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(54) Title: METHOD OF CHEMICAL-MECHANICAL TREATMENT OF WASTE WATERS FROM OPERATION OF TANNERIES

(57) Abstract: A method of chemical - mechanical treatment of waste waters from operation of tanneries which includes the mutual coagulation of pollutants by the way of joint treatment of waste exhausted process baths in concentrated state.



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Method of chemical-mechanical treatment of waste waters from operation of tanneries

Technical Field

The invention relates to a method of chemical-mechanical treatment of waste waters from processing of raw hides of farm animals, such as sheep, beef cattle, goats, horses, and others.

Background Art

Hides processed in tanneries are an intermediate product intended for further processing. In the case of intermediate products for fur products, there is used a technology of chrome tanning, where raw hides are treated in a bath containing chromium(III) salts. In order to obtain pelts, i.e. hides without hair, raw hides are treated in an alkaline bath, containing alkalis, and, in particular, sodium sulphide, by which subcutaneous tissues and hair are removed from the raw hides. The both technologies produce waste waters containing harmful, and, in the concentrations in question, toxic substances. For this reason, these waters must not be discharged into public watercourses, and not even into a public sewerage system leading the waste waters into a community waste water treatment plant for final treatment. Because of that, the waste waters must be brought in line at least with the local sewerage system regulations.

According to the state of the art, waste waters from tanneries producing the above-mentioned kinds of waste waters are treated, on the one hand, together in a mixture, namely in the mixture of concentrates of waters from chrome tanning, and of leach waters, together also with washing waters from the above-mentioned tanning processes (see FIG. 1), qualitative composition of which is similar to the concentrates but concentration of which is many-times lower than in the original concentrates. During that, pollution is reduced simply by diluting, but this reduction is insufficient from the point of view of the requirements. Joint treatment of this mixture of waters is uneconomical and shows low efficiency. Because of that, some of the tanneries are using the method of treatment of waste waters from tanneries separately according to their kind (see FIG. 2).

Disclosure of Invention

Through this method, higher treatment effect is achieved, but at the expense of much higher costs for operational chemicals and investments.

In accordance with the method of chemical-mechanical treatment of waste waters from operation of tanneries (see FIG. 3 and FIG. 4), according to our invention, waste exhausted process baths are treated in the concentrated states, namely in the way that, at first, sulphides (S^{2-} , SH^-) are removed separately from the leach water, preferably through oxidation by air oxygen or through chemical oxidation using an oxidation agent, and this water is mixed with the exhausted concentrated bath polluted with Cr^{3+} salts, and together with that, it is subjected to chemical coagulation. The remaining (wash out) waters are then added to the treated mixture in the end.

The method of treatment according to the invention provides the following advantages:

1. Improvement of the efficiency of the treatment process;
2. Improvement of final level of treatment of waste waters from tanneries ;
2. Reduction of consumption of operational chemicals;
3. Reduction of investment by lowering of requirements on operational equipment,;
4. Reduction of energy consumption. and staff of the treatment plant;
5. Reduction of requirements on the built-up area;
6. Reduction of production of waste sludge;
7. A consequence is also lowering of the need for maintenance and spare parts.

The invention will find use in tanneries using the both basic processes: treatment by chromium(III) salts in weakly acid pH for production of intermediary products for fur products, and production of hairless leathers through action of alkaline sulphides in strongly alkaline baths.

Detailed Description of the Invention

A method of chemical-mechanical treatment of waste waters from operation of tanneries, through which there are treated waste exhausted process baths in concentrated state, and, at first, there are removed sulphides from the bath containing them via an oxidation

process known as such, characterized in that, at first, the concentrated waste bath from chrome tanning is mixed with the concentrated bath, from which sulphides were removed, in the volume ratio from 3 : 1 to 2 : 3, and, under permanent mixing, there are added a coagulating agent based on iron, and calcium hydroxide in order to keep the resulting pH of the mixture in the range from 9.5 to 10.5, and, subsequently, there is added an auxiliary flocculating agent on the basis of a polymeric organic substance, for example, polyacrylamide, and the resulting sludge is removed from the liquid phase by sedimentation.

When the method of the invention is carried out (FIG. 3 and FIG. 4), it is proceeded in the way that a volume of concentrated waste bath from the production of pelts, from which sulphides were removed, for example, via catalytic oxidation using air oxygen, is pumped into a reaction tank equipped with a mixing device, to which a volume of concentrated tanning bath comprising chromium(III) salts is added under permanent mixing, and, simultaneously, there is added a solution of ferrisulphate in an amount according to the level of organic pollution, and, further, calcium hydroxide in order to keep the reaction pH of the mixture in the range from 9.5 to 10.5, and, subsequently, there is added an auxiliary flocculating agent, for example, a high-molecular polyacrylamide, and, after concluding the mixing, the mixture is allowed to sediment. After 30 to 60 minutes of sedimentation, the settled sludge is discharged from the bottom of the tank, and the supernatant is pumped for further treatment, or optionally, mixed with the other waters from the tannery.

The main advantage of the method of the invention is its high efficiency of treatment, with simultaneous saving of reaction chemicals, and with lower requirements on the number and size of the treatment equipment.

Brief Description of the Drawings

The invention will be disclosed in accordance with the following Drawings in which:

FIG. 1 shows the method according to state of the art;

FIG. 2 shows another method according to the state of the art;

FIG. 3 shows the method according to the invention in comparison with the state of the art as drawn in FIG. 1 and in FIG. 2;

FIG. 4 shows the complete method according to the invention.

Best Mode for Carrying Out of the Invention

An embodiment of the method of the invention is illustrated by the following specific example:

EXAMPLE 1

In accordance with FIG. 4, a tannery processing raw hides of various farm animals, on the one hand, into fur products, and, on the other hand, into pelts to be further processed in the leather industry, there are produced, at the same time, two kinds of exhausted tanning baths:

on the one hand, waters from chrome tanning, the pollution of which is characterised by the following values: 2500 mg/l Cr^{3+} , and organic pollution expressed by the value $\text{COD} = 8500$ mg/l O_2 , and $\text{BOD}_5 = 4760$ mg/l O_2 at pH = 4.6, and leach waters from pelts production, with values $\text{S}^{2-} = 2100$ mg/l, $\text{COD} = 16500$ mg/l O_2 , and $\text{BOD}_5 = 9200$ mg/l O_2 at pH = 12.9.

Both kinds of waters are lead into a waste water treatment plant separately in the concentrated state, together with the first washing waters, the composition of which is similar to the original baths. From the both waters, coarse mechanical pollutants are removed by passing through mechanical sieves with mesh size 1 mm. Subsequently, sulphides are removed from the sulphide water through catalytic oxidation by air oxygen to residual values 0 to 5 mg/l. This water showing organic pollution level essentially in the original values is accumulated in tank /1/. Water with content of trivalent chromium accumulates in tank /2/. From tanks /1/ and /2/, the both waters are pumped into reaction tank/5/, in the way that the ratio of the water with chromium to the leach water free of sulphides in the total volume of the reaction tank is 3 : 2, and, subsequently, under permanent mixing via the mechanical mixer, there is added ferrisulphate in an amount 4 mval/l in order to support the coagulating process /6/, then calcium hydroxide is added in an amount 0.5 g/l /7/, and, finally, there is added an organic polymer based on polyacrylamide in an amount 2 mg/l, in order to speed up sedimentation of the produced sludge /8/. Subsequently, mixing is stopped and the content of the reaction tank is allowed to sediment. After 45 minutes of sedimentation, the layer of settled sludge from the bottom of the tank is pumped into tank/9/, and, subsequently, the separated water is pumped, using the pump /10/, through a sand filter /11/ into tank /12/, into which the other wash out waters from the tannery are lead.

Industrial Applicability

The invention will find use in tanneries using, at the same time, technologies of tanning of raw hides in baths comprising, as the effective component, salts of trivalent chromium, and of producing pelts in leach alkaline baths containing alkaline sulphides.

;

Claims

1. A method of chemical – mechanical treatment of waste waters from operation of tanneries which includes the mutual coagulation of pollutants by the way of joint treatment of waste exhausted process baths in concentrated state.
2. A method according to claim 1, wherein the sulfides are removed separately from the process bath from the production of pelts by removing via an oxidation process by air oxygen or through chemical oxidation using an oxidation agent .
3. A method according to claim 2, wherein the leach water from the oxidation process are collected separately.
4. A method according to claim 1, wherein the process bath from the chrome tanning containing chromium salts is collected separately.
5. A method according to claim 1, wherein exhausted concentrated bath polluted with chrome salts (claim 4) is mixed together with the concentrated leach waters from the oxidation process(claim 3) in a volume ration 3:1 to 2:3 according to the levels of pollution of both kinds of waters.
6. A method according to claim 5, wherein mutual coagulation reaction of both kinds of polluting waste waters is proceeding under permanent mixing and adding the of ferrisulphate in an amount according to the level of organic pollution and calcium hydroxide in order to keep the reaction pH of mixture in the range from 9,5 to 10,5 and auxiliary flocculating agent , for example , a high – molecular polyacrylamide.
7. A method according to claim 6, wherein after mixing and sedimentation process, the settled sludge is discharged and the supernatant is filtered and mixed with other flushing waters from tanneries.

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CHROMIUM WASTES CONCENTRATES

LEACH WASTES CONCENTRATES

OTHER WASTES

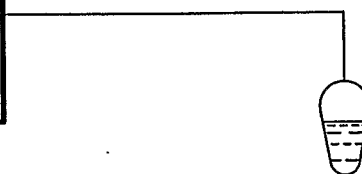
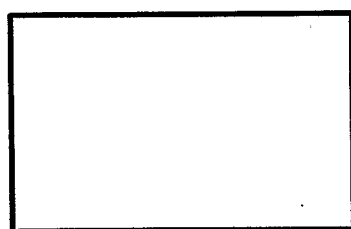


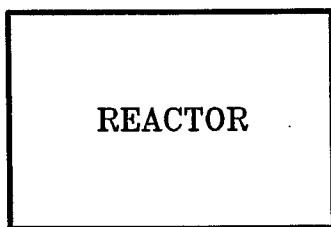
FIG. 1

STATE OF THE ART

CHROMIUM WASTES CONCENTRATES

Ca(OH)₂

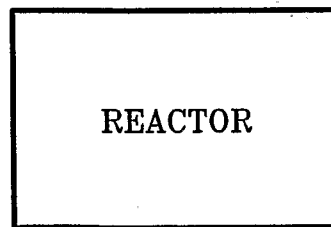
Fe₂(SO₄)₃



REACTOR

LEACH WASTES CONCENTRATES

Fe₂(SO₄)₃



REACTOR

OTHER WASTES

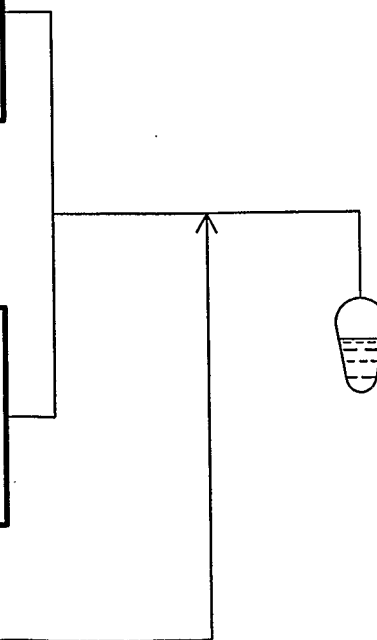


FIG. 2

STATE OF THE ART

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FIG. 3

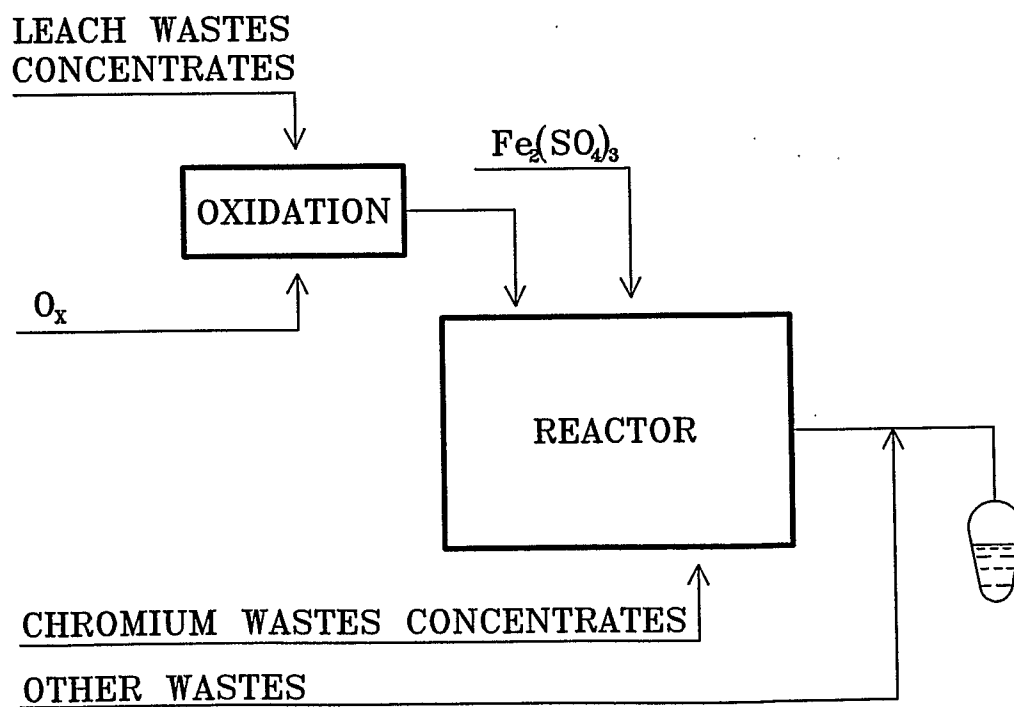
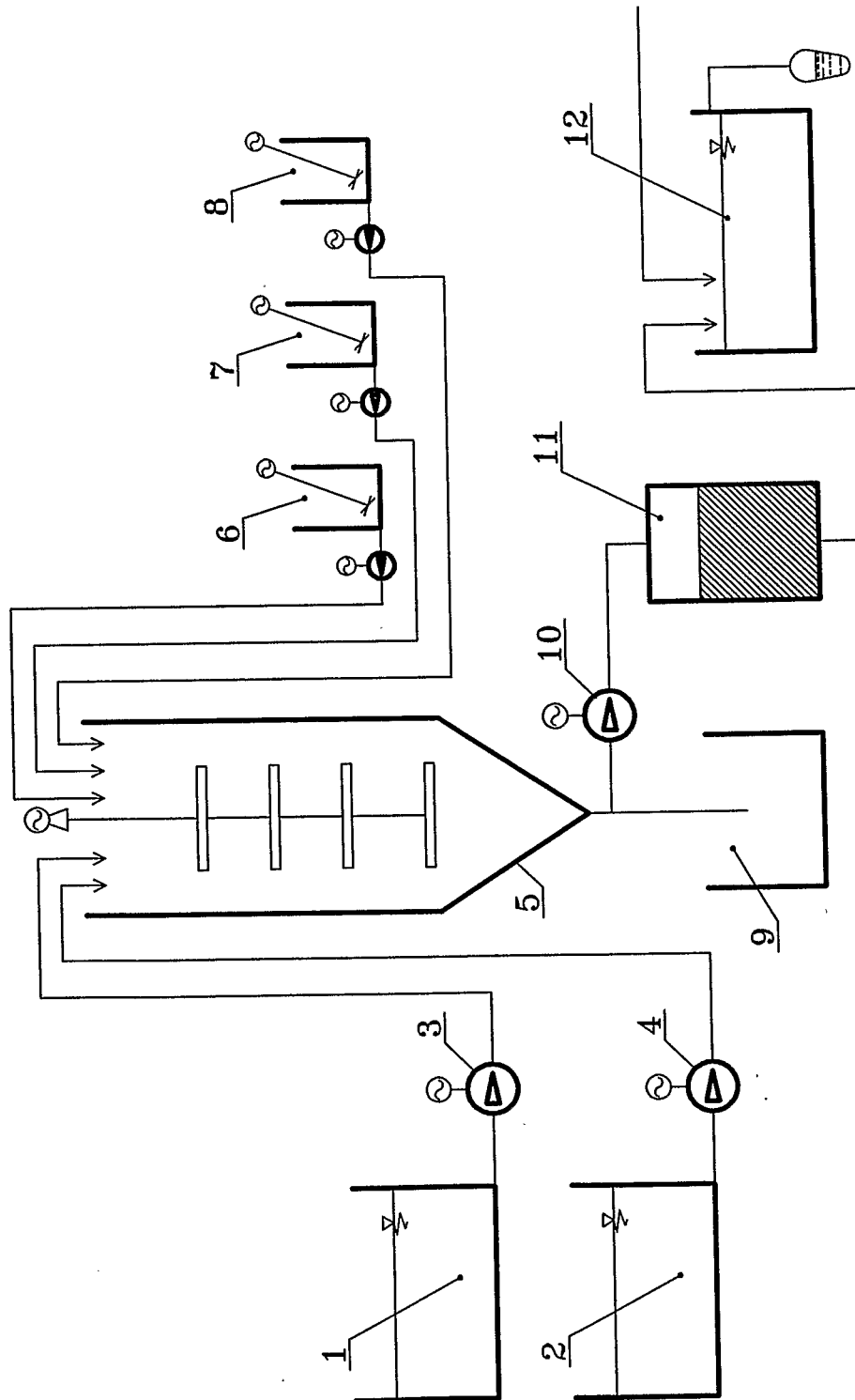


FIG. 4



INTERNATIONAL SEARCH REPORT

International application No
PCT/CZ2009/000093

A. CLASSIFICATION OF SUBJECT MATTER INV. C02F9/00 ADD. C02F1/52 C02F1/56 C02F1/66 C02F1/74 C02F101/22 C02F103/24 C02F101/10		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C02F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, COMPENDEX, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	P. MIJAYLOVA NACHEVA, G. MOELLER CHAVEZ, M. JUAREZ HERRERA: "Alternative treatment strategy for tannery wastewater reuse and material recovery" WATER SCIENCE AND TECHNOLOGY, vol. 50, no. 2, 2004, pages 121-130, XP002555494 page 126 - page 127 figure 2	1-7
A	----- DE 195 17 231 A1 (STOCKHAUSEN CHEM FAB GMBH [DE]) 21 November 1996 (1996-11-21) example 5 claim 13 -----	6-7
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents :		
A document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. * & * document member of the same patent family		
Date of the actual completion of the international search	Date of mailing of the international search report	
16 November 2009	07/12/2009	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Janssens, Christophe	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 19517231	A1	21-11-1996	NONE