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Reclamation treatment of the chrome leather scrap

JIANG Ting-da*, ZHANG Chun-ping, QIN Fei

(Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China)

Abstract: A novel method to extract protein and Cr(III) from the chrome leather scrap discarded by leather industry is described. Chrome leather scarp was hydrolyzed under basic condition to remove chromium compound and extract protein. The extracted protein was mixed with substrate and used as feed protein after being dried and ground. The basic residue was treated with sulfuric acid to obtain chrome(III) sulfate which can be used as tanning agent again after adjusting pH with base. The acidic residue was processed and used as flower fertilizer. The safety of the protein powder produced has been by toxicology and nutriology test. This reclamation method has been industrialized.

Key words: protein; chromium compound; tanning agent; solid-waste

Introduction

Chrome leather scrap is the solid-waste of leather industry. Its main composition is protein (mainly collagen protein, globulin and albumin), some Cr compound bonding with the protein, a little carbohydrate, fat and some inorganics.

The chrome leather scrap stacked will putrid gradually and generate foul smell. The green sewage produced in this process bears high concentration of Cr compound and protein, which will pollute air, ground water and surface water.

The chrome leather scrap was disposed as reclaimed leather in the past. With the development of leather industry, the amount of chrome leather scrap increased in contrast to the declining demand to reclaimed leather. Therefore, it became a new task to dispose chrome leather scrap in a better way. Although the chrome leather scrap can also be used to produce peptone, low-grade gelatin, dye fixative, or react with $SOCl_2$ after acidic hydrolysis to produce surfactant (Francis, 1978), these treatment will bring secondary pollution and are prohibited by many countries. Incineration and burail are the common methods to dispose chrome leather scrap now.

Early than 30's, some scientists in France have suggested that the protein in the chrome leather scrap should be extracted and used as animal protein additive of feed. This suggestion had obtained extensive attention. It had become the research focus in 70's. There are many research papers and patents(Nematllaev, 1982; Uziebio, 1979; Vishnyakov, 1984) in the countries with advanced leather industry. However, almost all these researches on the renewable resources of chrome leather scrap could not be industrialized because of two main problem. Firstly, the Cr(III) and Cr(VI) compound could not be removed completely. Secondly, the digestibility to the extracted protein could not be increased in a wide range.

We have thoroughly researched these problems for more than ten years and advocated a novel technological process(Jiang, 1991) which could resolve the two questions above completely.

The novel method has been industrialized in four special factories. The largest one can treat 6600 tons chrome leather scrap per year, the smallest one 1300 t/a. The protein powder they

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* Corresponding author

produced has been sold in provinces of China, and has never been detected to bear Cr(VI)(μg/g grade). Its safety has been proved by toxicology test. The nutriology research shows that its digestibility is higher than 91.7%, and can be used as a novel animal protein resource with higher nutrition.

1 Experimental section

The technological process is extracting protein from chrome leather scrap; mixing the extracted protein with subtract to produce adsorptive protein powder; extracting Cr(III) to produce tanning agent bearing basic chromium sulfate. The residue is processed and used as flower fertilizer.

1.1 Materials and methods

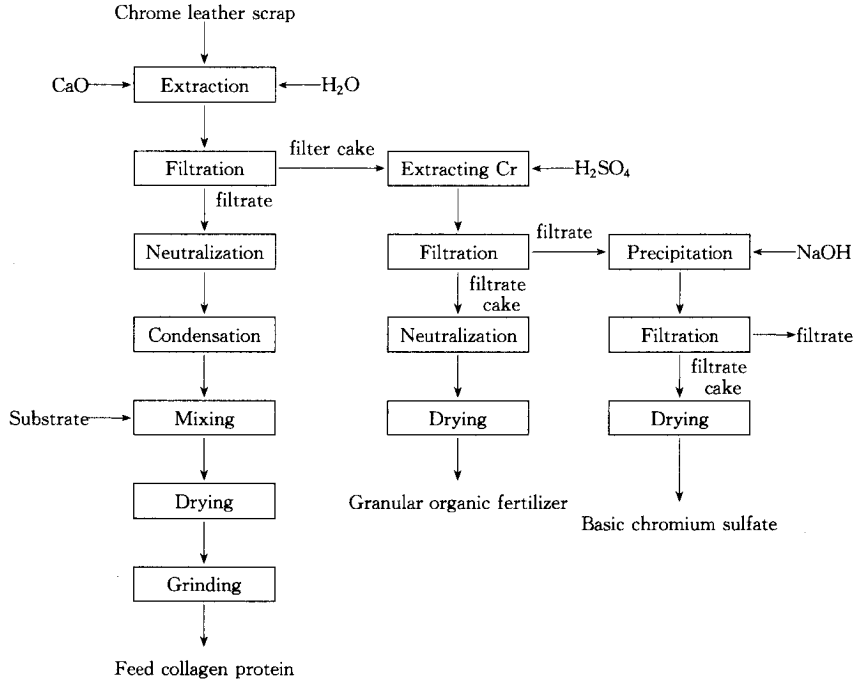

Fig. 1 Technological flow diagram

1.2 Extraction of protein and preparation of protein powder

10g dry chrome leather scrap and given quantity of CaO were put into flask and added given volume of water. The temperature was raised to the given degree. The product was filtered. The filtrate was cooled to room temperature, and neutralized with HCl, its concentration condensed to 50% in rotating thin film evaporator. The condensed protein solution mixed evenly with substrate (wheat bran) according to given ratio. The product was dried, ground and sieved with 60 mesh sift, which then could be used as feed collagen powder.

1.3 Preparation of basic chromium sulfate

The basic filter cake left by protein extraction process was mixed with water (5 times the volume of filter cake). H_2SO_4 was added as stirred. The solution pH was controlled to be lower than 2. The product was filtered. The filter cake was used to prepare granular organic fertilizer. The green filtrate was heated to 50— 60℃ as stirred. NaOH was added slowly till the pH was between 7.5 and 7.8. The product was cooled to room temperature and filtered. The filtrate

should be yellow or transparent, bearing no Cr compound. The filtrate bearing small amount of protein can be reused in the former extraction process. The main composition of green filtrate cake is basic chromium sulfate which can be used directly to tan leather or sold as tanning agent after being dried.

1.4 Preparation of granular organic fertilizer

The filter cake left by the chromium sulfate extraction process, bearing small amount of protein, was neutralized by lime milk, stirred and dried, then the granular organic fertilizer is produced, which could be used as flower fertilizer.

1.5 Measurement of chromium content(Jiang, 1992)

0.500g dry feed collagen protein, basic chromium sulfate and granular organic fertilizer with constant weight were respectively weighted (0.0001g accuracy). They were mixed with concentrated HNO_3 and H_2SO_4, then heated to boiling until the solution was transparent. The solution was neutralized with ammonia, transferred to 50.0 ml colorimetric cuvette(I), and added de-ionized water to graduation. 25.0 ml solution in cuvette(I) was transferred to another one(II). Cuvette(II) was added 0.01g$(NH_4)_2S_2O_8$, boiled for 15 min, and the Cr(III) was oxidized to Cr (VI). The solution was cooled to room temperature.

The two cuvette was respectively added de-ionized water to graduation. 2.5 ml 2,2'-diphenyl carbonic dihydrazide was added respectively and mixed evenly. Their optical density at 540 nm were measured with spectrophotometer. The contents of Cr(VI) in the cuvette(I) and (II) were calculated according to the following formula: $C_{[Cr(VI)]} = 2 \times m_{(Cr)}/W$, where, $C_{[Cr(VI)]}$(mg/kg) is the content of Cr(VI); $m_{(Cr)}$(μg) the quality of Cr(VI) from standard curve; W(g) the weight of sample.

Content of Cr(VI) in the sample equals the content of Cr(VI) in the cuvette(I). The quantitative difference between cuvette(I) and (II) equals the content of Cr(III) in the sample.

2 Results and discussion

2.1 Effect of pH

Tanning leather is a cross-linking process between leather protein and tanning agent. Extracting protein from chrome leather scrap is actually a process to break the cross-bond so that the cross-linked leather protein can become three protein molecular.

There are several methods to break cross-bond, such as enzymic(collagen protenase) one, acidic one and basic one. The operating cycle time of enzymic method is long, requiring large area and investment, which is not fit of treating chrome leather scrap at large scale. The operating time of acidic method is short, but the protein and Cr(III) dissolved in solution can not be separated easily. The basic method (pH>9) need non anticorruption equipment. The protein dissolves in solution and Cr(III) is precipitated as $Cr(OH)_3$, then they can be separated by filtration.

There are many basic reagent that can be used such as NaOH, MgO, etc., but CaO is the optimum one. It has three advantages: a. cheap and can be obtained easily; b. the lime milk produced by CaO and water can adsorb the tiny particle of $Cr(OH)_3$ and flocculate other impurity in the system; c. the Ca demand of feed is higher than Na and Mg.

The effect of CaO dose to the extraction process and Cr (III) concentration is shown in Table 1.

When the CaO dose higher than 3% of weight of chrome leather scrap(pH>11), the extraction ratio increased apparent. At the same time, the Cr(III) in protein solution increased too. The pH should be low than 11 in order to reduce the concentration of Cr(III) in the protein solution.

Table 1 Effect of pH(90℃, 10h)

CaO,g	Initial pH	Protein conc., mg/g	Cr(III) conc., μg/g
0.15	7.76	11.0	0.248
0.20	10.17	13.5	3.404
0.30	11.02	15.0	3.474
0.50	11.29	29.88	16.488
0.70	11.82	32.37	23.344
0.90	12.06	45.0	-

2.2 Effect of temperature

Raising the temperature can effectively accelerate the extraction rate, but it will also accelerate the decomposition rate of protein(Fig. 2).

The temperature has positive correlation to the amount of Cr(III) dissolved. The dissolving process included two steps: a. the cross bond is broke, and Cr(III) broke from protein molecular to form $Cr(OH)_3$ precipitation; b. part of $Cr(OH)_3$ precipitation dissolves in heat basis solution to from CrO_3^{3-}, resulting in the high content of Cr(III) in the dry protein powder.

The concentration of Cr(III) will decrease with the increase of precipitation. Therefore, the lower temperature is favorable(Fig.3).

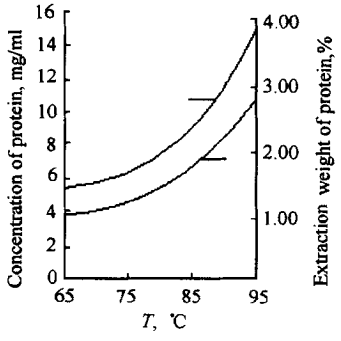

Fig.2 Effect of reaction temperature
1. concentration of protein; 2. extraction weight of protein

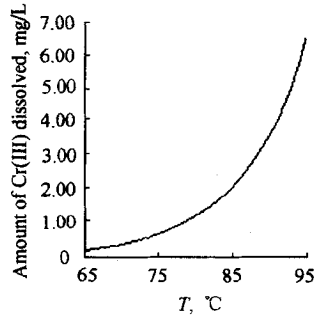

Fig. 3 Relationship between reaction temperature and the amount of Cr^{3+} dissolved

2.3 The effect of reaction time

The decomposition process of chrome leather scrap includes two steps: (1) the OH^- goes to the inside after the impregnation, swelling and soften of chrome leather scrap; (2) the OH^- break the cross-bond and form Cr $(OH)_3$. From Fig. 4 and Fig. 5, we can see that the protein concentration increased faster in the first hour and the Cr(III) dissolved is little.

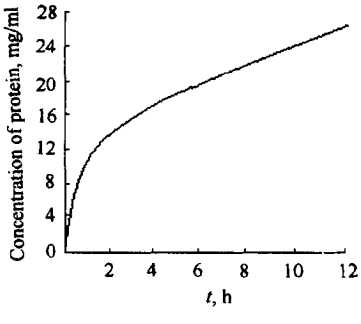

Fig.4 Effect of reaction time

With the lapse of time, the protein began to hydrolyze, molecular-weight of protein gradually became smaller. Table 2 shows the relationship between reaction time and molecular-weight (with gel permeation chromatography determination) and molecular weight distribution(d). We can find in Table 2 that the

average molecular-weight ($\overline{Mn}$) has positive correlation with the time, but the weight average molecular($\overline{Mw}$) has negative correlation with the time.

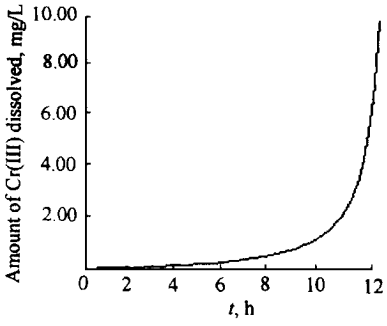

Fig. 5 Relationship between reaction time and the amount of Cr^{3+} dissolved

Table 2 The relationship between reaction time and molecular-weight and molecular weight distribution(d)

No.	Reaction time, h	$\overline{Mn}$	$\overline{Mw}$	d
1	4	2052	16576	8.35
2	8	2601	13912	5.35
3	12	2529	9294	4.60
4	16	2628	8372	3.19

We can see a main peak rented into double peak, and a minor peak with a dilatory shoulder peak. With the lapse of time, the former peak of main peak become lower than the later one gradually. Which shows the drop of $\overline{Mw}$. The dilatory shoulder peak of the minor peak become lower gradually with the lapse of time and disappeared at last(Fig. 6, Fig. 7).

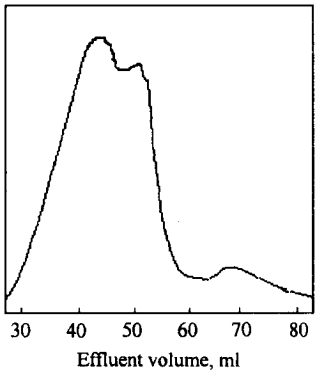

Fig. 6 GPC of No. 1 protein sample reaction time: 4h; $\overline{Mn}$ = 2052; $\overline{Mw}$ = 16576; d = 8.35

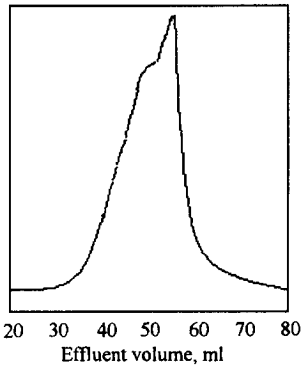

Fig. 7 GPC of No. 3 protein sample reaction time: 16h; $\overline{Mn}$ = 2628; $\overline{Mw}$ = 8372; d = 3.19

The reduction of molecular weight of protein can improve produced by the two factory proved its poisonlessness. Its $LD_{50} > 10$ g/kg, the accumulated rate $K > 5.8$. Ames test results showed the mutagenic action is negative. Micronucleus test dose higher than 5 g/kg is still negative. Sperm malformation test dose higher than 5 g/kg is still negative.

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