Study on a Simple Method Removing Cd from Scallop Processing Waste

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***Abstract*—In order to make effective use of the processing waste of scallops as resources such as fertilizer and feed, a simple and low cost method was developed to remove cadmium (Cd) of hazardous metal. The waste was treated with 1%, 2% or 4% citric acid, acetic acid or water respectively, then the concentration of cadmium in the waste was compared. At the same time, the effect of cadmium on the adsorption and washing liquid was discussed. The results are as follows: 1, the Cd concentration in the waste decreased after citric acid, acetic acid and water washing treatment, the best washing condition is 4% citric acid and double weight water which can make the concentration of Cd decreased from 5.95mg / kg to 1.22mg/kg. 2, The eggshell had ability to adsorb the Cd, the Cd concentration in citric acid washing liquid decreased from 2.22 mg/kg to 0.39 mg/kg. The effect of eggshell adsorption on the washing liquid treated by 4% citric acid and double weight water was significant. The method has the advantages of simple operation, convenient operation, low cost and good application.**

***Index Terms*—scallop, waste, cadmium, washing, eggshell**

I. Introduction

The scallop is one of the major aquaculture resources in world. In China and in Japan, the amount of farmed scallops were 1.6 million [1] and 0.5 million tons [2], ranking first and second in the world, respectively. The adductor muscle, the edible part of the scallop, is the only part of the shellfish consumed, just accounting for just 15% of the total weight of the shellfish meat.

Processing waste (hereinafter abbreviated as waste), including the testis, ovary, mantle and midgut gland, accounts for 25%-35% of the total waste. The waste not only contains a variety of nutrients, such as protein, fat, vitamins, minerals and so on, but it also contains a lot of biologically active substances. Therefore, there is high value in its use and is expected to be reused. However, cadmium (Cd) is a toxic heavy metal that accumulates in the gut gland in high concentration, which makes the reuse of waste impossible. For this reason, the waste is primarily as industrial waste and is incinerated. Consequently, incineration of the processing industry is a great burden, with a cost of ￥35,000/ton.

In China, some waste is processed into fertilizer, most buried, which not only wastes resources but also pollutes environment. Whether in Japan or China, the treatment of waste is on the contrary of the valuable resource recycling pursuit. In recent years, in order to reuse the biological resources and to prevent the environmental pollution, great progress has been made in research on the effective utilization of waste materials and entire midgut gland. Some of the methods studied have been the sulfuric acid soaking method, electrode decomposition [3], competitive adsorption [4], enzyme treatment [5], [6], subcritical water treatment method [7], [8], weak acid washing method [9]. However there are many items that need to be addressed, such as low efficiency, high cost, and lack effective method to dispose the waste liquid containing Cd. Usually after separating protein and cadmium, free cadmium was collected by adding adsorbent or precipitant. Such as ion exchange resins [10] and chelating adsorbent [2], however, the cost of these adsorbents is high. Earlier investigations have shown that then eggshell membrane (ESM) was capable of binding various metal ions from aqueous solutions [11]. Therefore, in this study, eggshell was used as an adsorbent.

As a part of the international collaborative research and with reference to previous studies [2], the waste is washed with citric acid, acetic acid or water and then the effect of each washing condition on Cd concentration in the waste residue is compared. Then the washing liquid containing Cd was treated with eggshell and the removal rate of Cd was analyzed. The goal of this study was to establish a simple low-cost environmentally friendly method that the Cd removal rate was high and was feasibly applied to factory setting.

II. Materials and Methods

Materials: Aomori aquaculture scallops were purchased from the market in Tokyo, Japan. From the market to the laboratory about 10min by car. The scallops

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were placed in a polystyrene box filled with crushed ice at 2℃. The waste including overcoat, catgut in testis and ovary was immediately collected in the laboratory and prepared for testing. The scallops were stored in the crushed ice about 3 hour until they were fully processed.

Methods: Washing conditions for removing Cd from the waste Citric acid, acetic acid or water was used to remove Cd from waste as a washing agent to remove Cd from the waste, respectively. The concentration of the washing agent was 1%, 2% or 4%, accounting for the weight of the materials.

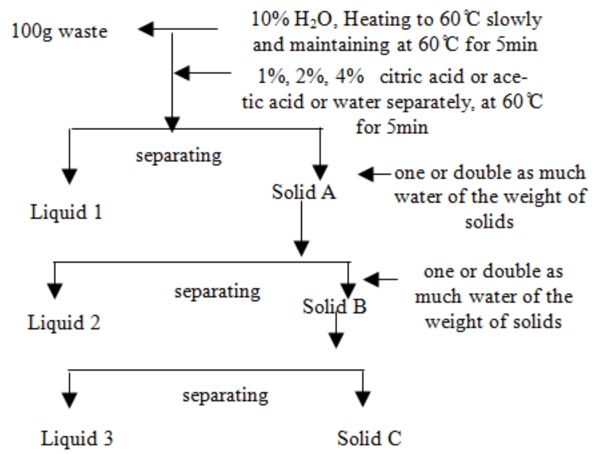

Figure 1. Washing procedure of the scallop processing waste

First, the 1 / 10 (w / w) water was added to the waste, stirring while heating the temperature slowly after reaching 60℃, in order to destroy the visceral membrane and then maintaining at 60℃ for 5 min. Thereafter, 1%, 2%, 4% citric acid or acetic acid or water was added to the mixture respectively, heating at 60℃ for 5min. Then the mixture was separated with a gauze. Solid A and liquid 1 was obtained. Next，one or double water as much of the weight of solid A was added, washing at 60℃ for 5min continually and then separated to obtain solid B and liquid 2. The same procedure was repeated once to obtain solid C and liquid 3. In the processing , the waste liquid 1, liquid 2 and liquid 3 was produced and then was mixed with the washing liquid, upon which the Cd concentration in the washing liquid was examined.

The Cd concentration in each solid and liquid was determined in order to investigate the influence of washing conditions on the removal of Cd from waste.

Treating method of the washing liquid containing Cd

Egg shell was used as an adsorbent. A certain amount of washing liquid was weighed and the eggshell was added (corresponding to 3% of the weight). After vibrating for 1 hour then centrifuging at 7000g, the supernatant was obtained. Next, the adsorbent was added (accounting for 2% of the weight of the the supernatant), vibrating for 1 hour, then centrifugal separation at 7000 g. The adsorbent was added (accounting for 1% of the weight of supernatant), then vibrated for 1 hour followed by centrifugal separation. Cd concentration of the third supernatant liquid was analyzed. The eggshell absorption the Cd was assessed.

Cd determination method: About 0.5 g of the measurement sample was precisely weighed and 8 mL of concentrated nitric acid for measuring the heavy metal was added and decomposed by microwave. The dissolved solution was adjusted to 20 mL with distilled water, and then the Cd concentration was measured by Inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher).

Statistical analysis: Results were expressed as the mean of triplicate determinations. Significance tests between samples were evaluated using one-way ANOVA using SPSS 17.0 (SPSS Inc., Chicago, IL, USA).

III. Results and Discussion

Influence of washing conditions on the removal of the Cd from waste

The Cd concentration in the waste after washing with citric acid was shown in Fig. 2. The Cd concentration in the waste was 5.95 mg/kg. The greater the amount of citric acid was used, the better the washing effect was obtained. After treatment with 4% citric acid, Cd concentration reduced to 1.22 mg/kg, the reduced removal rate reached to 80%. The effect of 2 times water washing is better than those washed by one times water.

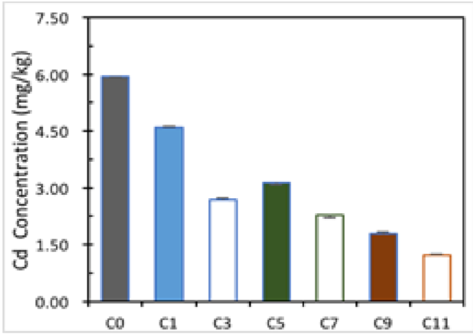

Figure 2. The Cd concentration in the waste after washing with citric acid, C0 : materials, C1: 1% citric acid and 1 time water washing; C3 :1% citric acid and double water washing; C5: 2% citric acid and 1 time water washing; C7: 2% citric acid and double water washing; C9: 4 % citric acid and 1 time water washing; C11:4% citric acid and double water washing.

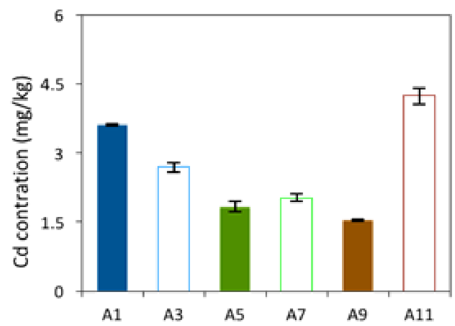

Figure 3. The Cd concentration in the waste after washing with acetic acid, A1: 1% acetic acid with 1 time water washing; A3 :1% acetic acid with double water washing; H5: 2% acetic acid with 1 time water washing; A7: 2% acetic acid with double water washing; A9: 4 % acetic acid and 1 time water washing; A11:4% acetic acid with double water washing.

Wang *et al*. used citric acid to remove the Cd in shellfish meat homogenate, when the citric acid concentration was 0.08 mol/L, pH was 3, reaction time was 4 h, the extraction rate of heavy metal cadmium reached 89.31% [12]. In the homogenate, the removal rate of Cd was relatively high, in this study, in order to make full use of the waste, the waste has not been homogenized, the Cd removal rate can also reach to 80%, which indicates that the method is effective.

To compare the capacity of citric acid removal of Cd, the same amount of acetic acid was used to wash the waste. As shown in Fig. 3, with 4% acetic acid as the cleaning agent, the removal efficiency of Cd was better, after disposal, the Cd concentration was 1.52mg / kg, removal rate was 73.6%. Removal effect was lower than that of citric acid. However, under the condition of only adding water, the removal rate of Cd did not increase even when the amount of water was increased. When 1% water was added, the efficiency was the best, but the maximum removal rate is only about 57%.

The three cleaning agents, the highest cleaning effect was obtained at the condition of 4% citric acid with double of washing water.

The effect of eggshell adsorption using different washing agents and concentration

Cd concentration in the waste liquid after cleaning with the citric acid washing agents and the Cd concentration in the supernatant after treatment with eggshell were shown in Fig. 4. The Cd concentration in the citric acid washing liquid was 1.87 to 2.63 mg/kg, The higher the Cd content in the wash liquor, the better the removal effect. Meanwhile, the content of Cd in waste liquid after double water washing was lower than that after one times water washing. The concentration of Cd decreased because of the increase of the amount of water. After the adsorption of eggshell, the content of Cd in waste liquid is greatly reduced. The adsorption efficiency was best in the 4% citric acid one times water washing liquid. The Cd concentration decreased from 2.63 to 0.39mg/kg. 85% of the Cd in the waste liquid can be adsorbed.

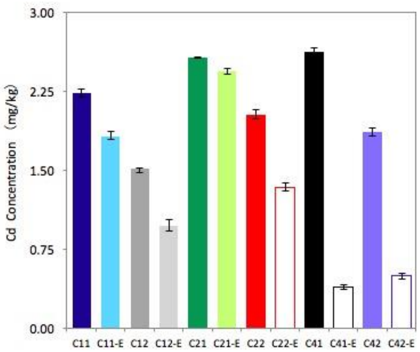

Figure 4. The Cd concentration in the waste liquid and supernatant after treatment with eggshell, C11, C21, C41: 1%, 2%, 4% citric acid and 1 times water washing; C12, C22, C42: 1%, 2%, 4% citric acid and 2 times water washing, -E the liquid treated with egg shell.

The Cd concentration in the acetic acid washing liquid was 1.32 to 2.76 mg/kg, after eggshell adsorption, the Cd concentration was 0.83-1.55 mg/kg (Fig. 5). The Cd concentration in the water washing liquid was 0.9 to 2.3 mg/kg (Fig. 6). After eggshell adsorption, the Cd concentration decreased to 0.53 and 1.28 mg/kg respectively. The effect of eggshell adsorption on the waste liquid treated by 4% citric acid and double weight water was significant.

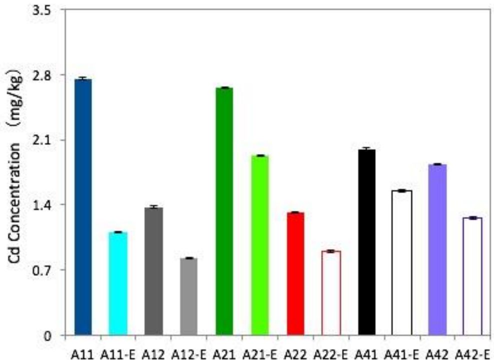

Figure 5. The Cd concentration in the waste liquid and supernatant after treatment with eggshell, A11, A21, A41: 1%, 2%, 4% acetic acid and 1 times water washing; A12, A22, A42: 1%, 2%, 4% acetic acid and 2 times water washing, -E the liquid treated with egg shell.

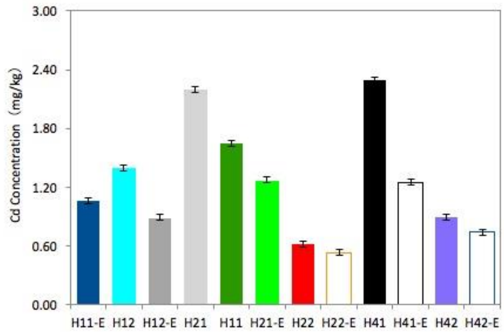

Figure 6. The Cd concentration in the waste liquid and supernatant after treatment with eggshell, H11, H21, H41: 1%, 2%, 4% citric acid and 1 times water washing; H12,H22, H42: 1%, 2%, 4% citric acid and 2 times water washing, -E the liquid treated with egg shell.

IV. Conclusion

The goal of this study is to develop a simple and low-cost method to remove the harmful components in scallop waste in red to recover the useful components. When the waste was washed with 4% citric acid, removal rate of Cd was more than 80%. When the waste liquid was treated with eggshell, the Cd concentration decreased to 0.39mg/kg, providing evidence that, if the waste liquid can bright to a low enough concentration, then it can be reused.

In Japan, the cost of citric acid is ¥300/kg, and the cost of the waste treatment method is ¥12000/ton, therefore, about half of the current processing cost is reduced. Achieving a low Cd concentration in the washing water and waste liquid would allow the scallop waste to be reused thereby reducing the overall cost of the scallop harvesting process. If Cd adsorbed on the egg shell can be recovered, it seems that the total processing cost can be further reduced.

Meanwhile this method is simple, cheap and suitable for industrial production, in further studies, the need for determining effective components and nutrient substance in the waste in order to establish effective reuse method.

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