ACTA SCIENTIARUM POLONORUM Acta Sci. Pol., Technica Agraria 3(1-2) 2004, 69-77

PROCESSING OF MIXTURES CONTAINING CHROMIUM--FREE TANNERY WASTES. PART II. FERTILISING VALUE OF COMPOSTS

Maciej Urbaniak
Leather Research Institute, Technical University of Łódź

Abstract. In previous studies (part I) it has been established that methane fermentation of chromium-free tannery wastes results in partly stabilised post-fermentation sludges, rich in nitrogen and phosphorus. This part of the investigations have confirmed that in view of the quality of fertilising material, the composting of post-fermentation sludges is most beneficial; and composting of non-fermented wastes is less beneficial. The sludges from short fermentation (only partly stabilised) and after prolonged fermentation were subjected to composting. The composting of sludges allowed to obtain material, rich in basic fertilising components and organic soil-forming components. The paper shows that it is possible to reduce the arduousness of direct composting (with the omission of fermentation) of chromium-free tannery wastes. The dependence of the quantity of basic fertilising and soil-forming components in the obtained material on the applied processing conditions has been shown.

Key words: post-fermentation sludge, composting, fertilising components, soil-forming components, stabilisation of organic material

INTRODUCTION

As it has been shown in earlier papers, Aloy et al. [1989], Anonymous [1994], Urbaniak [2003], Urbaniak and Hillebrand [2003], Urbaniak [2004], methane fermentation can serve as a method of stabilisation and utilisation of nasty chromium-free tannery wastes. When compared to traditional organic fertilisers, post-fermentation sludges obtained as a result of fermentation contain huge amounts of nitrogen and high amounts of phosphorus. The content of fertilising components calculated per unit of dry substance increases in time of fermentation process. Simultaneously, the content of organic soil-forming components decreases, and losses of nitrogen increase. On the other hand, short fermentation does not give fully stabilised material.

Corresponding Author – Adres do korespondencji: Maciej Urbaniak, Leather Research Institute, 73 Zgierska Street, 91-462 Łódź, Department of Environmental Engineering of Technical University of Łódź, Al. Politechniki 6, 93-590 Łódź, Poland, e-mail: dyr-ips@mazurek.man.lodz.pl

It has been assumed that composting may be a valuable solution. It should allow to obtain stable materials of high fertilising value (resulting from the content of nitrogen and phosphorus in wastes) and an increased value of soil-forming components (as a result of the addition of structural materials). In order to confirm the above assumptions, composting was applied to non-fermented wastes and to post-fermentation sludges from fermentation of chromium-free tannery wastes.

MATERIALS AND METHODS

Initial experimental material included ten types of wastes from different stages of hides processing; six wastes from cattle hides processing, and four from pig hides processing. From cattle wastes and separately from pig wastes "averaged cattle waste, and "averaged pig waste" were prepared. There were also studied two homogeneous protein wastes. One was cattle splits from limed hides as a typical collagen waste. In some tests crushed splits were subjected to partial thermal gelatinisation to make collagen more susceptible to biodegradation. The other homogeneous waste was cattle hair as a typical keratin waste. Cattle hair was separated from technological bath as a waste after the so-called conservative liming.

The analytical characteristics of chromium-free tannery wastes as the initial experimental material have been presented in part I (tab. 1) of the paper [Urbaniak 2004] The method of the preparation of wastes for fermentation , conditions of fermentation, and separations of sludges have also been described. The wastes for direct composting (without fermentation) were crushed once in a grinding machine with Ø 5 mm outlets.

Table 1. Post-fermentation sludges obtained after 35 days of fermentation of some chromium-free tannery wastes (Urbaniak 2004) selected for tests in this part of the study
Tabela 1. Osady pofermentacyjne uzyskane po 35 dniach fermentacji niektórych odpadów garbarskich bezchromowych [Urbaniak 2004] wytypowane do badań w tej części pracy

Type of waste which was subjected to 35-day fermentation at pH 7.0-7.2 and 35°C Rodzaj odpadu, który poddano 35-dniowej fermentacji przy pH 7,0-7,2 i 35°C	Symbol of sludge Symbol osadu	Basic components of sludges dewatered to the standardized ds content; up to 35±1%[1)] Podstawowe składniki osadów odwodnionych do zawartości sm ujednoliconej; do 35±1%[1)]				
		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
Averaged cattle (bovine) waste / Odpad bydlęcy uśredniony	AB-F35	904	177	69	4.00	1.03
Averaged pig waste / Odpad świński uśredniony	AP-F35	886	281	29	2.71	0.71
Cattle hair / Włos bydlęcy	H-F35	642	3	121	5.71	1.74
Cattle split / Dwoina bydlęca	SP-F35	903	3	106	4.66	0.89

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

In this part of the work, sludges after 35-day fermentation (thus not fully stabilised), and some crushed wastes, were selected as experimental material. These sludges are characterised in table 1.

Wastes from softwood processing (sawdust), were used as structural additive for samples intended for composting. Bio-Kompost, made by Atlas-Planta (from Bydgoszcz), was used to enrich the samples with composting micro-organisms. To one of the composting mixtures, hydrated lime, containing 68% of lime calculated per CaO, was added as an alkalising agent.

Abbreviations for the experimental material

The following symbols were used for the description of the materials: (1) letters referring to the kind of waste: AB – averaged cattle (bovine) waste, AP – averaged pig waste, H – hair, SP – split; (2) letters representing fermentation – F, or composting – K; (3) digits referring to the time of fermentation and/or composting; and (4) letters Ca in brackets referring to the addition of lime, or pH representing neutralisation of waste. For example, symbol SP-F35-K20 stands for the material from split waste fermented for 35 days and composted for 20 days.

Procedures

Composting mixtures were prepared from sludges obtained as a result of tannery wastes fermentation and from original wastes (not subjected to fermentation). Post-fermentation sludges, dehydrated down to 35% of dry substance (ds), were mixed with sawdust in the proportion of 3:1 (dry substance). The majority of wastes selected for tests were mixed with sawdust in the proportion of 1:1. One mixture, containing averaged cattle waste, was prepared in the proportion of 3:1, and 2 kg of lime were added per every 100 kg of the mixture. Another mixture was prepared with averaged cattle waste neutralised to 7.2 pH.

To every mixture Bio-Kompost was added in the amount of 2.5 g per 100 g of ds of a mixture, and the humidity of the mixture was corrected to 55 ± 1%. Mixtures from post-fermentation sludges were composted for 20 days; the process was treated as a complementation of anaerobic stabilisation. The mixtures from non-fermented wastes were composted for 120 days. The process was carried out at 21 ± 1°C in the conditions of controlled humidity of the air and composted mixtures.

pH values of the mixtures prepared for composting measured in water extract (time 0) were the following: (1) mixtures with sludges: 6.9–7.1, (2) mixtures with non-neutralised averaged (cattle or pig) wastes: about 10.5, (3) a mixture with averaged cattle waste and an addition of lime: 13.9, and (4) a mixture with neutralised averaged cattle waste: 7.1. Samples prepared for composting are characterised in table 2 (time of composting 0 days).

Methods of analytical tests

The content of dry substance (ds), organic dry substance (ods), inorganic dry substance (ids), ethereal extract (ee), protein content (pc), the amount of collagen, total nitrogen (N_{tot}), total phosphorus (K_{tot}) were determined according to Polish Standards compatible with EU procedures.

The content of pc was calculated from organic nitrogen by using the following coefficients: 6.25 for hair (keratin), 5.62 for a split (collagen), and 5.8 for averaged waste. 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).

RESULTS

Soil-forming influence versus composting conditions

Adopting a very simplified approach, it can be assumed that the soil-forming influence of an organic fertiliser is based on the enrichment of soil with compounds that have a positive impact on the structure of soil, its sorptive properties and nutrient abundance, etc., which, in turn, causes the development of biological life. Both direct composting of tannery wastes and composting of sludges obtained from earlier fermentation of tannery wastes require the addition of structural material into the composting mixtures. Structural material increases the amount of ods, mainly by oos fraction. Celluloses and chemicelluloses inserted together with structural material produce stable ods (oos fraction), that is gradually transformed mainly into humus compounds of compost and then humus of soil. Ods of structural material of composts forms a substance conducive to the maintenance of fertilising components that are released from non-fibre proteins of leather. Non-fibre proteins are highly susceptible to biodegradation.

Table 2. Results of composting of sludges from the fermentation of some chromium-free tannery wastes and direct composting of tannery wastes (without fermentation)
Tabela 2. Wyniki kompostowania osadów z fermentacji niektórych odpadów garbarskich bezchromowych oraz kompostowania bezpośredniego odpadów garbarskich (z pominięciem fermentacji) – składniki kompostów

Symbol of sludge or waste Symbol osadu lub odpadu	Time of composting, days Czas kompostowania, dni	Initial content of components in a mixture (time 0) and in a compost after the end of composting (20 or 120 days) Zawartość początkowa składników w mieszance (czas 0) i w kompoście po zakończeniu kompostowania (20 lub 120 dni)								Symbol of obtained compost Symbol uzyskanego kompostu
		ods smo	ids smn	ee	pc bu	oos pso	N_{tot} N_{og}	P_{tot} P_{og}	K_{tot} K_{og}	
		g/kg of ds								
a	b	c	d	e	f	g	h	i	j	k
AB-F35	0 20	917 901	83 99	133 79	143 138	641 684	53 52	3.03 3.61	1.07 1.28	AB-F35-K20
AP-F35	0 20	904 887	96 113	211 186	41 40	652 661	23 23	2.06 2.43	0.83 0.98	AP-F35-K20
H-F35	0 20	721 695	279 305	2.25 0.00	249 228	470 467	92 75	4.31 4.71	1.61 1.76	H-F35-K20
SP-F35	0 20	916 898	84 102	2.25 0.00	264 272	650 626	81 78	3.52 4.26	0.97 1.18	SP-F35-K20
AB	0 120	950 886	50 114	221 10	206 93	523 783	38 61	0.76 1.73	0.69 1.57	AB-K120
AP	0 120	948 869	52 131	329 8	105 29	514 832	20 35	0.41 1.03	0.65 1.64	AP-K120
AB(Ca)	0 120	926 884	74 116	325 207	304 279	297 398	52 41	1.05 1.65	0.42 0.66	AB-K120(Ca)
AB(pH)	0 120	949 815	51 185	221 1	206 33	522 781	39 102	0.76 2.76	0.69 2.50	AB-K120(pH)

Due to the above properties, it seems particularly reasonable to compost sludges separated from mixtures after fermentation of tannery wastes. The duration of composting should be matched to allow the following: a complete change of strongly reduced environment of sludges into aerobic environment of composts; a multiplication of aerobic microflora; and complementary biodegradation of the residues of compounds susceptible to arduous and intensive decomposition, including the biodegradation of ee fraction undesirable in soil. (ee fraction is an efficient raw material in the biological production of methane, yet it is undesirable in soil environment. When introduced into soil in larger amounts, it requires additional agrotechnical procedures aimed at the acceleration of decomposition). The optimum duration of usually short composting of sludge depends on the advancement of prior anaerobic biodegradation.

Direct composting of chromium-free tannery wastes (without their fermentation) has to last much longer. In this study, the applied time was 120 days. Composts obtained as a result of direct composting (AB-K120, AP-K120, and AB-K120(pH)) can possibly have a positive impact on soil environment, due to, among others, the use of larger amount of structural material (that is 50% of ds of a mixture – tab. 2).

In case of (mixed) averaged wastes, direct composting process may be nasty due to the presence of huge amounts of organic compounds susceptible to rapid decomposition. The disagreeableness may be reduced by the acceleration of composting process. For this purpose the following can be done: 1) lowering of pH value to approximately 7.2 before composting (sample of waste AB(pH) in table 2 was prepared in this way), and 2) increasing of the "permeability" of a composting mixture by adding more structural material, for example, in the amount equivalent to 50% of ds (the amount added to mixtures from which composts AB-K120, AP-K120, AB-K120(pH) in table 2 were obtained). It is important to meet technological requirements concerning air supply. In case of piles a solution is a proper frequency of shifting.

A special solution is composting of averaged wastes with an addition of lime (compost AB-K120(Ca), tab. 2). In the composting process a very limited and prolonged biodegradation of organic compounds took place. After 120 days of composting in the compost with lime (AB-K120(Ca)) the loss of ee and pc content was 60% and 41%, respectively, and in the remaining composts (AB-K120, AP-K120, and AB-K120(pH)) it was over 98% and over 80% (tab. 3). It appears that the addition of lime causes a partial hygienisation of the mixture by increasing pH value up to 13.9 (at the beginning of composting process). Such an organic material introduced into the soil may prove to be a good source of fertilising components transmitted with delay. The assessment of soil-forming influence of this compost requires, however, additional tests. Certainly, it will alkalise soils, which may be favourable in view of the acidification of many soils.

Due to a very low susceptibility of keratin and rather low susceptibility of collagen to biodegradation, it is necessary to consider the reasonability and the degree of possible preliminary chemical and thermal processing of wastes containing almost exclusively these proteins (waste hair and waste splits). Slow decomposition of keratin and collagen in soil (taking a few years, in case of native keratin) may be very useful for the soil environment. The problem is so interesting that it may become a subject of separate studies. In averaged wastes, the content of keratin and collagen is considerably lower and, surely, they do not need to be biodegraded in composting processes, or in fermentation carried out before composting.

Fertilising components

The content of basic fertilising components (NPK) in the composts from sludges is high, despite the fact that a part of these components remained in sludge liquid and a part of nitrogen passed into gaseous phase in the process of fermentation and later, another part passed into air in the process of composting. When compared with the manure, in all composts from sludges (SP-F35-K20, H-F35-K20, AB-F35-K20 column h tab. 2) the amount of nitrogen is higher (3.9, 3.8, 2.6, 1.2 times, respectively). The content of phosphorus (column i tab. 2) in three composts (AB-F35-K20, H-F35-K20, SP-F35-K20) is also larger than in the manure. In one compost (AP-F35-K20), the content of phosphorus is smaller. The contents of potassium (column j tab. 2) are considerably smaller. Average contents of nitrogen, phosphorus, and potassium in manure calculated per N, P, K, are accepted as 2% of N, 0.3% of P, and 1.16% of K in ds.

Assessing the amount of nitrogen as the most important fertilising component, it was noted that during 35-day fermentation of wastes [Urbaniak 2004] its losses were smaller than later, during a short period of composting. It can be assumed that in the first stage of composting, when the "reduced" environment (anaerobic conditions of fermentation) is changed into aerobic one, there mostly takes place the phenomenon of "blowing away" of ammonia nitrogen, and only partly its oxidisation.

In the lower part of table 2, basic components of composts obtained from direct composting (without previous fermentation) of chromium-free tannery wastes are presented. In order to increase their aeration, to two mixtures sawdust was added in amounts equivalent to 50% of ds of every mixture (composts AB-K120 and AP-K120). A positive influence of an increased addition of structural material on the process of tannery wastes composting was confirmed in earlier paper [Urbaniak 1997]. Higher permeability accelerates the composting by, among others: (1) lowering of pH value of a mixture as a result of the formation of carbonates from lime present in wastes and CO_2 from the air (if wastes have not been neutralised beforehand); (2) satisfaction of a growing demand for oxygen to develop aerobic biodegradation; (3) successive oxidation of released nitrogen to the final nitrate form. Consequently, despite the "dilution" of wastes with sawdust, the two composts (AB-K120, AP-K120) contained more nitrogen than the comparable composts (AB-F35-K20, AP-F35-K20), obtained from the same wastes but in an indirect way (from sludges), from mixtures containing a half less of sawdust. The differences are presented in column h table 2.

Neutralisation of wastes accelerates the composting process, and neutralisation combined with the increase of the amount of structural material accelerates the process even more. As a result of intensive biodegradation, compost AB-K120(pH) contains the largest amount of nitrogen, over 10 times higher than the manure (column h tab. 2).

As it has been mentioned before, very specific compost is obtained from the mixture with the addition of lime (AB-K120 (Ca). The assessment of this compost is ambiguous. The amount of nitrogen found in it was 2 times higher than in the manure, as well as the amounts of phosphorus and potassium were smaller than in the manure. Disadvantageous differences can be explained by the smallest loss of ods among all composts obtained

Table 3. Amounts of components in mixtures prepared for composting (time 0) and in composts obtained from them (time of composting 20 or 120 days). Components were calculated per inorganic dry substance (ids) as a value relatively constant and, besides, losses of components were calculated

Tabela 3. Ilości składników w mieszankach przygotowanych do kompostowania (czas 0) oraz w otrzymanych z nich kompostach (kompostowanie 20 lub 120 dni). Składniki przeliczono na suchą masę nieorganiczną (smn) jako wielkość względnie stałą oraz wyliczono ubytki składników

Symbol of obtained compost Symbol otrzymanego kompostu	ods smo		ee		pc bu		oos pso		N_{tot} N_{og}		P_{tot} P_{og}	K_{tot} K_{og}
	g/10 g of ids and losses given in % / g/10 g smn oraz ubytki wyrażone w %											
a	b		c		d		e		f		g	H
AB-F0-K0	111		16.0		17.2		77.2		6.39		0.37	0.13
AB-F35-K20	91.0	18 %	7.98	50 %	13.9	19 %	69.1	11 %	5.25	18 %		
AP-F0-K0	94.2		22.0		4.27		67.9		2.40		0.22	0.09
AP-F35-K20	78.5	17 %	16.5	25 %	3.54	17 %	58.5	14 %	2.04	15 %		
H-F0-K0	25.8		0.08		8.93		16.9		3.30		0.16	0.06
H-F35-K20	22.8	12 %	0.00	100 %	7.48	16 %	15.3	10 %	2.46	26 %		
SP-F0-K0	109		0.27		31.4		77.4		9.64		0.42	0.12
SP-F35-K20	88.0	19 %	0.00	100 %	26.7	15 %	61.4	21 %	7.65	21 %		
AB-K0	190		44.2		41.2	80 %	105		7.60		0.15	0.14
AB-K120	77.7	59 %	0.88	98 %			68.7	34 %	5.35	29 %		
AP-K0	182		63.3		20.2		98.9		3.85		0.08	0.13
AP-K120	66.3	64 %	0.61	99 %	2.21	89 %	63.5	36 %	2.67	30 %		
AB-K0(Ca)	125		43.9		41.1		40.1		7.03		0.14	0.06
AB-K120(Ca)	76.2	39 %	17.8	60 %	24.1	41 %	34.3	15 %	3.54	50 %		
AB-K0(pH)	186		43.3		40.4		102		7.65		0.15	0.14
AB-K120(pH)	44.1	76 %	0.05	100 %	1.78	96 %	42.2	59 %	5.51	28 %		

[1)]In columns from b to f (on the right) losses of ods, ee, pc, oos, N_{tot} (expressed in %) in composting process are given. The losses of P_{tot} i K_{tot} in columns g and h are not given as they are close to 0.

[1)]W kolumnach od b do f (po prawej stronie) podano ubytki smo, ee, bu, pso, N_{og} (w %) w procesie kompostowania. Ubytków P_{og} i K_{og} w kolumnach g i h nie podano, gdyż są one bliskie 0.

directly (without fermentation) from wastes (column b tab. 3). The process of composting was not stinking and the organoleptic assessment was very positive. The assessment of the fertilising value of this special compost and the assessment of its influence on the soil environment require further studies.

Due to a large addition of structural material (50% of ds), in composts derived directly from wastes (AB-K120, AP-K120) the amount of phosphorus is smaller (column i tab. 2), and the amount of potassium is larger (column j tab. 2), than in composts derived indirectly from the same wastes, i.e., in composts from sludges (AB-F35-K20, AP-F35-K20). The amount of potassium increased because its content in sawdust was much higher than in wastes, and the amount of phosphorus decreased because its content in sawdust was very low.

CONCLUSIONS

1. The composting of sludges separated from mixtures after the fermentation of chromium-free tannery wastes very significantly increases total fertilising value of the final product. Structural material added to mixtures increases the amount of ods of the mixture with carbon compounds like cellulose and chemicellulose, which are absent from the sludges but contribute to the formation of humus. The composting of biologically unstable sludges (e.g., from short fermentation) allows to obtain a more stabilised product.

2. Depending on the degree of biodegradation of easily decomposable organic compounds in the process of fermentation, the composting of sludges may be shorter or longer, and more or less intensive. If a larger amount of ee fraction remained in the sludge, then it should decrease to no more than a few percent in the process of composting.

3. The intensity of direct composting of chromium-free tannery wastes may be increased by the following: (a) a larger addition of structural material (for instance, 50% instead of 25% of ds) and technologically adequate air supply to the mixture, (b) neutralisation of wastes to the level of approximately 7.2 before the preparation of a composting mixture.

4. Composts from chromium-free tannery wastes are very rich in fertilising components, particularly nitrogen and phosphorus, whose content is larger than in the manure. The content of nitrogen is several times higher. However, the manure contains a larger amount of potassium. They may have a prolonged fertilising influence, if fibre proteins have been preserved, as they undergo slow biodegradation in the soil environment.

5. The compost of specific properties is derived from mixtures of chromium-free tannery wastes with structural material and lime. The determination of its fertilising properties requires additional tests.

REFERENCES

Aloy M., Mermet R., Sanejouand J., 1989. Biomethanization of tannery waste on industrial experiment, J. Am. Leather Chem. Assoc. 84, 97–109.

Urbaniak M., 1997. Przerób i wykorzystanie osadów ze ścieków komunalnych, Wyd. Ekoinżynieria, Lublin-Łódź.

Urbaniak M., 2004. Processing of mixtures containing chromium-free tannery wastes into fertilisers. Part I. Methane fermentation. Acta Sci. Pol. Technica Agraria, 3 (1–2), 57–68.

Urbaniak M., 2003. Chromium-free tannery wastes stabilized by methane fermentation in sewage treatment plants installations, Environmental Engineering Studies, Kluwer Academic Plenum Publishers, N. York, 185–198.

Urbaniak M., Hillebrand B., 2003. Technological remarks to methane fermentation of mixtures containing chromium-free tannery wastes and dewatering of post-fermentation sludges, Environmental Engineering Studies, Kluwer Academic Plenum Publishers, N. York, 309–322.

Vulliermet B., Aloy M., 1983. Biomethanisation de residus de tannerie, Technicuir. 17, 8, 132–135.

PRZETWARZANIE MIESZANIN ZAWIERAJĄCYCH BEZCHROMOWE ODPADY GARBARSKIE. CZĘŚĆ II. WARTOŚĆ NAWOZOWA KOMPOSTÓW

Streszczenie. We wcześniejszych badaniach (część I) ustalono, że wynikiem fermentacji metanowej odpadów garbarskich bezchromowych są osady pofermentacyjne częściowo ustabilizowane, bogate w azot i fosfor. W tej pracy potwierdzono, że z punktu widzenia jakości materiału nawozowego bardzo korzystne jest kompostowanie osadów pofermentacyjnych, a mniej korzystne kompostowanie odpadów niefermentowanych. Kompostowaniu poddano osady z krótkiej fermentacji (jedynie częściowo ustabilizowane) oraz po fermentacji przedłużonej. Kompostowanie osadów pozwoliło uzyskać materiał bogaty w podstawowe składniki nawozowe oraz bogaty w organiczne składniki glebotwórcze. Wykazano, że istnieje możliwość ograniczenia uciążliwości kompostowania bezpośredniego (z pominięciem fermentacji) odpadów garbarskich bezchromowych. Wykazano zależność ilości podstawowych składników nawozowych i glebotwórczych w materiale nawozowym od przyjętych warunków przetwarzania.

Słowa kluczowe: osady pofermentacyjne, kompostowanie, składniki nawozowe, składniki glebotwórcze, stabilizacja materiału organicznego

Accepted for print – Zaakceptowano do druku: 23.09.2004