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PROCESSING OF MIXTURES CONTAINING CHROMIUM--FREE TANNERY WASTES. PART I. FERTILISING VALUE OF POST-FERMENTATION SLUDGES

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Abstract. One of the ways of the utilisation of chromium-free tannery wastes may be their processing into organic fertilisers. Two methods are taken into consideration: methane fermentation and composting. It has been found that alongside gas recovery, methane fermentation of chromium-free tannery wastes allows to obtain material that is dewatered in different degree, with various, but always high, content of fertilising components. The final properties are determined by the kind of wastes (proportions in which various wastes have been mixed), and by conditions of the process. The paper offers a preliminary fertilising characteristics of various sludges and sludge liquids. The results confirm that it is possible to obtain biologically stable fertilising products of big, or even very big, fertilising value from nasty chromium-free tannery wastes.

Key words: sludge, sludge liquid, fertilising value, soil-forming value, stabilisation of organic material

INTRODUCTION

Chromium-free tannery wastes should not be deposited unprocessed in the landfill site due to sanitary reasons. Therefore, subjecting chromium-free tannery wastes to methane fermentation and alternatively using the remains as a fertiliser was introduced in some studies. In Denmark [Anonymous 1994] a separated methane fermentation plant was constructed. In this plant, miscellaneous (not only tannery) wastes underwent processing.

Urbaniak [2003], and Urbaniak and Hillebrand [2003] presented results concerning possibilities of using installations commonly applied in methane fermentation of sludges from municipal sewage. Supported by some auxiliary appliances, the installations can be used for fermentation of chromium-free tannery wastes. They also pre-

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sented new possibilities of much more effective sludges dewatering after fermentation of tannery wastes. Dewatering is very important for using sludges as fertilisers.

In this paper, attention was paid to the content of fertilising and soil-forming components in post-fermentation sludges and liquids, and to the loss of these components in the process of fermentation. Moreover, the distribution of fertilising and soil-forming components between the sludge and liquid, depending on the type of waste and selected conditions of the process, was assessed.

MATERIALS AND METHODS

Basic experimental material included 10 wastes from various kinds of hide processing; 6 from cattle hide processing, and 4 from pig hide processing. Particular wastes (excluding hair) were broken up. Wastes intended for fermentation were crushed 10 times in a grinding machine with Ø 5 mm outlets.

From cattle waste and separately from pig waste 'averaged cattle waste' (item 4 in table 1) and 'averaged pig waste' (item 5 in table 1) were prepared . The wastes were mixed in proportions similar to those obtained in tanneries when processing hides into grain (footwear) leather and in such a state of hydratation in which the waste was obtained.

Two homogeneous protein wastes were studied additionally. One was cattle splits from limed hides, as a typical collagen waste (item 1 and 2 in table 1). To make collagen susceptible to biodegradation in conditions of anaerobic fermentation, the crushed splits were partially gelatinised by 20-minute heating on a water bath up to the temperature of waste of + 90 ± 1^0 C; this temperature was maintained for 20 minutes.

The other homogeneous waste was cattle hair as a typical keratin waste. Native keratin is highly resistant to biodegradation. The hair was separated from technological bath after a conservative liming. The hair, along with hides after an alkaline (calciferous) bath, which causes the so-called hair immunisation (partial inurement to reducing agents), was subjected to partial destruction with sodium sulfide. A part of hair obtained in the above way was flushed with water solution of degreasing agent (Rokafenol-N8) and neutralized (item 3 in table 1). As a result of such a procedure, the latter part of hair (item 3 in table 1) differed from the other parts (item 4.6 and 5.4) in an amount of the ethereal extract (ee). The presence of ee fraction is due to the fact that, together with hair, a large amount of fatty contaminations is separated from technological bath (the hair is fatty).

The analytical characteristics of the studied materials is presented in table 1.

To enrich fermentation environment (chromium-free tannery wastes are typical protein or fat-protein wastes) preliminary sludge from domestic municipal sewage was added to samples intended for fermentation (dry substance (ds) of sludge 8.1%, organic dry substance (ods) 75% of ds, and total N, P, K respectively; 60,15,4.4 $g \cdot kg^{-1}$ of ds). As a source of microflora characteristic for the anaerobic environment of fermentation, the fermented sludge was used (ds 2.7%, ods 58% of ds, and total N, P, K; 38, 18, 2.1 $g \cdot kg^{-1}$ of ds). It was taken from the same sewage treatment plant as the preliminary sludge. The content of heavy metals in the preliminary sludge: Zn 201, Cu 76, Cd 3, Ni 18,

Table 1. Characteristics of chromium-free tannery wastes used to obtain organic fertilisers
Tabela 1. Charakterystyka odpadów garbarskich bezchromowych wykorzystanych do uzyskania nawozów organicznych

Type of waste or material Rodzaj odpadu lub materiału	pH	Share in averaged waste Udział w uśrednionym odpadzie %	Waste component – Składnik odpadu						
			ds., % sm, %	ods % ds smo % sm	ee	pc bu	N_{tot} N_{og}	P_{tot} P_{og}	K_{tot} K_{og}
					g/kg of ds. – g/kg sm				
a	b	c	d	e	f	g	h	i	j
1. Cattle splits from limed hides (collagen waste) /Dwoiny bydlęce ze skór zwapnionych (odpad kolegenowy)	13.1	-	40	96	6	939	170	3.2	0.2
2. Gelatinised cattle splits / Dwoiny bydlęce zżelatynizowane			like waste 1/ jak odpad 1						
3. Cattle hair (keratin waste) / Włos bydlęcy (odpad keratynowy)	7.2	-	24	88	52	750	139	1.6	0.6
4. Averaged cattle waste / Odpad bydlęcy uśredniony	10.7	100	54	93	442	413	72	1.4	0.8
4.1. cuttings from preserved hides / cyplowiny ze skór zakonserwowanych	6.5	10	76	82	280	466	93	1.8	
4.2. fleshings from washed hides /odzierki ze skór moczonych	6.9	33	65	96	665	215	38	0.9	
4.3. fleshings from limed hides / odzierki ze skór zwapnionych	12.9	27	50	93	470	392	65	1.1	
4.4. cuttings from limed hides / cyplowiny ze skór zwapnionych	13.0	7	48	93	190	670	110	2.1	
4.5. splits from limed hides, neutralised / dwoiny ze skór zwapn. zobojętnione	3.1	9	56	96	5	930	169	3.2	
4.6. hair from conservative liming / włos z wapnienia zachowawczego		14	25	88	190	610	105	1.4	
5. Averaged pig waste / Odpad świński uśredniony	10.8	-	58	94	658	211	37	0.7	0.1
5.1. fleshings from washed hides / odzierki ze skór moczonych	6.4	45	69	96	800	79	14	0.3	
5.2. fleshings from limed hides / odzierki ze skór zwapnionych	13.0	32	55	93	650	213	37	0.9	
5.3. cuttings from limed hides / cyplowiny ze skór zwapnionych	13.1	10	49	96	140	710	125	2.4	
5.4. hair from conservative liming / włos z wapnienia zachowawczego		13	28	86	190	630	115	1.5	

Pb 29, Hg 1, Cr 37 mg·kg^{-1} of ds, was considerably lower than this allowable in organic and mineral fertilisers according to legal regulations in most countries.

Analytical tests. The contents of dry substance (ds), organic dry substance (ods), and inorganic dry substance (ids), as well as ethereal extract (ee), protein content (pc), the amount of collagen, total nitrogen (N_{tot}), total phosphorus (P_{tot}), total potassium (K_{tot}), and the content of heavy metals, were determined in accordance with Polish Standard procedures, consistent with the procedures of EU. The content of pc was calculated from organic nitrogen with the use of the following coefficients: cattle hair (keratin) 6.25, splits (collagen) 5.62, and averaged waste 5.6. The amount of collagen was calculated basing on the content of hydroxyproline. The index called 'other organic substances' (oos) is the following difference oos = ods – (ee + pc).

Procedures. Prior to fermentation all tannery wastes (1:1 water : ds of mixtures) were neutralised by a sulphuric acid solution down to pH 7.2. After 5 hours, pH value was checked and adjusted (if necessary) back to 7.2. The hair was neutralised in a bigger amount of water and then impressed.

To prepare fermentation mixtures, to every waste 20% of ds of preliminary sludge (proportion of ds of waste to ds of sludge = 4:1), and 2.2% of the final volume of the sample of fermented sludge were added, and pH value was adjusted, to 7.2, and, finally, water was added to 5 ± 0.1% of ds. Fermentation was carried out at 35° ± 1°C for 35 or 75 days, and pH was maintained within the range of 7.0–7.2.

The sludges were separated from post-fermentation mixtures by centrifuging (4,000 rotations per minute), which allowed to obtain sludges containing 13–25% of ds. Then, the sludges were frozen at –6°C for about 18 hours and next defrosted on a +35°C water bath up to +20°C and finally dewatered by centrifuging to over 40% of ds. All sludges were hydrated with previously separated sludge liquids to the same content of ds, i.e., to 35 ± 1% of ds.

The following symbols are introduced for the results description: averaged cattle (bovine) waste AB, averaged pig waste AP, hair H, splits SP. Thus:

– sludges from 35 and 75-day fermentation of averaged cattle waste: AB-F35 and AB-F75, respectively;

– sludges from 35 and 75-day fermentation of averaged pig waste, AP-F35 and AP-F75, respectively;

– sludge from 35-day fermentation of hair: H-F35,

– sludge from 35-day fermentation of splits: SP-F35.

RESULTS OF EXPERIMENTS

Fertilising value of organic fertilisers is determined by the following properties: 1) the abundance of fertilising components important for plant growth, 2) the assimilability and time of releasing of fertilising components, and 3) the soil-forming influence. Organic fertilisers have much better soil-forming influence than the mineral ones.

Soil-forming influence of post-fermentation sludges

Organic fertilisers enrich soil environment with organic components and micro-organisms, mainly aerobic, favourable for soil. A part of organic compounds is transformed into soil humus. Sooner or later, all of them are used as a source of components necessary for biological life. High organic matter content of the sludges obtained in this study meets the criteria of a soil-forming fertiliser. The content of ods in sludges separated from mixtures after 35 days of fermentation (column c tab. 2) is relatively high and accounts for about 90% of ds (AB-F35, AP-F35, SP-F35), or 64% of ds (H-F35). The losses of ods which confirm the effectiveness of biodegradation and biological stabilisation of the above sludges are 33%, 37%, 43%, and 70%, respectively (column e tab. 4). These data do not include certain amounts of ods, which remained in sludge liquids after the separation of sludges. The prolongation of fermentation of averaged cattle waste and averaged pig waste to 75 days resulted in the increase of losses of ods up to as much as 94% and 97% (samples AB-F75 and AP-F75 in table 4). Simultaneously, the amount of ee fraction in the above samples decreased to 4.1% and 7.6% of ds (41 and 76 $g \cdot kg^{-1}$ of ds – tab. 2).

Table 2. Results of the process of fermentation of crushed chromium-free tannery wastes with the addition of preliminary sewage sludge (20%)
Tabela 2. Wyniki procesu fermentacji rozdrobnionych odpadów garbarskich bezchromowych z dodatkiem osadu ściekowego wstępnego (w ilości 20%)

Time of fermentation days Czas fermentacji dni	Symbol of waste and obtained sludge Symbol odpadu oraz uzyskanego osadu	Content of components in mixtures prepared for fermentation (time 0) and after their fermentation (35 and 75 days). Process at 35°C, pH 7.0–7.2 Zawartość składników w mieszaninach przygotowanych do fermentacji (czas 0) oraz po ich fermentacji (35 i 75 dni). Proces przy 35°C, pH 7,0–7,2								
		ds sm	ods smo	ids smn	ee	pc [1)] bu [1)]	oos[2)] pso[2)]	N_{tot} N_{og}	P_{tot} P_{og}	K_{to} K_{og}
		%	% ds. – % sm		g/kg of ds. – g/kg sm					
a	b	c	d	e	f	g	h	i	j	k
0	AB	5	90.4	9.6	356	334	214	70	4.14	1.02
35	AB-F35	3.51	86.3	13.7	209	255	399	90	5.90	1.45
75	AB-F75	0.77	37.7	62.3	41	76	160	277	26.8	6.62
0	AP	5	90.1	9.9	529	172	200	42	3.6	0.96
35	AP-F35	3.33	85.1	14.9	412	81	358	58	5.4	1.44
75	AP-F75	0.64	22.1	77.9	76	8	137	243	28.3	7.55
0	H	5	85.5	14.5	44	604	207	123	4.31	1.38
35	H-F35	2.01	63.7	36.3	18	369	250	241	10.8	3.46
0	SP	5	91.7	8.3	12	750	201	148	5.57	1.05
35	SP-F35	3.02	86.2	13.8	3	447	412	210	9.22	1.74

1) Organic nitrogen × coefficient (5.6 – splits, 6.25 – hair, 5.8 – averaged wastes) / Azot organiczny × współczynnik (5,6 – dwoiny, 6,25 – włos, 5,8 – odpady uśrednione)
2) oos = ods – (ee + pc) / pso = smo – (ee + bu).

The ee fraction is undesirable in soil environment as it reduces soil biological activity. Therefore, in the process of anaerobic fermentation the amount of this fraction should be minimised to a few percents of ds. In the process of fermentation the elimination of non-fibre proteins susceptible to rapid decomposition should take place as well.

Due to the above reasons, 35-day fermentation may be regarded as sufficient for obtaining sludges that can be used directly as fertilisers only in case of waste hair and splits. 35-day sludges from averaged wastes, especially pig ones, should undergo further stabilisation, for example by composting. Their longer fermentation (for 75 days), though effective with regard to redundant ee fraction, results in the elimination of ods. It seems that 35-day sludges from waste hair or waste splits may also be subjected to a short-time composting. In this case, the aim is not to decompose the remains of collagen or keratin in sludges. These proteins may be useful in soil environment as they probably take part in soil-forming processes. The added structural material will enrich the mixture with stable soil-forming compounds (cellulose derivates) and form a substance absorbing fertilising components released in the process of composting.

Fertilising components of sludges

Due to the character of tannery wastes, the dominant fertilising component of the obtained sludges is nitrogen and, to the smaller extent, phosphorus. The amounts of these components can be estimated by comparing them with common manure. The contents of nitrogen, phosphorus and potassium in manure calculated per N, P, K oscillates within wide brackets. As average values 2% of nitrogen, 0.3% of phosphorus, and 1.16% of potassium in ds are accepted.

Results presented in tables 2, 3 and 4 allow to find a general interdependence. The more pc fraction and the less ee fraction in the mixture subjected to fermentation and the higher the degree of biodegradation of organic substance measured by the loss of ods (as well as by the loss of pc and ee fraction included in ods), the higher the amount of nitrogen, phosphorus and potassium in the sludge.

Table 3. Post-fermentation sludges dewatered to the uniform content of ds[1)] – basic components
Tabela 3. Osady pofermentacyjne odwodnione do ujednoliconej zawartości sm[1)] – podstawowe składniki

Symbol of obtained sludge Symbol uzyskanego osadu	ds sm	ods smo	ee	N_{tot} N_{og}	P_{tot} P_{og}	K_{tot} K_{og}
	%	g/kg of ds. – g/kg sm				
a	b	c	d	e	f	g
AB-F35	35 ±1[1)]	904	177	69	4.00	1.03
AB-F75		566	23	57	5.06	1.26
AP-F35		886	281	29.4	2.71	0.71
AP-F75		405	39	36.6	5.66	1.11
H-F35		642	3	121	5.71	1.74
SP-F35		903	3	106	4.66	0.89

[1)]Post-fermentation mixtures were centrifuged, then frozen, defrosted and centrifuged again. Final humidity (35%±1% of ds) was obtained by supplementing samples with previously separated sludge liquids / Mieszaniny pofermentacyjne odwirowano, następnie zamrożono, rozmrożono i wirowano ponownie. Ostateczną wilgotność (35%±1% sm) uzyskano, uzupełniając próby oddzielonymi wcześniej cieczami osadowymi;

[2)]As a result of dewatering, the amount of ods expressed in g/kg of ds increased, and the amount of ids decreased (a considerable part of components of ids remained in sludge liquids) / W wyniku odwodnienia ilość smo wyrażona w g/kg sm wzrosła, a ilość smn zmalała (składniki smn w znacznej części pozostały w cieczach osadowych)

Table 4. Amounts of basic components in mixtures prepared for fermentation (time 0) and after 35 and 75 days of fermentation in post-fermentation mixtures, calculated per inorganic dry substance (ids) as a relatively constant value – losses of components

Tabela 4. Ilości podstawowych składników w mieszaninach przygotowanych do fermentacji (czas 0) oraz po 35 i 75 dniach fermentacji w mieszaninach pofermentacyjnych, przeliczone na suchą masę nieorganiczną (smn) jako wielkość względnie stalą – ubytki składników

Time of fermentation, days Czas fermentacji, dni	Symbol of waste and obtained sludge Symbol odpadu oraz uzyskanego osadu	ds sm		ods smo		ee		pc bu		Oos Pso		N_{tot} N_{og}		P_{tot} P_{og}	K_{tot} K_{og}
		g/100 ml[1]	loss[2],% ubytek[2], %	g/10 g of ids and losses expressed in %[3] g/10 g smn oraz ubytki wyrażone w %											
a	b	c	d	e		f		g		h		i		j	k
0	AB	5		94		37		35		22		7.3		0.43	0.11
35	AB-F35	3.5	30	63	33	15	59	19	47	29	↑	6.6	10		
75	AB-F75	0.8	85	6.1	94	0.7	98	1.2	97	2.6	89	4.5	39		
0	AP	5		91		53		17		20		4.2		0.36	0.10
35	AP-F35	3.3	33	57	37	28	48	5.4	69	24	↑	3.9	8.3		
75	AP-F75	0.6	87	2.8	97	1.0	98	0.1	99	1.8	91	3.1	26		
0	H	5		59		3.0		42		14		8.5		0.30	0.10
35	H-F35	2	60	18	70	0.5	84	10	76	6.9	52	6.6	22		
0	SP	5		110		1.5		90		24		18		0.67	0.13
35	SP-F35	3	40	63	43	0.2	85	32	64	30	↑	15	15		

[1]content of ds in a mixture before fermentation and after 35 and 75 days of fermentation (g/100 ml) / zawartość sm w mieszaninie przed jej fermentacją i po 35 oraz 75 dniach fermentacji (g/100 ml);

[2]loss of ds in relation to the content before fermentation (time 0) / ubytek sm w stosunku do zawartości, która była przed fermentacją (czas 0);

[3]losses (expressed in %) are given on the right side of columns e, f, g, h, i; in columns j, k the losses are not given as the losses of phosphorus and potassium in fermentation process are close to 0 / ubytki (wyrażone w %) podano z prawej strony kolumn e, f, g, h, i; w kolumnach j, k ubytków nie podano gdyż ubytki fosforu i potasu w procesie fermentacji są bliskie 0;

[1]the arrow ↑ means the increase of the amount of oos / strzałka ↑ oznacza zwiększenie ilości pso.

Cattle hair is a typical protein waste that contains keratin in the pc fraction. As a result of its 35-day fermentation, from fermentation mixture the sludge (H-F35) containing 6 times more nitrogen than the manure (column e tab. 3) was separated. The biodegradation of a considerable part of keratin took place. As it has been proved by Urbaniak [2003], chemically unchanged keratin is almost absolutely resistant to biodegradation. The studied cattle hair separated from hides in the process of the so-called conservative dehairing. (Hides with hair are placed in lime liquor where keratin immunisation takes place, and then sodium sulphide is introduced causing the loosening of hair seating and, simultaneously, partial chemical degradation of keratin. The degree of degradation may differ, depending on the conditions of the process.)

The second typical protein waste (sp) contains almost exclusively collagen in the pc fraction. As it has been proved in earlier papers [Urbaniak 2003], chemically or thermally unchanged collagen does not undergo significant biodegradation during fermentation. The applied partial gelatinisation resulted in the separation of the sludge (SP-F35), in which the nitrogen content was 5 times higher than in the manure (column e tab. 3).

After 35-day fermentation of the averaged cattle waste a post-fermentation mixture was obtained. The content of nitrogen in the sludge (AB-F35) separated from the mixture was 3.5 times higher than in the manure. Averaged cattle waste contains considerably less pc fraction than the waste hair or splits. Averaged pig waste contains the smallest amount of pc fraction (column g in table 2 for 0 fermentation time). As a result of 35-day fermentation of averaged pig waste, a post-fermentation mixture was received, from which the sludge (AP-F35) was separated; the content of nitrogen in this sludge was only 1.5 times higher than in the manure.

The prolongation of fermentation of both averaged wastes to 75 days did not apparently increase the amount of nitrogen in separated sludges (AB-F75 and AP-F75 – column e tab. 3). However, prolonged fermentation lead to a considerable increase of nitrogen loss that shifted into gaseous phase: from 10% up to 39% for cattle waste, and from 8.3% up to 26% for pig waste (column i tab. 4). There was also a considerable increase in the amount of nitrogen left in sludge liquids after the separation of both sludges.

The content of phosphorus in sludges separated from mixtures after 35-day fermentations (column f tab. 3) was the following: two times higher than in the manure (sample H-F35), approximately 1.5 times higher (sample SP-F35 and AB-F35) and almost the same (sample AP-F35) as in the manure. The amount of potassium in all sludges was significantly lower than in the manure (column g tab. 3), however, it increased in the fermented deposits.

The increase of nitrogen was not correlated with the losses of ods, as a part of nitrogen passed into gaseous phase; however, the increase of the amounts of phosphorus and potassium in sludges was evidently correlated with the increase of biodegradation measured by the loss of ods.

Remarks on fertilising value of post-fermentation sludges

1. Methane fermentation of chromium-free tannery wastes allows to do the following:

a) neutralise very arduous protein and fat wastes,

b) obtain high efficiency of methane fermentation from a unit of ds of wastes,

c) separate sludges rich in fertilising components, particularly nitrogen and phosphorus,

d) obtain sludge liquid of high content of fertilising components.

2. Fermentation of chromium-free tannery wastes may be carried out until complete biodegradation of organic compounds takes place. The following conditions are necessary: 1) preliminary chemical treatment of keratin and chemical and/or thermal processing of collagen; 2) prolongation of fermentation time (the residue will be highly mineralised post-fermentation liquid).

Fermentation may be carried out until complete biodegradation of non-fibre organic compounds (ee and pc fractions except keratin and collagen) takes place. The necessary condition is the prolongation of the time of fermentation (the residue will be post-fermentation liquid mixture from which sludge abundant in fertilising components, i.e. nitrogen and phosphorus, may be separated).

Besides, fermentation may be carried out at the limited time until partial, more or less advanced, biodegradation of organic compounds takes place (the residue will be post-fermentation liquid mixtures which can be divided into not fully stabilised sludge with a considerable content of fertilising components and sludge liquid).

3. As a result of incomplete biodegradation of chromium-free tannery wastes in the process of fermentation, sludges and sludge liquids with various contents of nitrogen, phosphorus and potassium are obtained. The content of fertilising components in the sludge depends on the following: (a) the type of waste, and (b) the effectiveness of biodegradation of organic substance (e.g., time and conditions of fermentation).

4. The more pc fraction and the less ee fraction the waste contains, the more basic fertilising components the sludge will contain.

Even from averaged pig waste in which the proportion of ee:pc fraction is about 3:1, as early as after 35 days of fermentation, the sludge (35% ds) contains 1.5 times more nitrogen then in the manure, the same amount of phosphorus as in the manure, and definitely less potassium, can be obtained. After 35-day fermentation of averaged cattle waste considerably more abundant sludge is obtained, and the fermentation of protein wastes (e.g. waste splits) allows to obtain sludges with the content of nitrogen more than six times higher, and the content of phosphorus twice higher, (in ds.) than in the average manure.

5. When considering sludges obtained in the process of fermentation of tannery wastes for fertilising purposes, the following facts should be taken into account.

a) Sludges from tannery wastes are very rich in nitrogen and phosphorus, yet poor in potassium. N, P, K proportions do not correspond to proportions generally used in fertilisation.

b) The content of ee fraction in the sludge should not exceed a few percent, if agrotechnical treatments are to be typical.

c) Depending on the way of the preparation of wastes, sludges may contain different amounts of collagen and keratin, or they do not contain them at all. If collagen and/or keratin are present in the sludge, then its fertilising influence will be prolonged for the period of slow biodegradation of these proteins in soil. (Depending on various soil conditions, biodegradation may take a year or more, particularly that of keratin).

d) Sludges from fermentation of tannery wastes contain few soil-forming components. To some extent, this function can be performed by collagen and keratin.

e) Anaerobic microflora and deoxidised character of sludge should be changed, if possible, before the application for fertilisation purposes. The best solution seems to be composting.

Sludge liquids

The results of the separation of mixtures into post-fermentation sludges containing 35% of ds and sludge liquids containing from 0.4 to 1.3% of ds are presented in table 5.

Separated liquids contain certain amounts of nitrogen and phosphorus and smaller amount of potassium. Calculated per ds present in the sludge liquids, these amounts are tremendous in comparison with the manure. For example, sludge liquid after the separation of the sludge (AB-F 35) contained 21% of nitrogen in ds (above 10 times more than in manure), 1.9% of phosphorus in ds (6.5 times more), and 0.44% of potassium in ds (3 times less).

Table 5. Distribution of more important components contained in post-fermentation mixtures between sludges and sludge liquids separated from them

Tabela 5. Rozdział ważniejszych składników zawartych w mieszaninach pofermentacyjnych między wydzielone z nich osady oraz ciecze osadowe

Symbol of obtained sludge Symbol uzyskanego osadu	A Dewatered post-fermentation sludges (containing 35±1% of ds) Osady pofermentacyjne odwod–nione (o zawartości 35±1% sm)					B Volume of centrifuged liquid per 1 dm^3 of sludge with 35% of ds Objętość cieczy odwi-rowanej na 1 dm^3 osadu o 35% sm	C Sludge liquids (containing from 0.4 to 1.3% ds) Ciecze osadowe (o zawartości od 0,4 do 1,3% sm)				
	ods	ee	N_{tot}	P_{tot}	K_{tot}		ods smo	Ee	N_{tot} N_{og}	P_{tot} P_{og}	K_{tot} K_{og}
	g/dm^3					dm^3	g/dm^3				
a	b	c	d	e	f	g	h	i	j	k	l
AB-F35	317	62	24	1.4	0.4	10	3.4	11,	0.7	0.07	0.05
AB-F75	198	8	20	1.8	0.4	46	0.5	0.1	1.7	0.17	0.04
AP-F35	310	98	10	1.0	0.3	11	6.5	4.4	1.0	0.09	0.02
AP-F75	142	14	13	2.0	0.4	55	0.7	0.2	1.3	0.15	0.04
H-F35	225	1	42	2	0.6	18	0.6	0.3	2.4	0.10	0.03
SP-F35	316	1	37	1.6	0.3	12	6.7	0	3.2	0.14	0.03

Amounts of nitrogen are several times higher (even a few tens for liquids from fermentation of splits) than in sludges from municipal sewage (when calculated per ds). The amounts of phosphorus and potassium are also considerably bigger than in sewage sludges [Urbaniak 1997].

It is interesting to compare the content of fertilising components in sludge liquids obtained in this study with this of typical liquid organic fertiliser (e.g., in liquid manure). Although the content of fertilising components in the manure varies to great extent, the values given by Szymański [1998] calculated per N, P, K: 7.1% of nitrogen, 1.28% of phosphorus, and 1.36% of potassium in ds, and average ds of 4.3% (that means: 3.1 g N/dm^3, 0.56 g P/dm^3, 0.59 g K/dm^3) have been adopted as the average. The comparison of sludge liquid obtained from fermentation of tannery wastes (and then separation of sludges from post-fermentation mixtures) and liquid manure is favourable for liquid manure (part C of table 5).

However, the comparison with sludge liquids obtained from the fermentation of liquid manure is favourable for sludge liquids obtained in this study as a result of fermentation of tannery wastes. Whereas some liquids (from the fermentation of splits rich in protein) contained a similar amount of nitrogen to liquid manure, others contained less (up to 4.5 times). The content of phosphorus was from 3 to 8 times smaller. The content of potassium was much smaller (tab. 5). An undoubted advantage of sludge liquids from fermentation of tannery wastes is the absence of any undesirable chemical loads. Moreover, despite the lack of the rise of temperature observed in composting, the process of anaerobic stabilisation also shows limited hygenising influence [Urbaniak 1997].

If sludge liquids from the fermentation of tannery wastes are not used as a liquid fertiliser, for example, due to farmers' lack of interest, their components should be treated as losses in total balance. Then, nitrogen losses are from 23% to 50% for samples fermented for 35 days, and over 80% for samples fermented for 75 days. Phosphorus and potassium losses are from 30% to 50% for samples fermented for 35 days, and over 80% for samples fermented for 75 days.

RECAPITULATION

This paper is an element of comprehensive research conducted under the project of the State Committee for Scientific Research No. 5 PO6H 033 19. In previous papers the technical and organisational solutions of the processing of chromium-free tannery wastes were suggested and developed, and conditions of technological processes were determined [Urbaniak 2003, Urbaniak and Hillebrand 2003].

The results presented in this paper confirm that methane fermentation of chromium-free tannery wastes allows to obtain post-fermentation sludges exceptionally rich in nitrogen and very rich in phosphorus compared, e.g., with traditional manure or sludges from municipal wastewater. The amount of potassium is smaller. The amounts of fertilising components depend in an obvious way on the kind of waste (mixing proportions) and on the conditions of the realisation of fermentation process. Natural resistance of collagen and keratin to biodegradation suggests that the sludges from tannery wastes will have fertilising and soil-forming influence for a longer period of time. Their resistance to biodegradation may be decreased by thermal (collagen) or chemical (collagen and keratin) processing.

The next part of the research shall be published as Part II of this paper. It will present the possibilities and advisability of the composting of post-fermentation sludges and direct composting (without fermentation) of chromium-free tannery wastes.

The final stage of the research will be the application of the sludges and composts as fertilisers and the obtaining of relevant attestations.

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PRZETWARZANIE MIESZANIN ZAWIERAJĄCYCH BEZCHROMOWE ODPADY GARBARSKIE, CZĘŚĆ I. WARTOŚĆ NAWOZOWA OSADÓW POFERMENTACYJNYCH

Streszczenie. Jednym ze sposobów wykorzystania odpadów garbarskich bezchromowych może być ich przetworzenie na nawozy organiczne. Pod uwagę brane są dwie metody: fermentacja metanowa oraz kompostowanie. Stwierdzono że fermentacja metanowa odpadów garbarskich bezchromowych, niezależnie od uzysku gazu, pozwala na uzyskanie materiału o różnym stopniu odwodnienia, o różnej, ale zawsze dużej zawartości składników nawozowych. O ostatecznych właściwościach decyduje rodzaj odpadu (proporcje, w jakiej różne odpady zmieszano) oraz warunki prowadzenia procesu. W pracy podano wstępną charakterystykę nawozową różnych osadów oraz cieczy osadowych. Wyniki pracy potwierdzają, że z uciążliwych odpadów garbarskich bezchromowych można otrzymać produkty nawozowe w pełni stabilne biologicznie o dużej lub bardzo dużej wartości nawozowej.

Słowa kluczowe: osad, ciecz osadowa, wartość nawozowa, wartość glebotwórcza, stabilizacja materiału organicznego

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