Application of Deaerated Water in Extraction of Colorants from Dyer's Saffron Florets

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ABSTRACT: The efficiency of the application of deaerated water that has no dissolved gases in extraction of colorants from dyer's saffron (*Carthamus tinctorius* L.) was examined. Dyer's saffron contains about 7% yellow colorants, saffrole yellow, and 0.3% red colorants, carthamine. Saffrole yellow must be removed completely from dyer's saffron before the carthamine extraction, because if saffrole yellow is present in carthamine-red dyeing, the resulting color is yellowish. Carthamine is one of the colorants that decomposes with heat. The application of deaerated water in the extraction of these two colorants was examined. With the extraction of saffrole yellow, the maximum absorbances of extract solutions are the same as those in air-present water. The rate constants in deaerated water are lower than those in air-present water. With the extraction of carthamine, the ratios of the maximum value of cumulative absorbance in deaerated water to those in air-present water are $124 \pm 7\%$ at 0°C and $118 \pm 10\%$ at 25°C. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1701–1704, 1999

Key words: deaerated water; colorants extraction; kinetic parameters

INTRODUCTION

The extraction of colorants from natural materials is usually accelerated with an increase of temperature. However, some colorants decompose with heat. Carthamine, the red colorant contained in dyer's saffron (*Carthamus tinctorius L.*), is one of these colorants.[1–6] Therefore, carthamine must be extracted at low temperature. Because the extraction rate is reduced at lower temperatures, it is very inefficient.

In our studies of the interaction of hydrophilic polymers and water,[7–13] the degree of interaction between polymers and water, measured by dilatometry, was different in air-present water and in deaerated water that has no dissolved gases.[9,10] The dissolved gases affect the swelling of hydrophilic polymers, as well as the hydrobondings between water and polymers. The dissolution of ionic dissociable groups of polymers is increased in water with a low-dissolved oxygen concentration.[10]

We applied these results to the swelling of Konbu (*Leminaria Japonica*),[12] the swelling of cellulose and amylose,[13] and the cotton desizing with enzymes.[13] The maximum amounts of soluble components from Konbu[12] in deaerated water were greater than those in air-present water, this being more apparent at lower temperatures. The rate constants in deaerated water were slightly lower than those in air-present water. For the cotton desizing, a higher desizing effect was achieved in deaerated water than in air-present water. We concluded that this effect of deaerated water was caused by the acceleration of swelling of the substrates.

In this article, the effect of deaerated water on the extraction of colorants from dyer's saffron at

different temperatures was examined in comparison to the results in air-present water. Dyer's saffron contains yellow colorant, saffrole yellow, and red colorant, carthamine.[4–6,14–16] If saffrole yellow is present in carthamine-red dyeing, the resulting color is yellowish.[14–16] In this study, saffrole yellow was completely extracted from the dyer's saffron before the extraction of carthamine. The extraction of these two colorants were investigated.

EXPERIMENTAL

Water

Deaerated water and air-present water were used. The preparation of deaerated water was shown in previous articles.[10,13] The concentration of the dissolved oxygen, c_{DO} of deaerated water, was 0.8 ± 0.1 mg L^{-1}. Deionized water in equilibrium with air was used for air-present water. c_{DO} of air-present water was 7.0 ± 1.0 mg L^{-1} at 25°C, and 8.5 ± 1.0 mg L^{-1} at 0°C.

Extraction of Colorants from Dyer's Saffron

Dyer's saffron contains about 7% yellow colorants, saffrole yellow, and 0.3% red colorants, carthamine.[16] Saffrole yellow must be completely extracted by using water before carthamine extraction, because if saffrole yellow is present in carthamine-red dyeing, the resulting color is yellowish.[14–16]

In this study, deaerated and normal water were used for saffrole-yellow extraction with water, and the extraction of carthamine followed with a 4% sodium carbonate solution.[6,17] The quantity of extracted colorants was obtained by measuring the absorbance of the solution at the maximum absorption wavelength (saffrole yellow: 388.0 nm; carthamine: 483.0 nm). The absorbance of the extracted solution was measured by using a 120-40 spectrophotometer provided by Hitachi.

Dyer's saffron (0.1 g) was added to the sample solution in a Myer flask sealed with a silicone-rubber stopper. This flask was shaken at 100 rpm in a thermostating incubator. After shaking for 30 min, the dyer's saffron was separated from the extract solution, and the absorbance of solution was measured. A new sample solution was added to the dyer's saffron and the extraction was started again. The extraction was repeated until
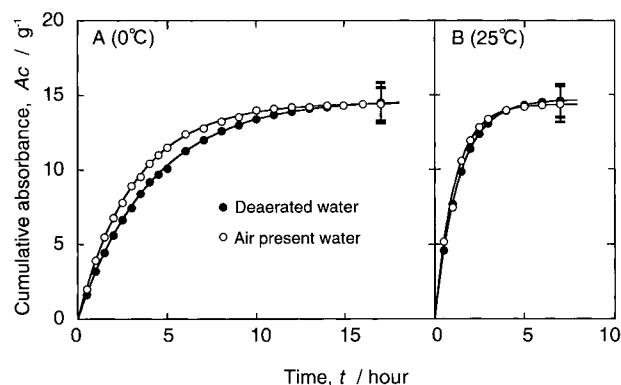
Figure 1 Time course of cumulative absorbance of extraction of saffrole yellow from dyer's saffron in deaerated water and air-present water at (A) 0°C and (B) 25°C.

the absorbance of the extract solution was <0.005.

RESULTS AND DISCUSSION

Figure 1 shows the time course of the extraction of saffrole yellow, plotting the cumulative value of the absorbance per gram of dyer's saffron, A, versus extraction time, t. Figure 1(A) shows the results at 0°C, and Figure 1(B) shows the results at 25°C.

The cumulative absorbances increase with extraction time, t, and show simple saturation curves. The saturation values of the cumulative absorbances were the same regardless of the solution or the temperature. It took longer for extraction at 0°C than at 25°C. Time to reach to the equilibrium state in deaerated water was longer than in air-present water.

Treating these results as apparent first-order reactions, the first-order kinetic parameters are obtained and listed in Table I. In Table I, the ratios of the results in deaerated water to those in air-present water are also listed.

The maximum values of the cumulative absorbance in deaerated water are similar to those in air-present water at both 0 and 25°C. The ratios of the rate constants in deaerated water to those in air-present water are as small as 0.77 ± 0.04 at 0°C, 0.84 ± 0.20 at 25°C. Although the difference of the swelling of the dyer's saffron substrate in deaerated water and in air-present water is not clear, if we assume the swelling of the substrate is

Table I   Apparent First-Order Kinetic Parameters of Extracting Saffrole Yellow with Deaerated Water and Air-Present Water at 0 and 25°C

Temp. (°C)	c_{DO} (mg L^{-1})	Maximum Value of Cumulative Absorbance		Rate Constant	
		Total Ac (g^{-1})	Ac_D/Ac_A	k (min^{-1})	k_D/k_A
0	8.5	Ac_A 14.4 ± 1.1		k_A 0.0053 ± 0.0001	
	0.5	Ac_D 14.7 ± 1.3		k_D 0.0040 ± 0.0001	
			1.02 ± 0.11		0.77 ± 0.04
25	6.9	Ac_A 14.4 ± 1.2		k_A 0.0148 ± 0.0021	
	0.5	Ac_D 14.7 ± 1.1		k_D 0.0124 ± 0.0012	
			1.02 ± 0.11		0.84 ± 0.20

different with these two solutions, the extraction of saffrole yellow is not the rate-determining step.

The extraction results of carthamine from dyer's saffron after the extraction of saffrole yellow are shown in Figure 2. The cumulative absorbance per 1 g of dyer's saffron was plotted against the extraction time, t. The result at 0°C is shown in Figure 2(A) and at 25°C in Figure 2(B).

All the cumulative absorbances increase with t and show simple saturation curves. The maximum values of the cumulative absorbances in deaerated water are higher than those in air-present water at both 0°C and 25°C.
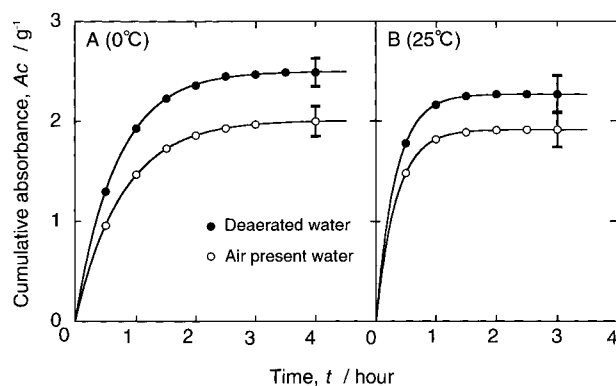
Treating these results as an apparent first-order reaction, the kinetic parameters are calculated and listed in Table II.

The ratios of the maximum value of the cumulative absorbances in deaerated water to those in air-present water are 124 ± 7% at 0°C and 118 ± 10% at 25°C. Furthermore, the maximum value

Figure 2 The time course of cumulative absorbance of extraction of carthamine from dyer's saffron in deaerated water and air-present water at (A) 0°C and (B) 25°C.

of the cumulative absorbance in deaerated water at 25°C, 2.27 ± 0.19, is higher than that in air-present water at 0°C, 2.01 ± 0.15. The use of deaerated water is very effective. The ratios of the rate constant are 113 ± 10% at 0°C and 104 ± 17% at 25°C, and the effect of deaerated water is insignificant.

These results suggest that the swelling of the dyer's saffron is different in deaerated water and air-present water in the extraction of carthamine because carthamine colorants are found in place of the dyer's saffron substrate, where it can hydrate easily. In the study on the color change of carthamine in the floral tissues of dyer's saffron, Fukushima et al.[18] pointed out that red carthamine was localized in the stigma and the peripheral region of the stylar canal. This result agreed with our results.

The extraction of colorants from dyer's saffron in deaerated water is compared to that in air-present water. With the extraction of saffrole yellow, the rate constants in deaerated water are lower than those in air-present water, and the maximum values of the cumulative absorbance are similar in deaerated water and air-present water. In the extraction of carthamine, the maximum values of the cumulative absorbance are higher in deaerated water than in air-present water and are higher at 0°C than at 25°C. The effect of deaerated water differs with the kind of colorant because colorants are found in different parts of the substrate. The effect of deaerated water in the extraction is significant when the colorant is present in the part of the substrate where the hydration can easily occur.

CONCLUSIONS

Dyer's saffron, a natural plant dye, contains the yellow colorant, saffrole yellow, and the red colo-

Table II   Apparent First-Order Kinetic Parameters of Extracting Carthamine with Deaerated Water and Air-Present Water at 0 and 25°C

| Temp. (°C) | c_{DO} (mg L^{-1}) | Maximum Value of Cumulative Absorbance | | Rate Constant | |
		Total Ac (g^{-1})	Ac_D/Ac_A	k (min^{-1})	k_D/k_A
0	8.5	Ac_A 2.01 ± 0.15		k_A 0.0218 ± 0.0015	
	0.5	Ac_D 2.50 ± 0.13		k_D 0.0247 ± 0.0022	
			1.24 ± 0.07		1.13 ± 0.10
25	6.9	Ac_A 1.92 ± 0.17		k_A 0.0494 ± 0.0056	
	0.5	Ac_D 2.27 ± 0.19		k_D 0.0512 ± 0.0072	
			1.18 ± 0.10		1.04 ± 0.17

rants, carthamine. Saffrole yellow must be removed completely from dyer's saffron before the carthamine extraction, because if saffrole yellow is present in carthamine-red dyeing, the resulting color is yellowish.

The application of deaerated water in the extraction of these two colorants was examined. The results are as follows. With the extraction of saffrole yellow, the maximum absorbances of extract are the same as those in air-present water. The rate constants in deaerated water are lower than those in air-present water. With the extraction of carthamine, the ratios of the maximum value of cumulative absorbance in deaerated water to those in air-present water are 124 ± 7% at 0°C and 118 ± 10% at 25°C.

The contents of saffrole yellow in dyer's saffron is 30% and carthamine is only 0.5%.[9] Furthermore, carthamine is easily decomposed thermally. The application of deaerated water at a low temperature such as this experiment is very effective, because this method can increase the maximum contents of carthamine extract.

REFERENCES

1. Saito, K.; Fukushima, A. Acta Soc Bot Pol 1986, 55, 639.
2. Kanehara, T.; Naruse, A.; Fukushima, A.; Saito, K. Z Lebensm-Unters-Forsch 1990, 190, 299.
3. Saito, K.; Fukushima, A. Int J Food Sci Technol 1991, 26, 21.
4. Fujii, M. Mem Tokyo Kaseigakuin Univ 1995, 35, 99.
5. Fujii, M.; Tsunoda, M.; Matsumoto, S. Mem Tokyo Kaseigakuin Univ 1991, 31, 117.
6. Wada, T. Mem Tezukayama J Coll 1993, 30, 178.
7. Ogawa, I.; Yamano, H.; Miyagawa, K. J Appl Polym Sci 1993, 47, 217.
8. Ogawa, I.; Yamano, H.; Miyagawa, K. J Appl Polym Sci 1993, 50, 35.
9. Ogawa, I.; Yamano, H.; Miyagawa, K. J Appl Polym Sci 1994, 54, 1971.
10. Ogawa, I.; Yamano, H.; Miyagawa, K. J Appl Polym Sci 1995, 58, 587.
11. Ogawa, I.; Yamano, H.; Miyagawa, K. Handbook of Applied Polymer Processing Technology; Marcel Dekker: New York, 1996; Chapter 13.
12. Yamano, H.; Ogawa, I.; Miyagawa, K. J Home Econ (Jpn) 1995, 46, 745.
13. Ogawa, I.; Yamano, H. J Appl Polym Sci to appear.
14. Yamaszaki, S. The Illustrated Book of Dye Plants; 202, Bijutu Shuppan-sha: Tokyo, 1985.
15. Kimura, M.; Shimizu, Y. Basic Words for Dyeing; Kansai-Iseikatu-Kenkyukai: Osaka, 1991; p 26.
16. Kobayashi, Y. Senshoku α (Dyeing and Wieving), 1990, No. 109, 68.
17. Saito, K.; Yamamoto, T.; Miyamoto, K. Z Lebensum-Unters-Forsch 1992, 195, 550.
18. Fukushima, A.; Homma, T.; Enomoto, Y.; Saito, K. J Plant Physiol 1997, 150, 697.