Pertraction of Cr(III) from Modeling Exhaustion Tanning Bath with a Bulk Liquid Membrane

by

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Abstract

The influence of chloride and sulfate ions as well as the age of the model test solution of the "tanning liquor" on the effectiveness of the chromium(III) pertraction with the use of a bulk liquid membrane has been investigated. Introducing SO_4^{2-} to the chromium solution causes the creation of stable sulfate complexes that limit the transport capacities of the investigated system with the liquid membrane. The presence of chlorines in the solution does not considerably influence the effectiveness of chromium(III) extraction and stripping. As a result of "aging" of tanning liquor the inhibition of the process was noticed. Such results restrict the direct application of liquid membranes for the pertraction of chromium from tanning liquors.

Resumen

La influencia de los iones cloruro y sulfato como también el añejamiento de una solución simuladora del "licor curtiente" se investigo en cuanto a la efectividad de extracción del cromo(III) por medio de una membrana líquida extensiva. La introducción de SO_4^{2-} en la solución provoca la creación de complejos estables que limitan las capacidades de transporte del sistema investigado por la membrana líquida extensiva. La presencia de cloruros en la solución no afecta la efectividad de la extracción y remoción del cromo(III). Como resultado del "añejamiento" del licor curtiente se detectó una inhibición del proceso. Tales resultados restringirán la aplicación directa de membranas líquidas en la recuperación del cromo de licores curtientes.

Introduction

During the tanning process the raw skins are converted into leather by means of particular mechanical and chemical operations requiring a lot of water and chemicals[1,2,3]. As a result the same amount of strongly polluted effluent is obtained. It is estimated that during the production process of one ton of skin about 30 m^3 of sewage is produced[4]. Until recently this amount has been twice as large[5]. The sewage composition is dependent on the type of skin put into the tanning processes, leather tanning technology as well as the type of the applied tanning agent. Since the XIX century the most popular tanning agent, applied in the majority of tanneries, has been the chrome tanning agent; which causes the sewage to contain chromium[6,7,8,9].

Presence of chromium in the exhaustion tanning bath results in two adverse effects: the extensive use of the tanning agent and the high concentration of chromium(III) in the sewage. This makes the process less economical and environmentally unfriendly. The conventional methods for the elimination of chromium from the tanning effluent giving satisfactory results require additional operations connected with the recirculation of the excessive deposit and the addition of coagulants. Moreover, they result in great amounts of deposits containing chromium, which make them useless for further application. Therefore, some efforts to introduce changes in the technology of leather production are made[10,11,12] and new technologies[13,14,15,16] for effluent treatment (e.g. those applying liquid membranes) are established to enable the reduction of hazardous factors.

The current studies on the liquid membranes show their applicability for the removal and recovery of chromium[17,18,19,20]. However, these studies concern the pertraction of chromium from pure water (without additional constituents) do not reflect the conditions observed in real effluent. Due to the complex character of tanning sewage, and in particular due to the presence of high concentration of chloride and sulfate easily generating the complex compounds with chromium[21,22,23,] it seems necessary to investigate this phenomenon in the presence of these ions influences the pertraction process.

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The paper presents the results of the studies on the influence of chloride and sulfate ions as well as the age of the model solution of the "tanning liquor" on the effectiveness of the chromium(III) pertraction process from water solutions with the use of a bulk liquid membrane.

EXPERIMENT

Transports experiments were carried out using a permeation cell described by Gawroński and Religa[24]. This cell was placed in thermostat and all experiments were performed at temperature t =25±1^{0}C. The feed phase (455 cm^3) was a model tanning bath solution containing chromium(III), sulfate and chloride ions. Cr(III) concentration was 0,058 M ($CrCl_3$ analytical grade, anhydrous, POCh), Cl^- concentration was 0,42 M (KCl analytical grade, Chempur) and SO_4^{2-} concentration amounted to 0,21 M (Na_2SO_4 analytical grade, anhydrous, Chempur). pH of the initial feed phase was 4. The pH was adjusted with 0,1 M NaOH (NaOH analytical grade, Chempur). These parameters and their concentration are characteristic for the real tanning bath. As a reference solution the chromium(III) solution (the initial Cr(III) concentration was 0,058 M) was used.

The age of the model solution of the "tanning liquor" was different from the "fresh" one either of 2 to 48 hours. The "fresh tanning liquor" is a solution prepared just before the testing and the 2-hour and 48-hour "tanning liquor" are prepared appropriately 2 and 48 hours before the begin of the testing. During this time the solutions are kept in room temperature without mixing. The stripping phase (300 cm^3) was an aqueous 4 M H_2SO_4 (95% H_2SO_4 analytical grade, Chempur) solution. Both aqueous phases were mixed by a magnetic stirrer at a rotary rate of 50 min^{-1}.

The bulk liquid membrane was an organic phase ca. 10 mm thickness. This phase contained the dinonylnaphthalenesulfonic acid (DNNSA, Fluka) as a carrier dissolved in the mixture of kerosene and o-xylene. The composition of the membrane phase was earlier investigated[18,19]. In this experiments used the optimal ones. The concentration of the carrier was 0,28 M. The membrane phase was unmixed. The interfaces were as follows: $A_{Feed\ phase/Membrane}$ = 54 cm^2, $A_{Membrane/Stripping\ phase}$ = 36 cm^2. The samples were taken from aqueous phases at scheduled time intervals and analyzed on chromium concentration with the SPEKOL 220 spectrophotometer at the wave length 595 nm. The corresponding chromium concentration in the membrane was established from the material balance.

RESULTS AND DISCUSSION

The influence of the feed phase composition on the transport kinetics

Figure 1 shows the graphic illustration of the course of chromium concentration changes in particular phases of the model solution of "tanning liquor" dependent on time. Additionally, to enable the comparison, the curves of the changes course of chromium concentration obtained for the "reference" solution, for the "reference" solution containing 0,42 mol/dm^3 of chloride as well as the "reference" solution containing 0,21 mol/dm3 of sulfate were presented.

In the "reference" solution in the first hour of the process a sudden decrease of chromium concentration in the feed phase and its sudden increase in the organic phase was observed. In the stripping phase chromium was not present during this time. In the later period the changes in chromium concentration in the feed and membrane phases were considerably smaller, whereas in the stripping phase its increase was observed. Moreover, in the membrane phase the concentration of chromium achieved maximum. The efficiency of the extraction and stripping after 12 hours of the process amounted to 64% and 21%, respectively.

A two-stage extraction process (look at Figure 1A) can result from considerable changes of pH in the feed phase during the process, and particularly, in its first hour when pH of the tested solution changes from 4 to 2,5 (look at Figure 2).

The chromium hydrolysis runs particularly effectively with these pH values. Lanagan and Ibana[21] as well as Pandey at al.[23] proved that strongly hydrolyzed chromium(III) ion easily creates stable complex compounds with acidic extractants. It results in high efficiency of chromium(III) extraction with the use of these compounds. Presumably in the case of dinonylnaphthalenesulfonic acid a similar dependence can be observed. Along with the decrease of pH value the form of chromium in the solution varies[25]. Nonhydrolyzed chromium is not so attractive for the carrier any more. At consequence the speed of the extraction process decreases. The changes of pH of aqueous phases are the consequences of the counter-transport case of a coupled transport mechanism appear in the studied system. In this process the chromium ions in the feed phase are substituted by an equivalent amount of counter-transport proton ions from stripping phase.

The delay of the stripping results probably from the considerable thickness of the membrane, that in the consequence leads to retention of the transported ions.

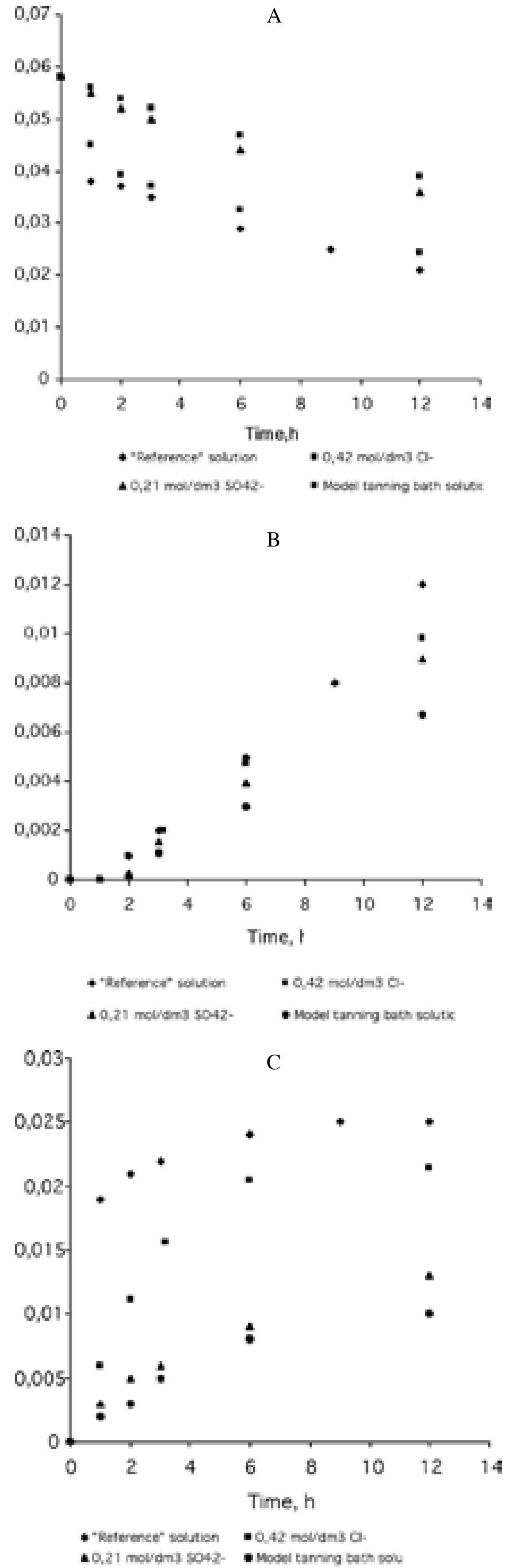

Figure 1: The changes of chromium concentration (III) in the: A) feed, B) stripping, C) membrane phase in time, dependent on the constitution of the feed phase.

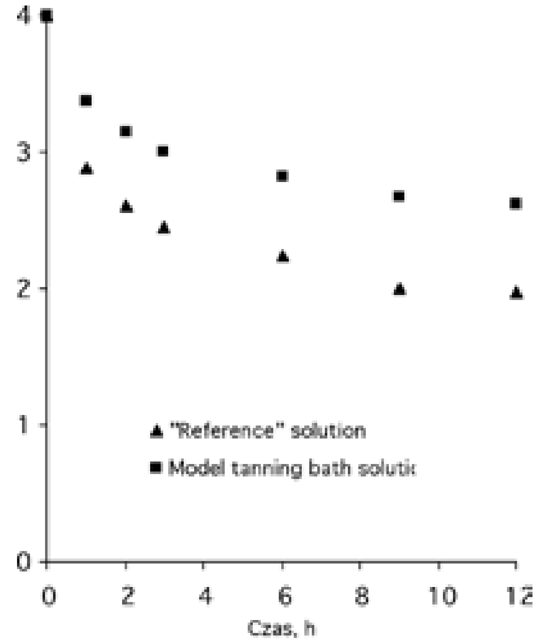

Figure 2: Variation of pH of the feed phase with time of experiment.

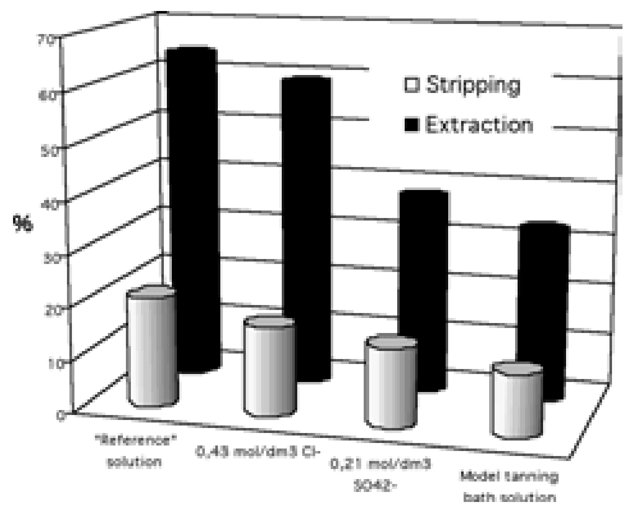

Figure 3: The changes of extraction and stripping dependent on the feed phase composition.

With regard to the solution containing chloride ions, the curves of changes of chromium(III) ions concentration in particular phases processed similarly as in the reference solution. It is a proof that the presence of chloride in the solution does not influence considerably the effectiveness of chromium(III) extraction and retrograde extraction (Figure 3). The obtained results indicate that hydroxy- and aqua- complexes of chromium(III) occurring for pH range in the first period, are much more stable than chloride complexes. These results are consistent with the data presented by Huheey[25], where in the case of chromium(III) the influence of anions can be ranged according to the following order:

$$NO_3^- < Cl^- < CO_3^{2-} < SO_4^{2-}$$

The presence of sulfate ions in the solution has a considerable influence on the effectiveness of the process. SO_4^{2-} ions have the ability to create stable complexes with chromium(III). The solution containing sulfate demonstrated considerably weaker chromium extraction than the "reference" solution. During 12 hours only 38% efficiency of this stage of the process was obtained. In the first hour of the process no sudden decrease of chromium concentration was observed, as it was in the case of the "reference" solution and even the solution containing chloride. The picture of changes of chromium concentration in the membrane phase shows its slow and stable accumulation (Figure 1C). No clear maximum chromium concentration in the membrane was observed. Slight chromium concentration in the membrane caused the extension of the delay time of the chromium penetration to the stripping phase, slowed down the re-extraction and also caused the decrease of its effectiveness only to 15%.

Chromium(III) extraction from the model solution of tanning liquor, which is a mixture of sulfates and chlorides, demonstrates features similar to the extraction from solutions containing sulfates. It confirms the thesis about the good complexing properties of sulfate ions and the little stability of chlorine complexes of chromium(III).

The influence of the feed phase composition on the transport kinetics

Due to the complex constitution of the tanning liquors, forming them the particular components (including chromium), undergo constant changes. We speak here about the so-called "ageing" process. Figure 4 presents the chromium(III) concentration in particular phases depending on time and the age of the model "tanning liquor". When analyzing the obtained results we can undoubtedly state that conducting the permeation in the "aged" solutions (2 and 48h) is ineffective. After 12 hours of the process, for both analysed cases the decrease of chromium concentration in the feed phase was achieved only to 1%. Presumably, as a result of changes undergoing in the tanning liquor the form of chromium(III) varies. This limits and even completely inhibits the pertraction process. Furthermore, it was observed that the curves drawn for the 48-hour solution had similar course to those obtained for the 2-hour solution. Probably, the equilibrium in the „tanning liquor" solution was achieved already after two hours that proves that the "ageing" process is a fast process.

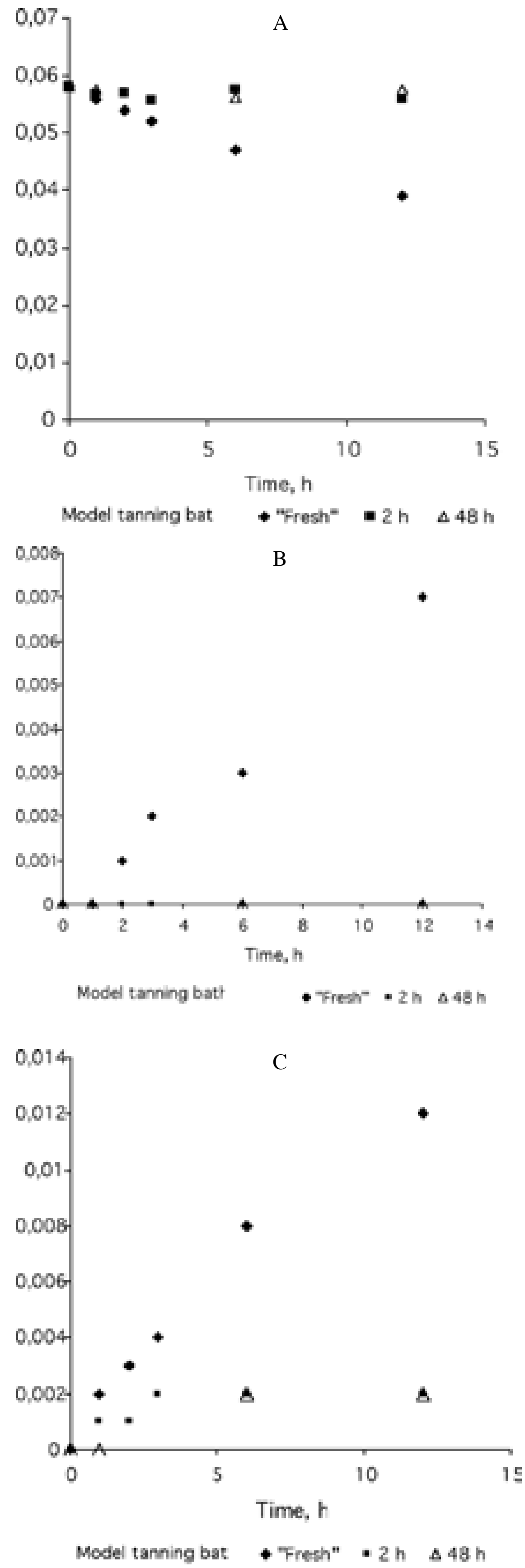

Figure 4: The changes of chromium(III) concentration in the A) feed, B) stripping, C) membrane phase dependent on time and on the age of "tanning liquor"

The changes of chromium concentration in the membrane phase are small. It is undoubtedly the result of the slight grade of extraction. Due to the slight concentration of chromium in the membrane and considerable thickness of this layer no stripping of chromium was observed.

CONCLUSIONS

The course of changes in chromium(III) concentration in time for the water solution indicates a great influence of pH of the water phase on the speed and the effectiveness of the transport. The chromium(III) hydrolysis process was especially effective for the pH range of 3 - 4. Strongly hydrolysed chromium(III) ion easily creates stable complexes with DNNSA. It has a clear reflection in the high efficiency of chromium(III) extraction. Introducing SO_4^{2-} to the chromium solution causes the creation of stable sulfate complexes that, to a large extent, limit the transport capacities of the investigated system with the liquid membrane.

The presence of chlorines in the solution does not considerably influence the effectiveness of chromium(III) extraction and stripping. Hydroxy- and aqua- complexes of chromium(III) are much more stable than chlorine complexes. Unfortunately, such results substantially restrict the application of liquid membranes intended for the release of chromium from tanning liquors.

Furthermore, as a result of "aging" of tanning liquor the inhibition of the process was noticed. Starting the process, even after 2 hours from the preparation of the tanning liquor, practically no chromium pertraction can be observed. Therefore, a possible use of liquid membranes intended for the release of chromium from tanning sewage is possible only for fresh solutions.

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