Separation and Purification Technology 81 (2011) 237–242

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Recovery of chromium(III) from wastes of uncolored chromium leathers. Part II. Solvent extraction of chromium(III) from alkaline protein hydrolyzate

Barbara Wionczyk [a,*], Wiesław Apostoluk [b], Witold A. Charewicz [b], Zbigniew Adamski [b]

[a] Institute of Leather Industry, Zgierska 73, 91-462 Łódź, Poland
[b] Division of Chemical Metallurgy, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

ARTICLE INFO

Article history:
Available online 22 July 2011

Keywords:
Protein hydrolyzate
Chromium(III)
Recovery
Extraction
Aliquat 336

ABSTRACT

Experimental studies were made on the solvent extraction of chromium(III) with Aliquat 336 from the protein hydrolyzate obtained by the alkaline hydrolysis of wastes of uncolored chromium-tanned leathers. The effects of NaOH concentration in the protein hydrolyzate, contact time of the organic and aqueous phases, the aqueous/organic phase volume ratio, and temperature on the extraction of chromium(III) and collagen proteins/peptides were examined. Stripping of chromium(III) from the loaded organic phase is also presented. Chromium(III) can be efficiently removed (99%) from the alkaline hydrolyzate by the solvent extraction with Aliquat 336 after 60–90 min at temperature 50 °C and at the aqueous/organic phase volume ratio equal to 5/1. Moreover, it was found that during one cycle of the alkaline hydrolysis followed by the extraction and stripping operations, chromium(III) can be separated from the source leather wastes with the total yield over 90%. The final products are: the protein hydrolyzates contaminated with traces of Cr(III) (less than 5 ppm) and the solutions of chromium(III) sulfate containing small quantities of protein substances.

1. Introduction

Recently, in Part I of the paper [1] we have reported the studies on determination of some mild conditions of alkaline hydrolytic decomposition of the selected wastes of chromium-tanned uncolored leathers. Under conditions established in those studies, chromium(III) passes from the examined solid leather wastes to an alkaline solution in the form of soluble hydroxocomplexes, which gives a possibility for their separation from the resulting alkaline hydrolyzate by the solvent extraction.

Therefore, in this work, we have attempted to apply for this purpose the solvent extraction with Aliquat 336 containing trioctylmethylammonium chloride (TOMACl) as a main active component.

Our previous studies [2–6] revealed that quaternary ammonium compounds effectively extract chromium(III) from the model alkaline aqueous solutions [2–5] and from appropriately prepared industrial spent tanning chromium liquors [6]. It was demonstrated for the first time that under optimal conditions, the extraction of chromium(III) with Aliquat 336 from alkaline media is quick and with yield exceeding 99%. So, these and other interesting results obtained in our previous studies, i.e. the large loading capacity of the organic phase containing trioctylmethylammonium chloride as well as the efficient and fast stripping of Cr(III) with sulfuric acid [4,6], authorize us to examine of this method for separation of chromium(III) from the alkaline protein hydrolyzate obtained by hydrolytic decomposition of the leather wastes.

On the other hand, it is generally known that Aliquat 336, is a non-specific extractant because it can extract simultaneously various anions (organic and inorganic) present in a solution. For example, Aliquat 336 was applied for the recovery of anionic complexes of different metals as well as anions of organic and amino acids from aqueous solutions. Hano et al. [7] have studied the extraction equilibria of 13 amino acids (tryptophane and 12 of these that belong to collagen i.e. glycine, alanine, valine, leucine, isoleucine, methionine, phenylalanine, tyrosine, histidine, arginine, serine, and threonine) with TOMACl in kerosene from aqueous solutions of KOH at pH 11–12. The highest extraction constant (8.89) established under examined conditions at 25 °C was observed for tryptophane while those determined for other amino acids changed from 0.036 for glycine to 0.97 for phenylalanine.

As it is known, collagen is a main fibrous protein of animal hide. Native collagen, irrespective of its origin, contains 19 amino acids which kind and composition is characteristic feature of that protein [8]. However, complete decomposition of collagen to free amino acids undergoes under severe conditions, e.g. heating with concentrated 6 M HCl solution at 140 °C for 3 h [9]. Hydrolysis of collagen under milder conditions, for example, at lower temperature and with acid or base of lower concentration for a longer period of time, leads in generally, to the partial non-specific

* Corresponding author. Tel.: +48 42 25 36 132(7); fax: +48 42 657 62 75.
E-mail addresses: wionczyk@ips.lodz.pl, wionczyk@mazurek.man.lodz.pl (B. Wionczyk).

1383-5866/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.seppur.2011.07.024

degradation of that protein to gelatin which renders the collagen water-soluble. Under such conditions, only part of the peptide bonds in a protein chain is disrupted, giving a mixture of oligopeptides and/or polypeptides of shorter chains containing sequence of amino acids with N-terminal and C-terminal amino acid residues. Courts [10–12] shown that glycine is the predominant N-terminal amino acid residue of gelatin hydrolyzate because that amino acid occurs the most frequently in collagen. Peptides with serine, threonine, alanine, aspartic acid, and glutamic acid residues also occurred in such hydrolyzates but in the small quantities. In the studies on constitution of gelatin, Schroeder et al. [13] obtained hydrolyzates containing 34 peptides (mainly dipeptides) using a mild partial acidic (with 3.6 M hydrochloric acid at 37 °C for a week) or alkali (with 0.5 M sodium hydroxide at 37 °C for a week) hydrolysis of gelatin.

From a different side, it should be mentioned that determined in our previous studies at temperature 25 °C, the extraction constants of chromium(III) with Aliquat 336 in *n*-heptane from the aqueous solutions at pH $\geqslant$ 12, varying from about 10–2000 according to the ionic strength of the aqueous phase [4]. Then, the extraction constants of chromium(III) are many times larger than these determined under similar conditions for the 12 amino acids [8] being components of collagen as well. Taking into account the considerable differences between the extraction constants of chromium(III) and amino acids, and resulting from that, their various extraction affinities towards Aliquat 336, it can be assumed that the selective separation of chromium(III) from the alkaline collagen hydrolyzate will be possible by the extraction with that quaternary ammonium extractant.

Consequently, in Part II of the paper we present the laboratory studies on the separation of chromium(III) by the solvent extraction with Aliquat 336 from the feed aqueous solutions originating from the alkaline hydrolysis of the leather wastes. The effects of NaOH concentration in the aqueous phase, contact time of the organic and aqueous phases, volume phase ratio, and temperature on the extraction of chromium(III) and collagen proteins/peptides are described. The stripping of chromium(III) from the resultant loaded organic phases is also reported. Moreover, concerning the results from Part I of the paper [1], a flowchart of process for the recovery of chromium(III) and protein substances from uncolored chromium-tanned leather wastes is proposed.

2. Experimental

2.1. Reagents and materials

The aqueous phases were freshly prepared alkaline protein hydrolyzates containing on the average 244 mg/dm^3 (0.0047 M) of chromium(III), 1550 mg/dm^3 (0.1107 M) of nitrogen and sodium hydroxide (p.a., from POCh, Poland) of concentration varying from 0.2 to 0.4 M.

The composition of the tested leather wastes and details concerning their hydrolysis were described in Part I of the paper [1].

The extractant was 0.05 M solution of Aliquat 336 (Merck-Schuchardt) containing 90% of trioctylmethylammonium chloride (TOMACl) in *n*-heptane (p.a., POCh, Poland) modified with 1% (v/v) of n-decanol (>99%, Merck-Schuchardt).

Sulfuric acid (p.a., from POCh, Poland) of concentration 0.5 M was applied as stripping solution. Distilled water was used in all experiments.

2.2. Extraction of chromium(III)

A series of conical flasks closed with glass stoppers, containing definite volume of the freshly prepared alkaline protein hydrolizate (V_a) and appropriate volume of the extractant (V_o), of compositions given in Section 2.1, were placed in a thermostatic water bath shaker type Elpin 357 (Poland) and shaken mechanically for established experimentally time and at constant temperature. Next, the both liquid phases were transferred into funnels to separate and clarify. Sometimes, these phases were separated by centrifuging at 4000 rpm for 5 min.

The influence of NaOH concentration in the aqueous feed solution on the extraction of chromium(III) was studied at the constant temperature (50 °C) and at constant ratio of phase volume $V_a/V_o = 2/1$.

The effect of temperature on the chromium(III) extraction was examined at two ratios of phase volume $V_a/V_o = 1/1$ and 2/1 and at temperature varying from 30 to 50 °C.

The effect of shaking time on the Cr(III) extraction was tested at temperature 50 °C and at the aqueous/organic volume phase ratios (V_a/V_o) equal to 2/1 and 5/1.

The dependence of the extraction of chromium(III) on the ratio of phase volume was checked at temperature 50 °C after shaking time equal to 90 min.

2.3. Re-extraction of chromium(III)

Chromium(III) was stripped from the loaded organic phase with 0.5 M sulfuric acid at the volume ratio of phases equal to one. Both phases were shaken for 40 min at constant temperature (25 ± 0.5 °C), and thereafter, were left to clarify and separate into a funnel.

Composition of the loaded organic phases used for the stripping was the following: 1196–1205 mg/dm^3 (about 0.023 M) of chromium(III) and 713–814 mg/dm^3 (0.051–0.058 M) of nitrogen.

2.4. Analysis

Contents of chromium(III) and collagen proteins/peptides in the alkaline hydrolizate prior and after the extraction as well as in the aqueous phase in the re-extraction system were determined by the methods given in Part I of the paper [1].

2.5. Calculations

Each single experiment of the liquid–liquid extraction of chromium(III) as well as its stripping from the loaded organic phase was repeated twice under identical conditions. Then, analysis was performed to determine the content of chromium(III) and total nitrogen in the hydrolyzate and/or in the aqueous phase (raffinate). The reproducibility estimated for the measurements of content of chromium(III) and total nitrogen was within the range of ±2%.

The content of chromium(III) and the collagen proteins/peptides in the organic phase was calculated from mass balance.

Moreover, it was assumed that content of the total nitrogen determined in the hydrolyzate before and after the extraction is directly proportional to the content of proteins/peptides originating from hydrolyzed collagen of definite type of leather wastes. However, it should be noted that trioctylmethylammonium chloride (Aliquat 336) used as an extractant distribute itself between the organic and aqueous phases in an extraction system. Therefore, one might suppose that a part of nitrogen, which was determined in the aqueous phase after the extraction, originates from the distribution of this quaternary ammonium salt. In the previous studies Wionczyk [14] has found that values of the distribution constant (K_D) of Aliquat 336 depend on kind of the extraction system and on the ionic strength of the aqueous phase as well. Their logarithmic values determined in the *n*-heptane–water and in the *n*-heptane–0.5 M NaOH extraction systems at the tempera-