvement in pH stability was noted due to the reversible behavior of pigments in terms of color-changing ability, wherein the pigments can change from one color to another and vice versa by exposing the pigment in an acidic or basic atmosphere. The improvement in light, thermal, and color stability was noted due to the decreased amount of fading or destruction under the light of the hybrid pigment. The increased stability is due to the inorganic component of the hybrid pigments, which were combined with the natural pigment through the methods mentioned. With the intercalations that occurred in the process, the mineral clays used were able to create another layer of protection which improved the overall stability of the hybrid pigment.

The pigments produced in the cited literature are shown to be useful in different applications. The saponite hybrid pigments are applicable as color-changing pigments as well as atmospheric acidity sensors. The montmorillonite hybrid pigments are useful as lake pigments, pH indicators, or colorants. The halloysite hybrid pigment is useful as a pH indicator. The palygorskite hybrid pigment was mentioned to be potentially useful in the development of an intelligent film that can detect the freshness of food. Lastly, the sepiolite hybrid pigment is useful as a fluorescent hybrid pigment. Based on the information, it was observed that most of the applications of the pigments are connected to the ability of the pigments to change color depending on the pH level, as the recommended applications were based on the mentioned observations.

3. CONCLUSIONS

This paper provides a systematic review of different research on hybrid pigments created with anthocyanins and several clay minerals. Hybrid pigments have been studied due to their environmentally friendly properties from natural pigments combined with the stability from synthetic pigments. Different research papers regarding hybrid pigments made with anthocyanins combined with different mineral clays, particularly saponite, montmorillonite, halloysite, palygorskite, and sepiolite, were discussed and elaborated. A comparison between the processes and interactions has shown that all the cited research utilized adsorption to combine the components, which led to the occurrence of intercalation between the anthocyanin and stabilizer, thus forming the hybrid pigment. It was observed that all the pigments, regardless of stabilizer used, exhibited color-changing properties, wherein the color of the pigment can be manipulated by changing the pH level of the environment. The pigments produced a variety of colors, which included pink, blue, red, brown, yellow, orange, purple, and several more colors. The stability of the pigments has improved, as described through each of the respective research cited, which included improvements in chemical stability, light stability, color stability, and thermal stability. With that in mind, the different possible applications of the hybrid pigments include acidity sensors, colorants, general-use lake pigments, and may also lead to the development of intelligent film capable of detecting the freshness of food. Overall, the paper has shown the development and improvement in hybrid pigment research, particularly with anthocyanin hybrid pigments.

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