Extraction of carotenoids from crustacean waste using organic solvents

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ABSTRACT

Carotenoid pigments are divided into two groups, xanthophylls (which contain oxygen) and carotenes (which are pure hydrocarbons, and contain no oxygen) having a strong antioxidant ability. Thus, they are applicable in food, pharmaceutical and cosmetic industries. It has been reported that astaxanthin has up to 10 times antioxidant activity than other carotenoids such as zeaxanthin, lutein, canthaxanthin and β-carotene; and 100 times more that than of α-tocopherol. For carotenoid extraction, polar solvents such as isopropyl alcohol (IPA), acetone and etc., non-polar solvents such as petroleum ether, hexane and etc. or the mixture of them are used.

Keywords: carotenoids, crustacean waste, organic solvents, extraction

INTRODUCTION

Animals are not able to produce carotenoids, so they have to get it from food chain with feed from algae and plants. These pigments are found in aquatic animals such as salmons, birds such as flamingo, in microorganisms and algae. The carotenoid pigments are the main and important pigment in nature; more than 600 kinds of carotenoids are available. The aquatic animals such as crustacean are known to contain various carotenoids and are considered as one of the important sources of natural carotenoids. Astaxanthin and its esters are the main pigment in crustacean. Astaxanthin is in the group of xanthophylls that have an O_2 or OH instead of H in carotene. Astaxanthin is the main component that makes an orange – pink color in salmon and crustacean. These waste products are economically recoverable, because they have high quality protein, chitin, minerals, carotenoids, such as astaxanthin, and lipids that are high in ω-3 fatty acids. It has been reported that astaxanthin has up to 10 times the antioxidant activity than other carotenoids such as zeaxanthin, lutein, canthaxanthin and β-carotene; and 100 times more that of α-tocopherol. In general, carotenoids and lipids are soluble in non-polar solvents and these types of solvent have

traditionally been used to extract them. Thus, several organic solvents have been permitted for use in food industries such as acetone, ethyl acetate, hexane, isopropanol, methanol, methyl ethyl ketone and ethanol. Other normally used solvents like dichloromethane, dimethyl sulfoxide and chloroform are not allowed, because of their toxicity. However, the disadvantage is that this method of extraction generally decreases the stability of carotenoids due to oxidation, if antioxidants are not used during and after processing. Environmental issues represent another concern (large volumes of solvent are required) and also the low extraction yields achieved using these types of solvent (almost 50% of the carotenoids are lost), stimulating studies directed at finding alternative extraction processes for this functional food and pharmaceutical supplement.

Sachindra *et al*. (2005) used organic solvents for extraction carotenoids from shrimp waste. In this research, polar, non-polar and the mixture of solvents were used. Hexane and isopropyl alcohol was the best solvent (Table 1).

Table 1. Yield of carotenoids from shrimp waste in different solvents and solvent mixtures (Sachindra *et al*., 2005)

Solvent/solvent mixture	Yield (μg/g waste) (WWB)*
Acetone	40.6 ± 1.6^{a}
Methanol	29.0 ± 3.3^{b}
Ethyl methyl ketone	36.8 ± 1.9^{c}
Isopropyl alcohol (IPA)	40.8 ± 3.0^{a}
Ethyl acetate	36.9 ± 2.9^{c}
Ethanol	31.9 ± 2.2^{d}
Petroleum ether	12.1 ± 1.8^{e}
Hexane	13.1 ± 0.9^{e}
Acetone:hexane (50:50)	38.5 ± 1.0^{ac}
IPA:hexane (50:50)	43.9 ± 0.7^{f}

* WWB – wet weight basis; values are means ± SD ($n = 6$); values with different superscript (a–f) differ significantly ($p \leqslant 0.05$).

Khanafari *et al*. (2007) used chemical and microbial methods for extraction astaxanthin from shrimp waste. In this research, they used hexane for extraction of astaxanthin.

Sachindra *et al*. (2005) used acetone to extract carotenoids from marine and fresh waters crabs of Indian (Table 2, 3). They extracted carotenoids in different body components of Indian shrimps (Table 5). Sachindra *et al*. (2006) extracted carotenoids in *Solonocera indica* and *Aristeus alcocki* (Table 4).

Table 2. Yield and total carotenoid content in meat and shell of crabs (Sachindra *et al.*, 2005)

	Marine crab (*C. cruciata*)		Fresh water crab (*P. potamon*)	
	Meat	Shell	Meat	Shell
Yield (g/100 g)[a]	29.7±3.9	34.4±1.2	28.8±1.5	35.7±1.0
Total carotenoid content (μg/g)(wwb)[b]	3.4±0.6	11.0±0.5	4.1±0.4	6.9±0.6

Values are mean±S.D ($n = 6$).
$P \leqslant 0.05$ in meat between species.
$P \leqslant 0.001$ in shell between species.
[a] $P \geqslant 0.05$ between species.
[b] $P \leqslant 0.001$ between meat and shell within species.

Table 3. Composition (g/100 g of total carotenoids) of major carotenoids in the carotenoid extract from marine and fresh water crab (by HPLC) (Sachindra *et al.*, 2005)

	Marine crab		Fresh water crab	
	Meat	Shell	Meat	Shell
Astaxanthin	17.3±1.1	23.6±1.4	9.3±0.6	7.2±1.0
Astaxanthin monoester	26.4±2.0	15.2±1.3	11.2±1.0	3.7±1.2
Astaxanthin diester	23.9±2.1	26.7±2.8	16.0±1.1	3.8±1.1
β-Carotene	3.6±1.3	5.1±1.4	7.4±1.6	3.6±1.2
Zeaxanthin	0.49±0.35	5.0±1.7	42.0±2.6	74.8±4.2
Unidentified	27.6±3.9	24.4±2.8	14.1±1.1	6.9±2.1

Values are mean±SD ($n = 3$).

Table 4. Total carotenoid content (μg/g) in two species of deep-sea shrimp (Sachindra *et al.*, 2006)

Species	Body Component		
	Meat	Head	Carapace
S. indica	15.9 ± 2.1^{xa}	67.7 ± 6.3^{ya}	116.0 ± 11.8^{za}
A. alcocki	21.4 ± 1.7^{xb}	185.3 ± 17.0^{yb}	117.4 ± 6.7^{za}

Values are mean ± SD (n = 4); Different superscripts on values in individual columns (a, b) and rows (x, y, z) indicates significant difference ($p \leq 0.05$)

Table 5. Total carotenoid content (μgg^{-1}) in different species of shrimp (Sachindra *et al.*, 2005)

Species	Meat	Head	Carapace
Penaeus monodon	17.4 ± 5.99xa	58.4 ± 7.73yab	86.6 ± 13.88za
Penaeus indicus	10.4 ± 0.92xb	35.8 ± 6.83yb	59.8 ± 11.02zb
Metapenaeus dobsonii	11.1 ± 1.61xb	51.3 ± 4.09yb	83.3 ± 13.87za
Parapenaeopsis stylifera	16.0 ± 2.21xa	153.1 ± 40.06yc	104.7 ± 11.39zc

Values are mean ± SD (n = 6).
a–c (columns), x–z (rows): significant difference ($p \leq 0.05$).

Coral-Hinostroza and Bjerkeng (2002) used acetone:methanol for extraction of astaxanthin from red crab langostilla (*Pleuroncodes planipes*).

CONCLUSIONS

Iran has proximately 2400 km shoreline which makes it rich in crustacean such as crabs and shrimps. Iran fisheries organization announced that 1300 tons of shrimp fishing in 2000-2009 years. It shows that Iran have a strong potential in seafood industry. The crustacean wastes are rich in protein, carotenoid, chitin and etc. that can be recycled and make economical improvement in fisheries industry. In order to extract carotenoids from crustacean wastes, polar solvents such as isopropyl alcohol and acetone are used, however non-polar solvents must be used for the phase separation, or instead the mixture of polar and non-polar solvents can be used.

REFERENCES

1. Charest DJ, Balaban MO, Marshall MR, Cornell JA.2011. Astaxanthin Extraction from Crawfish Shells by Supercritical CO2 with Ethanol as Co solvent. Journal of aquatic food product technology, 10, 79-93.
2. Coral-Hinostroza GN, Bjerkeng B.2002. Astaxanthin from the red crab langostilla (Pleuroncodes planipes): optical RyS isomers and fatty acid moieties of astaxanthin esters. Comparative Biochemistry and Physiology Part B, 133, 437–444.

3. Felix-Valenzuela L, Higuera-Ciapara I, Goycoolea-Valencia F.2001. Supercritical cojethanol extraction of astaxanthin from blue crab shell waste. Journal of Food Process Engineering, 24, 101-112.
4. Handayani AD, Sutrisno, Indraswati N, Ismadji S.2008. Extraction of astaxanthin from giant tiger (*Panaeus monodon*) shrimp waste using palm oil: Studies of extraction kinetics and thermodynamic. Bioresource Technology, 99, 4414-4419.
5. Hwan Lee S, Koo Roh S, Hwan Park K, Yoon K.1999. Effective extraction of astaxanthin pigment from shrimp using proteolytic enzyme. Biotechnology Bioprocess Engineering, 4, 199-204.
6. Khanafari A, Saberi A, Azar M, Vosooghi Gh, Jamili Sh, Sabbaghzadeh B.2007. Extraction of astaxanthin esters from shrimp waste by chemical and microbial methods. Iran Journal Environment Health Science Engineering, 4, 93-98.
7. López M, Arce L, Garrido J, R´ıos A, Valcárcel M.2004. Selective extraction of astaxanthin from crustaceans by use of supercritical carbon dioxide. Talanta, 64, 726–731.
8. Sachindra NM, Bhaskar N, Mahendrakar NS.2005. Carotenoids in different body components of Indian shrimps. Journal of the Science of Food and Agriculture, 85, 167–172.
9. Sachindra NM, Bhaskar N, Siddegowda GS, Sathisha AD, Suresh PV.2007. Recovery of carotenoids from ensilaged shrimp waste. Bioresource Technology. 98, 1642–1646.
10. Sachindra, NM, Bhaskar N, Mahendrakar NS.2005b. Carotenoids in crabs from marine and fresh waters of India. Lebensmittel-Wissenchaft und-Technologie, 38, 221–225.
11. Sachindra NM, Bhaskar N, Mahendrakar NS.2006. Carotenoids in *Solonocera indica* and *Aristeus alcocki*, Deep-Sea Shrimp from Indian Waters. Journal of Aquatic Food Product Technology, 15, 5-16.
12. Sachindra NM, Bhaskar N, Mahendrakar NS.2006. Recovery of carotenoids from shrimp waste in organic solvents. Waste Management, 26, 1092–1098.
13. Sachindra NM, Mahendrakar NS.2005a. Process optimization for extraction of carotenoids from shrimp waste with vegetable oils. Bioresource Technology, 96, 1195-1200.
14. Sánchez-Camargo AP, Meireles MÂA, Lopes,Fernando BLF, Cabral FA.2011. Proximate composition and extraction of carotenoids and lipids from Brazilian redspotted shrimp waste (*Farfantepenaeus paulensis*). Journal of Food Engineering, 102, 87–93.