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Release of bioactive active iodine in kelp

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Abstract: The release process and influencing factors of bioactive iodine of kelp are systemically studied by leaching experiment. The results showed that the bioactive iodine of kelp can be released rapidly and the principal form of iodine in lixivium is I^-. There is a dynamic process between the release and absorption of iodine. With the increase of leaching water, the gross amounts of released iodine rise. There also exists a transforming process among I^-, IO_3^- and organic iodine in lixivium.

Keywords: kelp iodine; absorption; release; lixivium

Introduction

Iodine is widely known as an intellectual factor for human being and it is a nutrient element just like protein, fat, saccharide and vitamin (Karen, 1997). Although the content is very low in body(30 mg on the average, that is, about two millionths of our body (Zaichick, 1997; Randhawa, 2001)), iodine is an essential micronutrient of thyroid hormones. Thyroid hormones play a very important role in somatic metabolism, growth and development, especially in cerebral development. Therefore, some kinds of diseases will occur if hormone is excreted insufficiently or excessively due to thyroid gland dysfunction (Randhawa, 2001).

Lacking iodine could bring on goiter and cretinism. Goiter is an endemic disease caused by compensated hyperplasia of hypothyroid tissue, when thyroxin synthesis is suffocated during a long time (Chi, 1993). The hyperplasia tissue can exert a pressure on trachea and esophagus, impair reflectibility nerve of throat to bring into voice hoarseness, or even cause malignant pathological changes (Ziegler, 1998), as well as damaging patient's appearance. Cretinism is the most serious syndrome resulted from iodine lacking, the obvious clinical symptoms of which are dementia (foolishness), lowness, deafness, dumbness and paralysis (Chi, 1993). Besides, dyslexia and neuromuscular obstacle might also take place in children of iodine-deficiency (Ziegler, 1998). All these syndromes caused by iodine lacking are called iodine deficiency disease(IDD)(Chi, 1993).

Kelp, a kind of large seaweed, can enrich a lot of iodine. Experimental studies on thyroxin synthesis and physiological processes of iodine show that iodide extracted from kelp can be absorbed directly by human's body and has distinct effects on IDD, moreover, even ingesting excessive iodine kelp would never result in iodine-plethora goiter through pathological experiments of animals. Therefore, this kind of iodine from kelp is called "bioactive iodine". Compared with other kinds of inorganic iodine, it has prominent advantages for man's health (Wang, 1998; Chi, 2002).

In this paper, by leaching experiment of kelp, we studied the effects of water quantity and soaking time on the leaching amounts and releasing process of bioactive iodine of kelp and the content variation of I^- and $I^- + IO_3^-$ along with soaking time in lixivium, meanwhile, the reason was also analyzed, which is important to reveal the activation of iodine in kelp and its biogeochemical transfer processes.

1 Materials and methods

1.1 Materials and sample preparation

The raw kelp is common sort collected from Hangzhou Aquatic Products Market. Kelp was dried at 45℃, then grounded into powder and mixed up. At room temperature (25℃), 1 g treated sample was marinated into deionized water under different time and different water quantity which are listed in Table 1. The solution samples for analysis were filtered by 8 layers sanitary gauze and then by 2 layers filter-paper. Treated kelp sample 0.5000 g(accurately weighed to 0.0001 g) was put into nickel crucible, and K_2CO_3 was added to fix iodine. After organic matters were destroyed by ashing, iodine would be released from the sample. Furthermore, calcined residue was ground, then washed and filtered using hot water for several times. Filtrate was gathered in 50 ml volumetric flask and mixed up after fixing capacity with deionized water. Thus, this kind of solution would be used to determine total iodine of kelp.

Table 1 Designed parameters of soaking water volume and time

300 ml soaking water under different soaking time												
Soaking time, min	5	10	15	20	25	30	45	60	75	90	120	150
	180	240	300	360	420	480	540	600	720	900	1080	
30 min soaking time under different soaking water volume												
Water volume, ml	400	300	200	150	100	75	50	25				

1.2 Determination methods

Spectrophotometry was used to determine I^-, IO_3^- and total iodine (Wei, 2001; GB/T, 13882-92), after filtrate and lixivium were diluted to a certain extent.

1.2.1 I^- determination

Solution sample V ml(containing $I < 1.2$ μg, $V < 5$ ml) was put into 10 ml volumetric flask, adding K_2CO_3(30 g/L)$(5 - V) \times 0.8/5$ ml after diluting it to 5.0 ml with deionized water, then 1.0 ml KSCN (0.0024 mol/L) was added and blended, in sequence, adding $NH_4Fe(SO_4)_2 \cdot 12H_2O \cdot HNO_3$ (0.16 mol/L) 2.0 ml and mixing up again. At last, $NaNO_2$(20.7 g/L) were added and stirred enough to make them react (GB/T 13882-92). If room temperature was 20—30℃, the reaction would last 20 min; if it was 15—20℃, the reaction would last 25 min; and if below 15℃, 40 min should be required. The absorbency of the reacted solution was determined using 1 cm cell at 460 nm wavelength with deionized water as reference solution. Then, the content of iodine was obtained from standard curve.

Iodine standard solution 0.00, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60 ml was imbibed into 10 ml volumetric flask respectively, then 0.8 ml of K_2CO_3 (30 g/L) were added after diluting it to 5.0 ml with

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deionized water. The following operations were the same as the above. Then, the standard curve of iodine was drawn.

1.2.2 I^- + IO_3^- and total iodine determination

Prepared solution V-ml($V \leqslant 10$ ml) was imbibed into 25 ml color comparison tube, then diluted to 10 ml with deionized water. Two drops of saturated bromine water were added, shaking and laying aside for 5 min. 1.0 ml of formic acid (10%, v/v) was added, shaking until achromatism. After keeping shaking for 1 min, 2.0 ml of H_3PO_4 (3 mol/L) and 2.0 ml of KI (100 g/L) was added, then diluted to 25 ml with deionized water and mixed up (Wei, 2001). The absorbency of the solution was determined using Ultraviolet-Visible Spectrophotometer with 1 cm cell at 345 nm wavelength with reagent blank as reference solution. The content of iodine was obtained from the standard curve.

Iodine standard solution 0.0, 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 ml was imbibed into 10 ml volumetric flask respectively, and then diluted to 10.0 ml with deionized water. The following operations were the ditto. Consequently, the standard curve of iodine was worked out.

2 Results and discussion

The content of total iodine in kelp is 4438 mg/kg dry weight.

2.1 Effects of soaking time to iodine releasing quantity from kelp

At room temperature (25℃), the variation of I^- concentration along with soaking time is shown in Fig.1, in which the ratio of kelp/water(m/m) is 1/300.

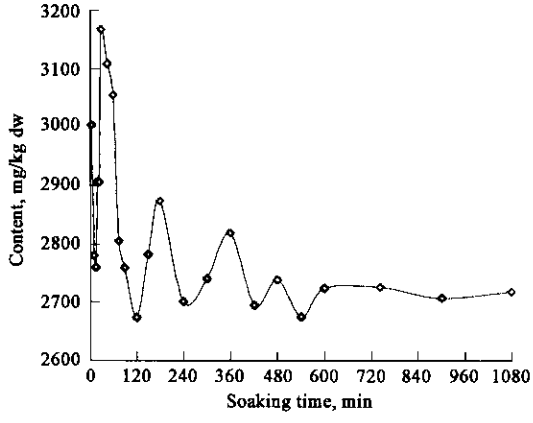

Fig.1 Variation of I^- content in solution at different soaking time

As shown in Fig. 1, the released amounts of I^- go through remarkable fluctuation from high to low and then rise rapidly to the maximum during the first 30 min, which demonstrates that the release of bioactive iodine of kelp is a dynamic process, and most of the active iodine can be released rapidly into water. In 5 min, the gross amounts of I^- in lixivium reached 68% of the total iodine of kelp sample(Table 2). Then, the concentration of I^- decreases, it manifests that a small part of released I^- is adsorbed by kelp again or is likely to transformed into other forms. After soaking for 30 min, the content of I^- reaches the maximum of 71% of total iodine(Table 2). During 30—60 min, it still remains high with decreasing gradually. With time going on, the concentration of iodine fluctuates at a low level and gradually approaches to a dynamic balance. Finally, the balance content keeps to 0.27 mg/kg dw and amounts to 61% of total iodine.

Table 2 shows that the remnant iodine in kelp sample is 29% of total iodine at 30 min, which is approximately 10% less than that at 75 min. It confirms that prolonging time will improve the remnants by 10%, which is consistent with the literature(Qin, 1995).

Table 2 Ratios of I^- in solution versus total iodine(TI) in kelp

Soaking time, min	5	10	15	20	25	30	45	60	75	90	120	150
I^-/TI	0.68	0.63	0.62	0.65	0.65	0.71	0.70	0.69	0.63	0.62	0.60	0.63
Soaking time, min	180	240	300	360	420	480	540	600	742	900	1080	
I^-/TI	0.65	0.61	0.62	0.63	0.61	0.62	0.60	0.61	0.61	0.61	0.61	

The maximums, minimums and mediums of iodine contents are respectively used to simulate the variation curves(Fig.2) which all follow some kinds of multinomial equations no matter what kind of value they are, that is, as time goes on, extrema and mediums approach to the same. This illustrated that the balance will be accessed between I in lixivium and bioactive iodine of kelp after 600 min.

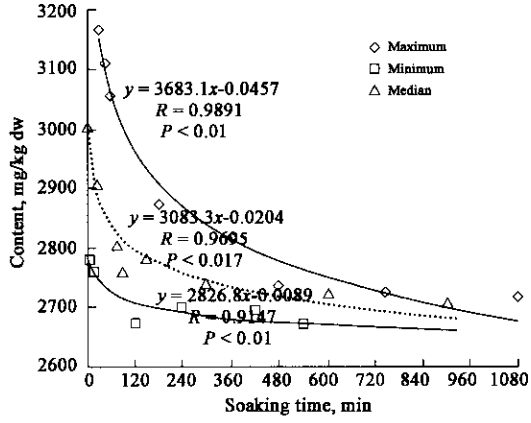

Fig.2 Simulation curves of extrema and mediums of I^- content

The researchers have studied the absorption mechanism of *Fucales Ascophyllum nodosun* and *Fucus ceranoides* to iodine respectively (Küpper, 1998). The results suggested that both of them followe Michaelis-Menten kinetic equation and also proved that it is not IO_3^- but I^- that is absorbed by the algae. Our study shows that more than 60% of iodine in the lixivium exists in the form of I^- and all of the extrema and mediums of iodine contents followe polynomial equations(Fig.2). It is hinted that there are some inherent relationships between the release of bioactive iodine in kelp and absorption of iodine during its growth.

It was found as early as 1926 that there was some insoluble substance in algae called Iodide Oxidation Enzyme (IOE) which is inlayed in the outside of the cell membrane. It took part in the iodine absorption of living alga as well as the release process after its death (Fan, 1994). As cells lose activity, being incapable of retaining iodine, bioactive iodine will permeate into water rapidly. During this process, IOE might have some influence on its release.

The dynamic process of the release and adsorption of bioactive iodine in kelp gradually approaches balance after 600 min. It means that there is little possiblity for kelp to physically adsorb iodine. Although the organism has died, it might still remain some substances of adsorbility or some kinds of iodides that are difficult to dissolve.

2.2 Effects of water quantity on the release of iodine

Since the released amounts of iodine reach the maximum value at 30 min according to the experiment, this time was chose to study the effects of the variation of water quantity on the release of bioactive iodine.

The results(Fig.3) show that if the ratio of water/kelp dw(m/m) is lower than 150∶1, the released amounts of I^- + IO_3^- fluctuate slightly between 3293—3416 mg/kg; if the ratio is from 150∶1 to 200∶1, the amounts of I^- + IO_3^- increase obviously; if the ratio is larger than 200∶1, the released amounts almost vary no more and get to the maximum.

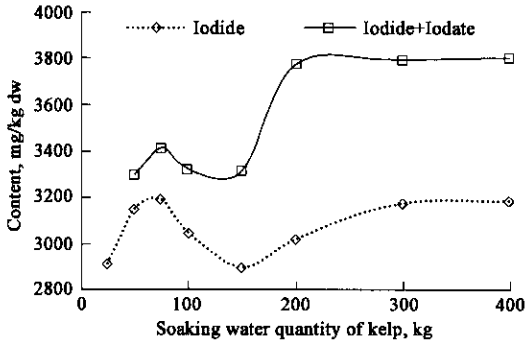

Fig.3 Content changes of I^- and I^- + IO_3^- in solution at different ratios of water/kelp

By contrast, the released amounts of I^- vary less, the maximum of which is 3000 mg/kg. As shown in Fig.3, at the ratio of 50:1, the content of iodide has approximately reached its maximum.

The ratios of I^- and IO_3^- versus total iodine in lixivium are listed in Table 3. It can be seen that the proportions of IO_3^-/total iodine and IO_3^-/I^- rise obviously with the increase of the ratio of water/kelp. Therefore, increasing water quantity will improve the gross amounts of IO_3^-, which suggest that the bioactive iodine in kelp exist not only as the form of organic and inorganic iodine compound from which I^- is easily dissociated, but also as some sorts of compounds from which IO_3^- is released. Only if the ratio of water/kelp increases to a certain degree, may IO_3^- be easy to be released, the maximal amounts of which versus total iodine are about 17%.

It can also be seen from Table 3 that if the ratio of water/kelp is less than 150:1, the remnant iodine in kelp is 23%—25%, which keeps on a stable state in kelp. As the ratio augments, about 10% of the residual iodine is released as the form of IO_3^-. Thus, as the ratio keeps on rising, the kelp residue still remains about 15% of insoluble iodine compounds.

Researches(Fan, 1994) illustrated that organic iodine exists nearly in all kinds of algae, combining with amino acid by I-C covalent bond. However, the ratio of organic iodine/inorganic iodine is very different in various sorts of algae, e.g., the percentage of organic iodine in *Echilonia bioylis* is 50%—80%, yet the ratio in *Laminaria saccharina* and *L. digitata* is 2:3. There rarely exist other forms of iodine except organic iodine, I^-, IO_3^- and little I_2(Hou, 1999). It seems from the experiment that I^- + IO_3^- may be released from organic and inorganic iodine and most of the residual iodine in kelp might exist as the form of organic iodine.

Table 3 Ratios of IO_3^-/I^- and (I^- + IO_3^-)/total iodine(TI) in solution

Water/kelp, m/m	400	300	200	150	100	75	50
IO_3^-/I^-	0.19	0.19	0.25	0.15	0.09	0.07	0.05
(I^- + IO_3^-)/TI	0.86	0.85	0.85	0.75	0.75	0.77	0.74
IO_3^-/TI	0.14	0.14	0.17	0.09	0.06	0.05	0.03
I^- in residue/TI	0.14	0.15	0.15	0.25	0.25	0.23	0.26

Küpper *et al.*(Küpper, 1998) indicated that I^- was the main species of iodine enriched by algae. It can be seen from this experiment that I^- is the chief form of the released iodine after kelp death, while IO_3^- in lixivium is less than 20%. A number of insoluble organic iodine is preserved in kelp's remains, which might play an important role in the elimination of iodine from ocean(Muramatsu, 2001; Wong, 2001a).

2.3 Variation of iodine content in lixivium

At room temperature, the variation curves of I^- and IO_3^- at different ratios of water/kelp are displayed in Fig.4. It can be seen that the variation extent of I^- is more than that of I^- + IO_3^-, and the extrema of I^- occur later than those of IO_3^-; as time goes on, the content of I^- + IO_3^- increases slowly, while the content of I^- fluctuates obviously. This phenomenon might have something to do with other forms of iodine in lixivium except I^- and IO_3^-, and there must be some slowly transforming process among these species. Organic iodine as well as I_2, HOI are the third, fourth and fifth species of iodine in seawater(Abdel, 1999). According to the determination of iodine in this experiment, the last two forms have been excluded. Thus, it can be inferred that the chief form besides I^- and IO_3^- in lixivium is organic iodine.

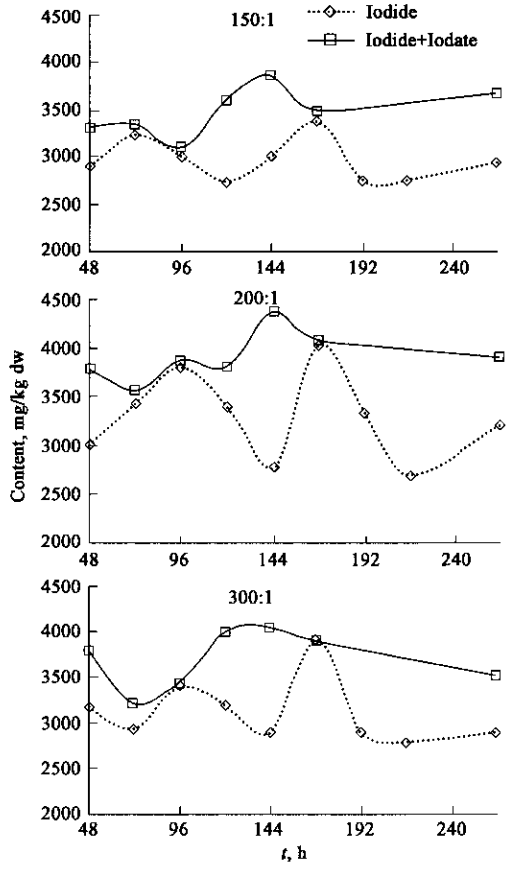

Fig.4 Variation curves of I^- + IO_3^- in solution

Studies(Wong, 2001b) showed that it is difficult for I^- to be reversibly oxidized into IO_3^- in ocean when IO_3^- have been reduced into I^-. Truesdale *et al.*(Truesdale, 2001a) believed that it is possible that I^- should be oxidized into IO_3^- under natural conditions. In our experiment, the reversible transformation between I^- and IO_3^- occurred in lixivium. In addition, transformation between two main forms of inorganic ion is related to biological activity in nature(Cook, 2000), but the biophilia of iodine is exclusively for some halobios (Farrenkopf, 1997; Truesdale, 2001b), thus, this factor was also overlooked in this experiment. Consequently, it could be inferred that photochemistry (Wong, 2001c) and some inherent components(Küpper, 1998; Fan, 1994) worked together during the transformation among I^-, IO_3^- and organic iodine, but it cannot be determined which one was the main reason as yet.

It is clear from Fig.1 and Table 2 that, although the maximum of released bioactive iodine is up to 71%, with time going on, there is about 10% released iodine absorbed again by kelp or transformed into

other forms finally. As shown in Fig. 4, the content of I^- fluctuates obviously, whereas $I^- + IO_3^-$ varies slightly. Moreover, there hardly exist other forms of iodine in organisms except I^-, IO_3^- and little I_2 (Hou, 1999). Therefore, according to our experiment and some known findings, it could be referred that the 10% of I^- in lixivium had been absorbed again by kelp and the form transformation could be excluded.

Some literature(Hou, 1999) reported that 51% of organic iodine in kelp associated with amino acid by C-I covalent bond, so iodic amino acid might be the main form of organic iodine in lixivium.

3 Conclusions

Bioactive iodine in kelp can be released rapidly after it is marinated into water, of which 60%—70% is in the form of I^- in lixivium.

There is a dynamic process between release and absorption of iodine during the leaching experiment of kelp. With time going on, the content of iodine in lixivium comes to stabilization, showing a trend of slow decline. Finally, dynamic balance approaches and the released amounts of iodine remain stable. All of the extrema or mediums follow the polynomial equation during the dynamic decrease of iodine in lixivium.

The ratio of water/kelp has an impact on iodine release. As the ratio increases from 150∶1 to 200∶1, the content of $I^- + IO_3^-$ rises rapidly, and the increased fraction mainly is IO_3^-. If the ratio is less than 150∶1 or more than 200∶1, it has little effect on the content of iodine. There exists form transformation among I^-, IO_3^- and organic iodine in lixivium.

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