Dyes and Pigments 100 (2014) 97–103

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Fluorescent colored material made of clay mineral and phycoerythrin pigment derived from seaweed

Yi-Hung Lin [a], Yumiko Hori [a], Saki Hoshino [a], Chiho Miyazawa [a], Yoshiumi Kohno [b], Masashi Shibata [a, *]

[a] School of Bioscience and Biotechnology, Tokyo University of Technology, 1404 Katakura-machi, Hachioji, Tokyo 192-0982, Japan
[b] Department of Materials Science and Chemical Engineering, Faculty of Engineering, Shizuoka University, 3-5-1, Johoku, Naka-ku, Hamamatsu, Shizuoka 432-8561, Japan

ARTICLE INFO

Article history:
Received 20 May 2013
Received in revised form
28 July 2013
Accepted 21 August 2013
Available online 5 September 2013

Keywords:
Phycoerythrin
Seaweed
Hectorite
Montmorillonite
Heat and light fastness
Fluorescence

ABSTRACT

In order to obtain a fluorescent colored powder, composites of phycoerythrin pigment extracted from seaweed and clays (hectorite and montmorillonite) were examined. The pigment adsorbed easily on synthetic hectorite in an aqueous solution and a composite with bright fluorescence was obtained. On the other hand, the adsorption of the pigment on natural montmorillonite was not sufficient, and a salt had to be added to the pigment solution to obtain the composite. Low heat and light fastness, which are serious drawbacks of phycoerythrin for practical usage, were increased by the adsorption to the hectorite clay.

1. Introduction

Fluorescent colored material is attractive as a cosmetic coloring material for makeup, such as foundation and blusher. However, some synthetic fluorescent pigments, which are widely used for cosmetics, e.g., Phloxine B and Acid red, have drawbacks and can cause problems such as skin staining and allergies [1–3]. A protein pigment called phycoerythrin present in the cells of red algae seaweed is vivid red and fluorescent [4–7]. This pigment is a type of food dye, and it is practically used as a medical marker [8,9]. However, this pigment has serious shortcomings as a cosmetic coloring material: it is easily discolored by light and heat [10] and it is water-soluble, which may lead to makeup deterioration.

It has been reported that clays can adsorb proteins and release the adsorbed proteins in a sustained manner [11–16]. They also stabilize pigments like anthocyanin by intercalation [17]. Hence, in order to overcome the aforementioned shortcomings of the phycoerythrin pigment for cosmetic usage, we have investigated the composites of clays and this pigment.

In this paper, we report the industrially practical method for preparing phycoerythrin and clay mineral composites and the properties of the obtained composites as fluorescent colored materials. The desired properties of the phycoerythrin/clay composite are as follows. First, it should be a vivid red and fluorescent powder. This means the clay has to adsorb a considerable amount of the pigment from its aqueous solution. Secondly, the color should not fade easily with exposure to heat or light.

In this study, two types of clay, natural montmorillonite and synthetic hectorite, were used. Both of them belong to the smectite group of clay minerals [18–20]. We investigated which clay is more suitable as the adsorbent of the phycoerythrin pigment.

2. Experimental

2.1. Materials

Raw edible seaweed (*Porphyra yezoensis*) was obtained from the sea near Kagawa, Japan, and was used as the raw material for phycoerythrin. The clays—natural montmorillonite (Kunipia F from Kunimine Industries) and synthetic hectorite (Wako Pure Chemical Industries, Ltd.)—were used as received.

* Corresponding author. Tel./fax: +81 42 637 2304.
E-mail address: mshibata@stf.teu.ac.jp (M. Shibata).

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http://dx.doi.org/10.1016/j.dyepig.2013.08.022

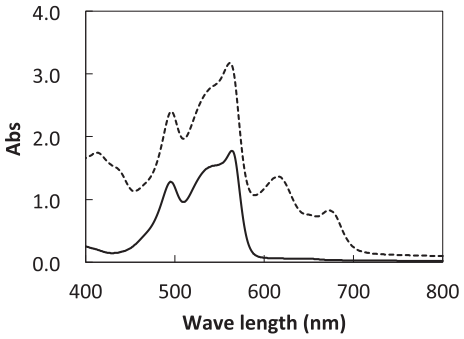

Fig. 1. UV–vis spectra of the solutions extracted from the seaweed. Solid line: before the surfactant treatment; dotted line: after the treatment.

Spherical silica gel (Sunsphere H-32, AGC SI Tech Co.) was used as the reference for the stability test instead of clays; the particle size of the gel was 3 μm, and specific surface area was 725 m^2/g.

2.2. Pigment extraction

Phycoerythrin was extracted by using an anionic surfactant (dodecyltrimethylammonium bromide) [21], which has the advantage that the pigment can be obtained by an easier and faster operation compared to other methods such as ammonium sulfate precipitation or column chromatography [11,22,23].

50 g of raw seaweed and 200 mL of deionized water were mixed, and the seaweed was ground to a paste using a homogenizer. It was subsequently centrifuged and filtrated with suction. Dodecyltrimethylammonium bromide surfactant (0.4 g, Wako Pure Chemical Industries, Ltd.) was added to the obtained the filtrate, and the solution was allowed to stand at ambient temperature for 1 h. The flocculants formed in the solution, which was a mixture of all pigments in the seaweed, were removed by centrifugation and filtration. Subsequently, in order to remove the surfactant in the filtrate, dialysis was performed. The solution was transferred to a cellophane dialysis tube (pore size = 2.4 nm), placed in deionized water (1 L) and then stirred for 5 h. The water was replaced every hour. Finally, the tube was buried in a drying agent powder (Aquacide II, sodium salt of carboxymethylcellulose, Wako Pure Chemical) in order to ooze water out through the cellophane membrane until the pigment solution in the tube became adequately concentrated for treatment.

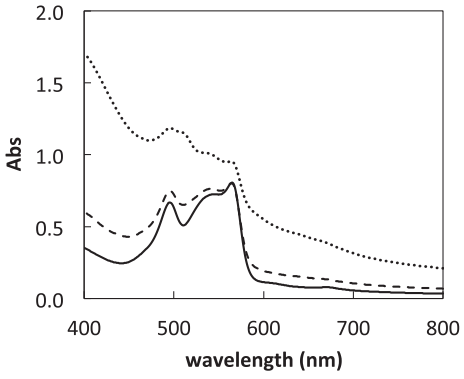

Fig. 2. UV–vis spectrum variation of phycoerythrin solution wchich was allowed to stand at 333 K. Solid line: initial, dash line: 1 day after, dotted line: 2 days after.

Table 1
Properties of the clays.

	Natural montmorillonite'	Synthetic hectorite
Adsorption of methylene blue	0.99 mmol/g	1.12 mmol/g
Swelling test	48 mL/2 g	45 mL/2 g
pH of the supernatant	9.5	10.1

2.3. Characterization of clays

The cation exchange capacities of the clays were compared by adopting a simplified methylene blue adsorption method [24,25]. 2 g of clay was added to deionized water (100 mL) and sonicated for 10 min. Methylene blue was added to obtain a concentration of 0.25–1.25 mmol/g of clay. The dispersion was allowed to stand at ambient temperature for 21 h and was then centrifuged. The amount of methylene blue adsorbed on the clay was calculated from the absorbance change of the supernatant.

2 g of clay was added quietly to 100 mL of deionized water in a graduated cylinder and was then allowed to stand for 21 h at ambient temperature. The apparent volume of clay gel in the cylinder was measured to estimate the swelling capacity of the clay.

After the swelling test, the top clear layer was collected and filtrated, and then the quantity of the cation species in it was determined by ICP analysis (Shimadzu ICPE-9000).

2.4. Preparation of pigment/clay composite

The pigment solutions were prepared with deionized water. In some experiments, in order to control the pH of the solution, sodium citrate buffer, phosphoric acid buffer, or aqueous glycine buffer was used. Alternatively, an appropriate amount of sodium chloride, potassium chloride, lithium chloride, magnesium chloride, or calcium chloride was added to the aqueous pigment solution (up to 30 wt% in the solution) before mixing with the clays.

The pigment/clay weight ratio was set to be 0.1, 0.3, or 0.5. 0.5 g of either clay was added to 15 mL of the pigment aqueous solution with an appropriate concentration and sonicated for 20 min. The dispersion was then allowed to stand for 21 h in the dark at 278 K. The amount of pigment adsorbed on clays was estimated from the change in the absorbance of the supernatant.

2.5. Characterization of pigment and pigment/clay composite

The isoelectric point and the molecular weight of phycoerythrin were measured by two-dimensional electrophoresis. For the first-dimension isoelectric focusing (IEF), a PROTEAN IEF system with ReadyStrip IPG strip (Bio-Rad) was used. The second-dimension SDS-Page was performed on a PROTEAN II XL cell (Bio-Rad).

X-ray diffraction patterns were measured with a Rigaku Mini-Flex X-ray diffractometer (Cu Kα, 15 mA, 30 kV, step angle = 0.05°, scan speed = 2°/min).

UV–vis spectra were collected with a JASCO V-550 spectrophotometer. To measure diffuse reflectance spectra, the spectrophotometer was equipped with an ISV-469 integrating sphere.

Table 2
Amount of cations eluted from the clays dispersed in deionized water (ppm).

	Natural montmorillonite	Synthetic hectorite
Potassium	n.d.	0.8
Sodium	62.1	404.0
Calcium	0.9	0.1
Magnesium	0.8	7.1
Aluminum	1.6	n.d.