TESTING AEROBIC DEGRADATION OF THE PROTEIN PORTION OF FILTER CAKE AFTER FILTRATION OF CHROME TANNED WASTE

by

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ABSTRACT

mple of utilizing tanning waste as a secondary ıaterial is enzymatic hydrolysis of chrome ʒs, the result of which is collagen hydrolysate ıercially applicable) and filter cake containing ed Cr_2O_3 contaminated with collagen residues. view to further potential utilisation of chrome the content of collagen portion has to be d to a minimum. A possible solution, the of this presented work, is removal of the ɔn portion through aerobic biological ation in an aqueous or soil environment. rocess was examined by means of biochemical consumption (standard CSN EN ISO 9408) carbon dioxide production expressed ercentage of theoretical production (standard 5209-92). The source of micro organisms was mmercially produced soil substrate and a soil prepared there from for inoculating aqueous nment. Using the described conditions, it was that the collagen portion is removed aqueous environment by 83% and from the 58% (in approximately 80 hours). Due to solubility, chromic oxide does not exhibit nfluence.

ABSTRACTO

emplo de utilización de los residuos curtidos una materia prima secundaria es la hidrólisis ática de las virutas de cromo, el resultado es el ɔno hidrolizado (comercialmente aplicable) torta de filtro que contiene Cr_2O_3 hidratado ninado con residuos de colágeno. Con el de la utilización potencial adicional de la torta ɔmo, el contenido de colágeno tiene que ser do a un mínimo. Una posible solución, que es ıa de este presente trabajo, es la remoción de la ɔn de colágeno a través de la degradación ɡica aeróbica en un ambiente acuoso o de suelo.

Este proceso se examinó por medio del consumo de oxígeno bioquímico (Norma CSN EN ISO 9408) y la producción del anhídrido carbónico expresada como un porcentaje de producción teórica (Norma ASTM 5209-92). La fuente de microorganismos fue el substrato de tierra producido comercialmente y un extracto de tierra preparados allí por inoculación del ambiente acuoso. Usando las condiciones descriptas, fue encontrado que la porción de colágeno es removida del ambiente acuoso por 83% y de la tierra por 58% (en aproximadamente 80 horas). Debido a su insolubilidad, el óxido crómico no exhibe influencia tóxica.

INTRODUCTION

Technologically viable processing of chrome shavings by enzymatic hydrolysis has been described in the literature[1]. Products are protein hydrolysate (ProtH) and chromium-enriched filter cake. The remaining collagen portion is partly present in the cake in free form; mainly, however, it is bound by coordination bonds with chromium. Removal of this portion may be realized by a number of procedures, for example, by washing with water after additional enzymatic[2] or alkaline hydrolysis[3] or by anaerobic digestion[4]. Managing the removal of the collagen portion of the chrome cake is an important step to utilizing chrome shavings, i.e. not only collagen hydrolysate (of relatively high purity) but also the filtration residue. Without this step, the chromium contained in the filter cake cannot be recycled for technological reasons; for instance, it cannot be added to freshly prepared chrome liquor[5].

This work is a complement to tests of biologically removing the collagen portion of filter cake under aerobic conditions in an aqueous and soil environment; changes in biochemical oxygen demand (BOD) were examined together with balance of produced carbon dioxide. It describes behaviour of the filter cake especially during its use as landfill. Biodegradability of protein hydrolysate was already subject of a number of works, particularly in connection with its use as an additive to PVA blends, for example[6,7]; this work is continuation of this research.

EXPERIMENTAL

All employed chemicals were of analytical purity, manufactured or distributed by Lachema Co, Brno, Czech Republic.

Mineral medium solution

A mixture of inorganic salts (mineral medium) was used as an aqueous environment, which was prepared according to standards valid for evaluating biological aerobic degradability of organic substances in an aqueous environment[8] and soil environment[9].

Quantities dosed into a 1-liter volumetric flask were 800 ml distilled water saturated with atmospheric oxygen, and always 1 ml. of stock solutions of $CaCl_2$ (27.5 g.L^{-1}), $FeCl_3$. $6H_2O$ (0.25 g.L^{-1}), $MgSO_4$.$7H_2O$ (22.5 g.L^{-1}), and of solutions of trace elements (0.75 g.L^{-1} H_3BO_3, 0.05 g.L^{-1} $(NH_4)_6Mo_7O_{24}.4H_2O$, 0.18 g.L-1 $CoSO_4.7H_2O$, 0.5 g.L^{-1} $CuSO_4.5H_2O$, 0.1 g.L^{-1} $ZnSO_4.7H_2O$, 3 g.L^{-1} $FeSO_4.7H_2O$). Quantities further added were 20 ml. solution of phosphate buffer (8.2 g.L^{-1} KH_2PO_4, 21.75 g.L^{-1} $K_2HPO_4.12H_2O$, 44.7 g.L^{-1} $Na_2HPO_4.12H_2O$) and 5 ml. $(NH_4)_2SO_4$ (10 g.L^{-1}) solution. All were mixed and filled to the mark with distilled water saturated with atmospheric oxygen.

Biological material

Work utilized two kinds of commercially supplied soil substrates from the AGRO CS Co., Ceska Skalice, CZ, gardening substrate A (pH 5-7, N 150-400 mg.L^{-1}, P_2O_5 80-250 mg.L^{-1}, K_2O 250-600 mg.L^{-1}) and gardening substrate B (pH 5-6.5, N 100-300 mg.L^{-1}, P_2O_5 100-300 mg.L^{-1}).

The inoculum used for the aqueous environment were soil extract prepared from gardening substrate A and gardening substrate B mixed in a ratio of 2:1, with the final moisture content 50%, which was shaken 1 hour in mineral medium and filtered through sterilized filter paper. Level of the extract pH was adjusted to 7 with 0.1M NaOH and extract was aerated 24 hours prior to use.

The inoculums used for the soil tests were gardening substrate A - gardening substrate B (see above) of moisture content approximately 60%, aerated 5 days prior to the test to remove residual organic carbon.

Tested material[10]

Protein hydrolysate(ProtH) Hykol E produced by the Tanex Co, Hrádek n/Nisou, CZ; filter cake (FC1, FC2 - containing 20-30% protein portion, TABLE I) and washed chrome cake (FC3 - containing residual TC 29%) from manufacture of ProtH.

Drying of sample was executed at 105°C to constant weight (approximately 17 h). Nitrogen in filter cake was determined by the Kjeldahl method. Results are given as percentage of total nitrogen (TKN) in solids, or as ratio TKN/Cr_2O_3. Chromium content in the filter cake was determined following mineralization in microwave oven (Mineraliser Milestone Mls 1200, Sorisole, Italy) using an atomic absorption spectrophotometer GBC 933A, Dandeong, Australia. Values are expressed as % Cr_2O_3 in solids. Possible traces of Cr^{6+} in filtrates were determined by photometry applying diphenylcarbazide. The amount of organic carbon (TOC) in filtrates was determined with a Shimadzu TOC 5000A carbon analyzer.

The tested substance was sole source of organic carbon for inoculum microorganisms. Results were compared with blank test (endogenous respiration of inoculum microorganisms) and with degradation of standard compound (sodium benzoate) for verifying activity of soil inoculum.

Respirometric test[8] in accordance with CSN EN ISO 9408

This manometric method is based on studying biological oxygen demand by aerobic microorganisms through changes in gaseous phase pressure (CSN EN ISO 9408)[8]. Concentration of tested material in volumetric flasks was 100 and 500 mg.L^{-1}, 5 mL soil extract (see above) and 10 mg.L^{-1} allyl thiourea for suppressing nitrification processes. To suppress biological processes, concentration of $HgCl_2$ in compensation vials was 200 mg.L^{-1}. At conveniently chosen time intervals, number of divisions on U-tube of the Bial BOD 10 apparatus (made by JZD AK Slusovice, CZ) were recorded.

Modified respirometric test[11,12] in accordance with standards ASTM D 5209-92 and CSN EN 29439

The bottle apparatus[10] consisted of 1- liter vessels containing reaction suspension in 0.7-L volume, interconnected through silicone hoses to cleaning (removal of atmospheric CO_2) arm and absorption arm of equipment. Actual concentration of sample in reactor was 100 and 350 mg.L^{-1}. Employed inoculum was 50 ml. soil extract. CO_2 production was examined daily following absorption in 1M NaOH; after precipitation with barium chloride, unreacted quantity was retitrated with 1M HCl. CO_2 production was also studied by means of GC after withdrawal from reaction flasks through septum. Determination of proper CO_2 content was carried out by means of gas chromatograph CHROM 5 apparatus (made by Laboratorni Pristroje, Prague, CZ) in glass packed column 3.6 m long and of 3-mm inside diameter. The column was packed with Porapak QS 80-100 mesh. Detection employed thermal conductance detector

TABLE I
Characteristic of Chromium Cake

Dry matter (%)	TOC (%)[1]	TKN (%)[1]	Cr (%)[1]	Mg (%)[1]	Cr_2O_3 (%)[1]	TC/Cr_2O_3	TKN/Cr_2O_3
17.27	27.05	7.60	4.24	3.43	6.17	4.07	1.23

1) % in dry matter
TKN - Total Kjeldahl Nitrogen
TC - Total Carbon

(TCD), helium 4.6 carrier gas, thermostat temperature 50°C, detector temperature 100°C. Main biodegradability criterion was ratio (D_{CO2}) of actually CO_2 production arising during microbial degradation to theoretical quantity (Th_{CO2}) given by balance of carbon present in sample;

$$Th_{CO_2} = \frac{[(TC_s.c_s)/100]}{Mw_{carbon}}$$

where Th_{CO2} is theoretical quantity of CO_2 in mol. L^{-1}; Mw_{carbon} is molecular weight of carbon in g.mol^{-1}; TC_s is concentration of total carbon in substrate in % (inorganic carbon content in tested samples is negligibly low); c_s is concentration of substrate in reaction suspension in g.L^{-1}.

Determining biodegradability in an aerobic soil environment[9]

Soil reactors (lysimeters) were of approximately 20-liter volume. Course of degradation was again examined by means of CO_2 production with a final titration determination. Air was drawn in through reactors with pumps after disposing of CO_2 by passing through absorber containing 2M NaOH. Actual biodegradation of substrate (reactor B) proceeded in soil of approximately 5 kg weight and approximately 60% water content placed in soil reactors. Testing was executed under two loads (60 and 180 g FC per lysimeter volume). Sorption solutions of hydroxides were exchanged in approximately one day intervals and partly exhausted solutions were titrated with HCl. Reactor A was employed in both cases to determine endogenous respiration.

Apparatus

Biological degradability of tested samples using GC and final titration determination utilized a so-called bottle apparatus (Fig.1). Biodegradability of samples took place in 1L bottles attached by means of silicone hoses to the cleaning and absorption arms of the apparatus. The cleaning arm consists of two washing flasks containing 2M NaOH (to catch atmospheric CO_2) and one indication flask with 0.02M $Ba(OH)_2$ (for signaling potential exhaustion of previous solutions). The absorption arm consists of absorbers with 1M NaOH which catch CO_2 produced from reaction suspensions proper. This arrangement and interconnection of the apparatus enables discontinuous aeration of the bottles. In their inactivity regime their gastightness is secured by clamps fastened to silicone hoses. Bottle closures are also provided with gastight septum by means of which gaseous phase samples may be withdrawn for GC

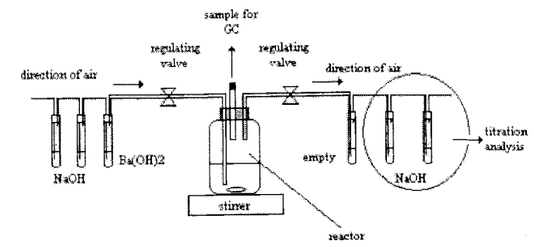

FIGURE 1. - Diagram of bottle apparatus for determining biodegradability of tested samples in aqueous environment by CO_2 production through GC analysis and titration

analysis[10]. Air is sucked into the apparatus by pumps and its rate of flow is set to approximately 200 mL.min^{-1}.

Determining biodegradability of tested samples in a soil environment at a laboratory temperature of 25 ± 2°C employed lysimeters (Fig.2). Course of degradation was examined by means of produced CO_2. Evolving CO_2 was trapped in two series-connected absorbers with 1M NaOH. A further safety absorber containing 0.025M $Ba(OH)_2$ was inserted behind these absorbers to signal exhaustion of two preceding solutions. Rate of air flow was set to approximately 100 mL.min^{-1}. Apparatus was connected to mains through switch clock; regime was set for cycles of 15 min aeration, 45 min pause.

Processing results

Measured dependencies BOD= f(t), D_{CO2}= f(t) were described in regression mode by an equation for first-order substrate kinetics;

$$D = D_{max}\left[1 - e^{-k.(t - t_{lag})}\right]$$

where D_{max} is the regression coefficient representing the limit value in infinite time in % - BOD_{max}, DCO_{2max}; k is negative value of rate constant - k_{BOD}, k_{DCO2} in h^{-1}; t_{lag} is the shift on time axis indicating lag phase in hours.

It must be emphasized that reaction order is only an empiric quantity and in the case of substrate kinetics has no objective significance. It should merely describe rather complex actions by simple power functions which are valid only within limits they were determined. Calculating regression coefficients was performed by the least squares method applying the Statistica CZ 6.1 program. All experimentally obtained dependencies were processed by regression in such manner that only those points were taken into account where substrate biodegradation (lag phase subtracted) already unambiguously proceeded. In actual regression analysis, a regression coefficient of 0.99 was always achieved.

RESULTS AND DISCUSSION

The date reported in this section are results obtained by examining aerobic biodegradation displayed by the protein portion of the studied filter cake in an aqueous and soil environment through methods described in the pertinent

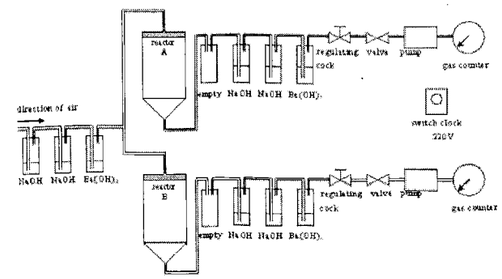

FIGURE 2. - Diagram of soil lysimeters - determining total biodegradability of tested samples in soil environment

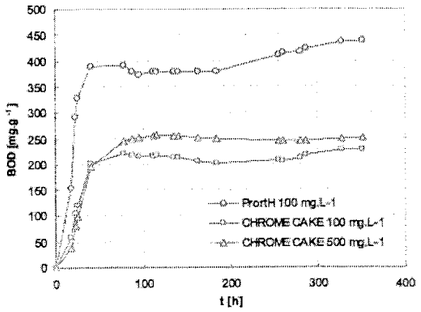

FIGURE 3. - Time course of chrome cake biodegradation according to BOD

preceding paragraph. Methods employed for the aqueous environment were Bial manometric method determining BOD, and bottle test with final determination by volumetry and gas chromatography.

Determining the course of BOD with Hykol E and two quantitatively different filter cake samples is shown in Fig.3.

Compared with ProtH, chrome cake naturally displays lower degradation ability. This is caused by the fact that merely the soluble part of chrome cake partly split after hydrolysis is degradable. Fig.3 shows both concentrations of filter cake exhibit roughly the same BOD ($mg.L^{-1}$) levels that correspond to approximately half the values of BOD measured with ProtH. Compared BOD levels show that average BOD level for filter cake approximately attains 48% of BOD value for ProtH. Even under a fivefold dose of chrome cake, degradation inhibition does not appear; it was also found[10] that under test conditions, oxidation of chromium to its hexavalent toxic form does not occur. The level of pH under a higher dose of chrome cake increased from approximately 7.5 to 8.2-9.6. It was brought about by an increased effect of alkali present in filter cake at higher concentration and under gradually degrading protein.

The extent of determination error (confidence interval) of chrome cake (and ProtH) degradation is shown in Fig.4. For given type of determination, the extent of k_{BOD} with a 95% confidence interval is satisfactory.

In the bottle test (Fig.5), degradation of ProtH evaluated by produced CO_2 (as compared to theory) with final volumetric determination, was about 6% lower than by BOD determination.

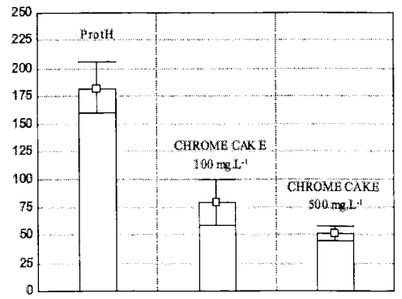

FIGURE 4. - Extent of $-k_{BOD}$ ± 95% confidence interval for biodegradability of ProtH and chrome cake of various concentrations

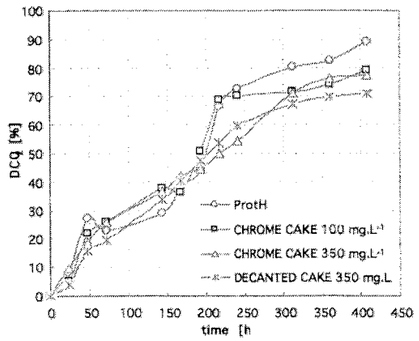

FIGURE 5. - Biodegradability of tested sample calculated from ratio (%) of actually CO_2 production to theoretically CO_2 production determined by means of titration

When employing gas chromatography (Fig.6), regardless of the quantity of produced CO_2 present in the system in a non-ionic form and of pressure, produced CO_2 occurs in gaseous phase as a constant fraction. At a given temperature, this fraction is defined as a constant value of CO_2 separation coefficient, which is defined as the quotient of CO_2 concentrations in liquid and gaseous phase. The dependence of separation coefficient on temperature is not too large, and its value at 20°C is 0.897. Under conditions of the experiment, 41.8% CO_2 of its totally produced quantity occurs in the gaseous phase.

TABLE II presents percentage of degradation of all samples on the basis of produced CO_2 determined by both methods. From

TABLE II
Determining Biodegradability in Aerobic Aqueous Environment

Analysis	ProtH	FC A	FC B	FC C
Gas chromatography (%)	83,0	73,2	83,7	54,6
Titration (%)	89,6	79,8	78,9	79,1

ProtH - collagen hydrolysate
FC A - filter cake - concentration of 100 $mg.L^{-1}$ in testing bottle
FC B - filter cake - concentration of 350 $mg.L^{-1}$ in testing bottle
FC C - washed filter cake - concentration of 350 $mg.L^{-1}$ in testing bottle

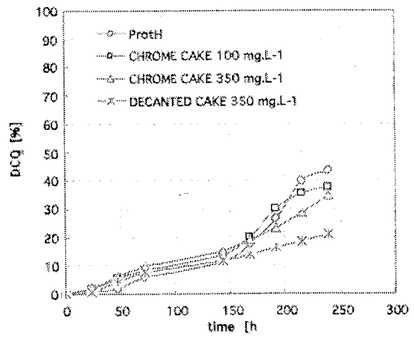

FIGURE 6. - Biodegradability of tested sample calculated from ratio (%) of actually CO_2 production to theoretically CO_2 production determined by GC

measured results it is shown that ProtH undergoes biodegradation most, chrome cake less and washed filter cake least. Determination through gas chromatography appeared as the more reliable as its results were in better accord with values obtained by the manometric test.

Samples used in a further test were chrome cake and washed chrome cake of approximately 100 $mg.L^{-1}$ concentrations so that same TC percentage in weighed-in quantities would be achieved. As already mentioned, cake after enzymatic hydrolysis still contains a part of free protein that was not removed. It was found this protein portion may be partly washed out of filter cake at elevated temperature and, thereby, chromium may concentrate even more[2]. On washing out protein and analyzing TC in solid sample, we may find the percentage of protein a sample contains. The only component not washed out of filter cake with pH being in the alkaline region is precisely chromium with which protein is stabilized. As the quantity of chromium in cake remains the same,

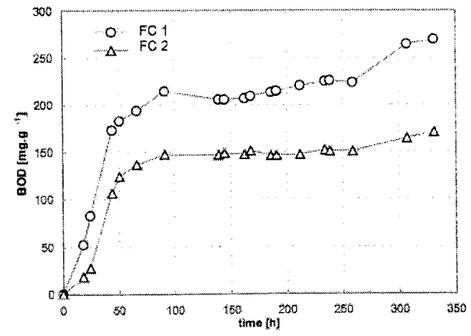

FIGURE 7. - Biodegradation course of filter cakes as examined through BOD

ratios that may be used for assessing the percentage of washed-out protein are TC/Cr_2O_3 (or TKN/Cr_2O_3).

Chrome cake was washed altogether four times with tap water and centrifuged. Every washing lasted about 20 minutes and the sample was heated over water bath with constant stirring. On conclusion of the whole procedure, sample was dried and homogenized in a mortar.

Sample TC value (29.2%) was subsequently determined, sample was mineralized and quantity of chromium determined on AAS. Ratio TC/Cr_2O_3 of washed sample was 3.5, which is a level 14.7% lower than that of unwashed. It follows that a part of free protein contained in original unwashed cake was removed. The proved lower content of free protein in washed sample was reason for also assuming lower BOD values.

In Fig.7 it is shown that BOD values of washed sample are lower than those of original sample, which confirmed our assumption. BOD value attained for ProtH was 51.1% with original sample

TABLE III
The Values of Determined Parameters

Parameter	F 1A	F 1B	F 2A	F 2B
% removed substrate[1)]	89.4	83.4	91.4	82.0
pH_{start}	7.46	7.69	7.45	7.64
pH_{final}	8.27	9.84	8.05	10.26
BOD_{max} ± SD[2)] ($mg\ O_2.g^{-1}$)	51.9 ± 0.36	51.4 ± 0.51	55.8 ± 0.54	60.1 ± 0.29
t_{lag} ± SD[2)] (h)	6.6 ± 1.49	12.4 ± 1.35	<1	8.9 ± 1.2
$-k_{BOD}$ ± SD[2)] ($10^{-3}.h^{-1}$)	40.5 ± 2.9	57.2 ± 6.2	41.9 ± 6.2	70.5 ± 6.4

[1)]accordinag to TOC
[2)]SD - standard deviation
F1A - filtrate 1, actual concentration of substrate in reactor 30 $mg.L^{-1}$
F1B - filtrate 1, actual concentration of substrate in reactor 100 $mg.L^{-1}$
F2A - filtrate 2, actual concentration of substrate in reactor 30 $mg.L^{-1}$
F2B - filtrate 2, actual concentration of substrate in reactor 100 $mg.L^{-1}$
BODmax - regression coefficient representing limit value in infinite time in %
t_{lag} - shift on time axis indicating lag phase in h
$-k_{BOD}$ - negative value of rate constant

TABLE IV
The Values of Detected Parameters in Start and Final of Experiments

Parameter	FC D	FC E
pH_{Start}	4.22	4.16
pH_{final}	3.95	3.84
DCO_{2max} ± SD[1)] (%)	65.52 ± 1.16	70.67 ± 2.56
t_{lag} ± SD[1)] (h)	178.9 ± 3.67	206.1 ± 3.73
$-k_{DCO2}$ ± SD[1)] ($10^{-3}.h^{-1}$)	3.7 ± 0.19	2.7 ± 0.19

[1)]SD - standard deviation
FC D - 60 g dry matter of filter cake on 5 kg soil substrate
FC E - 180 g dry matter of filter cake on 5 kg soil substrate
D_{CO2max} - regression coefficient representing limit value in infinite time in %
t_{lag} - shift on time axis indicating lag phase in h
$-k_{DCO2}$ - negative value of rate constant

(FC1), 32.5% with washed sample (FC3), which roughly corresponds to difference in washed-out protein content. At the start and end of the test, pH of all samples was measured; value increased from starting level 7.5 with FC to approximately 8.

In a further test, tested samples utilized products of chrome cake de-proteination produced by alkaline pressure hydrolysis with potassium hydroxide from previous work[3]. This method is one of the options of concentrating chromium in cake and removing residual protein from it. De-proteination products (filtrates F1 and F2) contained proteins removed from filter cake. Testing these samples ran in order to assess their potential application in the way of fertilizers.

In order to obtain filtrate F1, a temperature of 100°C was used, and KOH in a quantity corresponding to 1.5 times the equivalent quantity of KOH required to hydrolyze all peptide bonds in collagen; the same quantity of KOH as with filtrate F1 was used for filtrate F2, and a temperature of 116°C [3]. Filtrate F2 differs in composition from filtrate F1 by containing an approximately 2.5 times greater quantity of chromium (0.8‰). Results are presented in TABLE III.

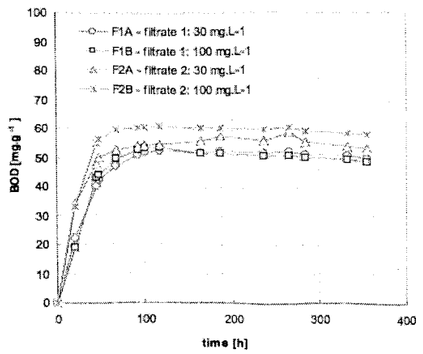

FIGURE 8. - Biodegradation of filtrates examined through BOD

Quantities weighed were selected so that all test bottles contained the same quantity of total carbon.

As shown in TABLE III, degradation degrees of all samples according to changes in TOC content are high (Fig.8); it follows that these de-proteination products are quite well degradable and potentially applicable as fertilizers.

Spectrophotometric determination employing diphenylcarbazide at end of test did not detect any present Cr^{6+} ($c < 0.1$ mg.L^{-1}) in these samples.

Calculated kinetic constants k_{BOD} with 95% confidence interval for discussed filtrates are shown in Fig.9. Results for the given kind of determination exhibit satisfactory scatter.

Fig.10 shows results of aerobic biodegradation time course of chief components under study, i.e. shavings, ProtH and chrome cake in an aqueous environment. Results prove "resistance" of chrome-stabilized material, i.e. shavings, and readiness of free protein portion (in chrome cake) to biodegradation.

Studying biodegradation in a soil environment

Testing in a soil environment used the apparatus of soil

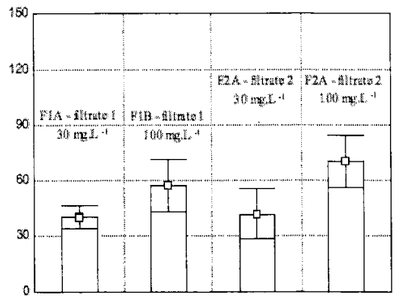

FIGURE 9. - Kinetic constants of 1st-order equation describing biodegradation of filtrates Extent of $-k_{BOD}$ ± 95% confidence interval

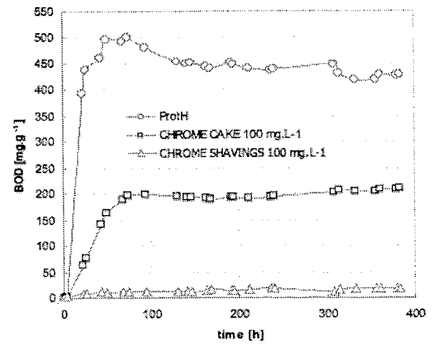

FIGURE 10. - Biodegradation course of chief assessed components

reactors. Degradation was investigated by means of actually CO_2 production and related in percentage to the level of theoretically possible CO_2 production. Principle of determination and description of apparatus are shown in Fig.2. The chief aim of these tests was to find the behavior of chrome cake in a soil environment, or to compare biodegradation course under various doses.

Biodegradation was studied under two different concentration doses. Testing employed gardening substrate B, whose characteristics and preparation are presented in the experimental section. Tests proceeded in such manner that approximately 5 kg blended and evenly moistened soil was dosed into each reactor and both reactors were then set in operation. For about 5 days, natural respiration was examined by catching evolved CO_2, after which the actual experiment of chrome cake degradation was launched. In the first experiment, soil in reactor B was contaminated with 60g dry matter of chrome cake; in the second experiment with a threefold quantity, i.e. 180 g. Reactor A served in both tests as a blank. Soils did not contain any added mineral nutrients.

CO_2 production was watched during test, and readings served to continuously evaluate degradation of chrome cake (Fig.11). At the beginning and end of both experiments, determinations checked actual water content of soils and pH values. As TABLE IV shows, levels of studied parameters did not markedly change during tests.

Maximum CO_2 production rates in both experiments already occurred about the first day following contamination.

In these tests, the same as with an aqueous environment, a higher dose of chrome cake was not found to cause inhibited degradation. It may be concluded from these results that the present chromium does not exert a toxic effect even in a soil environment and at an acid pH level. Hence, it is probable that under conditions of executed tests, oxidation of Cr^{3+} to Cr^{6+} did not occur.

In the first test, substrate degraded by 54.2% in 28 days, in the second test, chrome cake degraded by 58.1% in 35 days. These results are comparable. Calculated values of kinetic constants

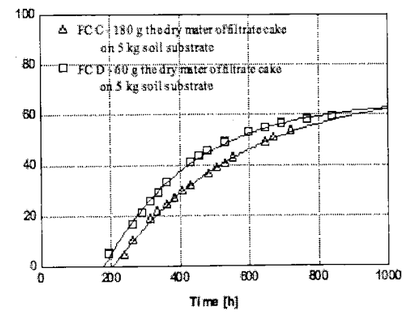

FIGURE 11. - Cumulative CO2 production expressed as percentage of theoretical production through degradation of filter cake, under various doses in lysimeter. Experimental values (points) are extrapolated by 1st order kinetics equation.

k_{DCO2} for the described experiments involving various doses of chrome cake in soil (± 95 % confidence interval) correspond with previous results.

CONCLUSION

The subject of this work was studying biodegradation of chrome-tanned leather waste in an aerobic biotic environment. Owing to the sizeable quantity of this waste, it is important to know what becomes of it on leaving the production process, above all in landfills where it is exposed to external influences. A further reason was study of potential de-proteination of sludge filter cake owing to its potential use regarding possible chromium recycling.

Materials tested were chrome cake, which is waste after enzymatic hydrolysis of shavings, and products of its de-proteination through alkaline pressure hydrolysis. Standard material was readily degradable collagen hydrolysate (ProtH), main product of enzymatic hydrolysis of chrome-tanned shavings under trade name Hykol E. Biodegradation of selected samples was examined in an aqueous as well as soil environment. Testing biodegradability in an aqueous environment used manometric determination on the Bial instrument, where degradation is inspected by means of BOD values. Owing to merely partial solubility of chrome cake and to difficult evaluation of its degradation by means of BOD values, further testing used a bottle apparatus with which biodegradation was evaluated by CO_2 production. Degradation in a soil environment was investigated in an apparatus of soil reactors also by means of CO_2 production. Source of microorganisms was commercially supplied soil substrates.

From the biodegradation course produced by manometric test on the Bial apparatus under given test conditions, it follows that chrome cake still containing residual protein after enzymatic hydrolysis is subject to biological degradation. It may be said that even this material, as based on the measured biodegradability course of tested shavings, is subject to a certain degree of degradation, however, requiring long time horizons. In the case of products of chrome cake de-proteination, their potential application in the form of fertilizers was confirmed.

tests employing the bottle apparatus, degradability based on O_2 production as determined by gas chromatography found ues of 83% with ProtH, 83.7% with chrome cake, and 54.6% h washed filter cake. According to volumetric results, ProtH s removed by 89.6%, filter cake and washed chrome cake approximately 79% alike. The difference is brought about by ferent methodology. All measured values were obtained after days of test.

the soil reaction apparatus, biodegradation of chrome cake was udied under two doses. When 60 g dry matter of sample was sed in 5 kg soil, observed degradation was 54%, when dosed reefold, degradation was 58%. Degradation rate when ntamination with chrome cake was higher was almost three mes greater than with the lower dose.

ested tanning wastes are subjected to degradation in an erobic biotic environment (aqueous as well as soil) depending n content and accessibility of protein component. As opposed o primary material (chrome shavings), the free portion of rotein in products of their hydrolysis is as biodegradable as the ther proteins.

ACKNOWLEDGEMENT

This work was supported by Research Project of the Ministry of Youth, Education and Sports of the Czech Republic No. MSM 7088352101.

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