POSSIBILITIES OF SLUDGE FROM THE EDIBLE OILS PRODUCTION UTILIZATION

Lucyna Przywara* and Jan Suschka*

*Insitute of Engineering and Environmental Protection, University of Bielsko –Biala, ul. Willowa 2, Bielsko – Biala, 43 -309
(E-mail:l.przywara@ath.bielsko.pl; jsuschka@ath.bielsko.pl)

Abstract This paper presented results of physical (pH, oxidation reduction potential, conductivity) and chemical (organic substances, phosphorus, calcium, magnesium, potassium and heavy metals) investigation on sludge from treatment wastewater from edible oils production. The content of heavy metals Pb, Cu, Zn, Ni in sludge samples was determined using ASA method. The investigated wastewater sludge was proved to have a high fertilizing value. The sludge contains a relatively high content of phosphorus, calcium and potassium.
Taking into account the fertilizing qualities of investigated sludge from the existing industrial wastewater treatment plant it can be favorable fertilizer, provided it do not contain heavy metals above standards. Evaluation the of presence and quantity of heavy metals is an important criteria in regard to natural recycling of sludge. Sludge originating from the wastewater treatment plant can be used as a fertilizer for cultivation without homogenization. The natural use of sewage sludge resolves problems of high cost fertilization as well as resolve the problem of excess sludge disposal.
Keywords heavy metals, nutrients, industrial sludge, utilization

Introduction

Wastewater treatment processes always generate a certain amount of sludge i.e. an organic-mineral solid phase extracted from treated the wastewater. In Poland, the total amount of sludge fluctuates around 1080 thousand tons (expressed as dry matter) (Statistical Yearbook, 2008).
The sludge management in each treatment plant should ensure rational and environmentally -friendly sludge disposal and/or reuse. According to the waste disposal Act from the 27 April 2001 about wastes, sewage sludges are classified as waste materials. The major possibilities of adequate sewage sludge management, which are simultaneously considered as main guidelines are included in the regulations (Bień, 2007).
Sludge management is always connected with technical, technological as well as economical problems. Moreover, the investment and maintenance costs are usually very high. In order to partially compensate the costs of their treatment it is necessary to perceive the sewage sludge as a potential source of energy and/or natural fertilizers.
Sewage sludge properties depended on both the characteristics of the wastewater treated as well as the nature of the processes involved (Bernacka i in.,1994).
In particular such factors as the content of organic matter and nutrients, heavy metals, toxic and hazardous (harmful) substances as well as pathogens, determine the procedures of their further treatment and/or reuse.
Organic matter content is considered as an important indicator which is commonly used to determine mass structure properties, energy value as well as potential odour nuisance of the landfilled or soil applied sludge. Based on organic matter content, it is also possible to determine the biogas production potential if the sludge is to be anaerobically digested (Bernacka i in., 1994). However, the products of the organic matter decomposition (proteins, fat and carbohydrates) in anaerobic conditions, i.e. sulphide, ammonia nitrogen, sulphur dioxide as well as volatile organic compounds (VOCs) etc. are a potential source of odour nuisance (Rosik-Dulewska, 2000; Marcinkowski, 2008).

Sewage sludges contain main nutrients (nitrogen, phosphorus, potassium), which are essential for plants growth. As compared to other organic fertilizers, sewage sludges are richer in phosphorus and nitrogen, however, potassium content is significantly lower. Phosphorus content does not exceed 6% (dry matter). Whilst nitrogen and potassium content usually fluctuates between 0,3 – 0,6 and 0,1- 0,6 % d.m. respectively (Bień, 2007; Rosik-Dulewska i in.,2006).

The above mentioned nutrients occur in various forms. Nitrogen can be found as organic, nitrate or ammonia nitrogen. The range of phosphorus forms includes: organic phosphorus, phosphates as well as polyphosphates. Compounds can change their form, however, the conversion in soil happens very slowly. For example, nitrates present in the sludge or coming from bioconversion of organic nitrogen are absorbed by plants or leachated into water reservoirs.

Taking into account fertilization management the amount of sulphur and magnesium are also important as they are usually present in insufficient concentration in polish conditions. As mentioned before the sludge contains certain amount of calcium, which also plays an important role in the soil. Calcium ions coming from sewage sludge can contribute to the calcium present in the soil. Moreover, it depresses the mobility of heavy metals and subsequently decreases their availability for plants. The concentration of calcium is usually high and fluctuates between 1,0- 10 % d.m. (average value - 2,5 % d.m.)(Bień, 2007; Czekała, 2009).

The amount of heavy metals present in the sewage sludge varies significantly and has an impact on the sludge soil application or disposal. Sludge includes both essential microelements for plants, such as: Cr, Sn, Zn, F, J, Co, Si, Mn, Cu, Mo, V (assuming that their concentrations do not exceed permitted concentrations) as well as heavy metals which are known to be toxic and harmful for the natural environment. The later includes: lead, mercury, cadmium, nickel and chromium. What is more, excessive level of zinc and copper can also pose a threat to the environment (Rosik-Dulewska i in.,2006). Table 1 presents of permissible contents of heavy metals in deposits meant for agricultural and non- agricultural utilization.

Table 1. Permissible contents of heavy metals in deposits meant for agricultural and non-agricultural utilization

Metals	Methods of sludge utilization		
	Fertilizing, cultivation land recovery		Applied in cultivation of plants intended compost production
	agricultural utilization	non- agricultural utilization	
	Heavy metals content [mg/kg d.m.]		
Pb	500	1000	1500
Cd	10	25	50
Cr	500	1000	1500
Cu	800	1200	2000
Ni	100	200	500
Hg	5	10	25
Zn	2500	3500	5000

Heavy metals at high concentration are toxic for humans, animals and plants. Municipal and industrial wastewaters (e.g. metallurgical industry, chemical industry) are considered as the potential source of relatively high levels of heavy metals. However, pretreatment facilities and effectiveness of the processes applied have an influence on the heavy metal content in the above mentioned wastewater. Additionally, surface water run – off contribute to the total amount of heave metal in the sludge (Bernacka i in. 2002; Bień, 2007; Rosik-Dulewska, 2000;).

The degree of heavy metals reduction from wastewaters has an influence on their subsequent content in the generated sludges. Additionally, heavy metals have the ability to accumulate in sludges. For example, combined mechanical and biological wastewater treatment processes can reduce the total amount of heave metals by between 50 – 80 %. Heave metals are present in sewage sludge in inorganic forms as well as a part of organic compounds. Considering constant sewage sludge agriculture application, the forms of heavy metals significantly influence chemical reaction occurring in the soil. As mention before, they can accumulate in the soil and cause a potential thread for cultivated plants.

Also heave metals present in sewage sludge can leachate especially when the landfill bed is acid in nature. Furthermore, accumulated heave metals in fly- ash after sludge sewage combusting can be easy released to the atmosphere (Bernacka i in., 2002). The potential methods to reduce heavy metals content in sludge include: controlling the incoming to the wastewater treatment plant amounts, controlling their sources of origin as well as applying effective sewage sludge treatment processes (chemical and biological)(Łomotowski i in., 2002; Marcinkowski, 2004).

Just like other branches of food industry companies, the production of edible oil and fats ensure complex production processing, which determine the quality of the wastewater generated. One of the final products is margarine, i.e. water in oil emulsion. It is usually produced from refined vegetable oils. It contains about 83% of fatty substances. The edible oils and fats processing companies generate effluents containing:

- semi – clean cooling waters,
- canola grain pressing and refining wastewater,
- fat hardening wastewater
- the main processing (industrial) wastewater
- waters coming from cleaning productions halls as well as equipment.

The main ingredients of the wastewater are fatty substances. Additionally, the wastewater contains: milk, fatty acids, sodium and potassium hydroxides, sodium chloride, nickel and phosphates. Due to the varied chemical composition as well as sticky consistence and specific properties, it is particularly difficult to neutralize the sludge generated at the various production stages and treatment processes (grids, sieves, settlers, fat traps, phosphates precipitation).

The article covers the management of sewage sludges coming from edible oils and fats processing company. The potential methods of utilization and disposal which do not pose a negative effect in the natural environmental have been discussed.

The pretreatment process of wastewater from the production of edible oils and margarine is based on phosphates and total phosphorus elimination. Technological process is divided into several stages. Raw wastewater flows by gravity to the main fat trap, where fatty substances are colleted from the surface of the chamber and directed to the fat storage container. Furthermore, the wastewater is pumped out of the last chamber of the fat trap and transferred into a reaction tank. Lime (10 % solution of lime milk) and a flocculant which facilitates coagulation are dosed into the tank. During this stage of treatment, calcium phosphates are precipitated. Next, the wastewater is transferred to the sedimentation chamber, where solid phase of the sludge precipitates. Next, the clarified wastewater is neutralized to a pH close to 7 by addition of 30 % HCl.

The generated sludge is mechanically dewatered by means of centrifuge to ensure the sludge moisture at the level of between 65 – 75%. The average monthly amount of the sludge generated fluctuates between 40 and 50 tons.

Materials and methods

The sludge after phosphates precipitation by means of lime was the substrate for our investigations. The sludges derivate from the plant treating wastewater from the edible oils and fats production. Physical and chemical analyses were conducted according to the Polish Standard as well as analytical rules and guidelines published in "Laboratory methods of water, wastewater and sludge quality determination" (in polish) (Gajewska-Stefańska, 1994).
Samples preparation encompassed: high temperature drying, grinding, and liquidizing.
All analyses were conducted in five series of measurement. The scope of analysis encompassed: waste structure determination, odour and color determination, pH, oxidation reduction potential (ORP), conductivity, hydration, total and volatile solids determination, nutrients (P, Mg, Ca, K) as well as heavy metals concentration.
During the current research project the concentrations of nitrogen, mercury, chromium, and cadmium content were not determined.

Results and Discussion

The analysed samples exhibited the following colors: beige, light brown, grayish and dark gray. The samples have had a characteristic odour of fats and calcium. The analyzed samples were free of sulphide hydrogen odour.
Moreover, sludge sample consistence was greasy and clayey.
Sewage sludge pH was found to be slightly alkaline to alkaline. The recorded pH value varied around 10. The highest value 12,82 was recorded for the sample no. 1. Whilst sample no. 6 exhibited the lowest pH value 7,54. The given pH values are obviously the result of the wastewater treatment technology applied, based on phosphates precipitation with lime.
The conductivity of the analysed sludge (supernatant) varied between 476 and 1021 μS/cm. It was assumed that the high conductivity was the result of inorganic compounds dissociation. This was also confirmed by the mineral characteristics of the sludge.
The recorded ORP levels changed in the range of between + 72,5mV do – 260,7 mV. In majority, the ORP values have been in the reductive range. However, one sample was characterized by oxidizing value.
The sludge moisture changed between 67 and 70 %. The latter is strictly connected with centrifugation process, which was applied in technological line to remove sludge water. The process also impacted the dry matter of sludge, which varied in the range of 29,5 to 36%. The average level of the parameter was about 33%. The ratio of volatile organic matter (VS) to total solids (TS) fluctuated between 0,33 and 0,40. The rest of the sludge dry matter constituted mineral matter.
Table 2 presents physical and chemical results of sewage sludge after lime treatment.

Tab.2. Physical and chemical results of sewage sludge after lime treatment

Parameter	Units	Sample No				
		1	2	3	4	5
pH		12,82	10,08	10,75	8,35	7,54
Conductivity	µS/cm	1021	494	660	564	762
Oxidation - reduction potential	mV	-11,5	72,5	-7,3	-260,7	- 172,6
Dry matter	%	36,75	33,34	31,79	33,16	36,55
Mineral matter	% d.m.	60	62	62	61	64
Volatile organic matter	% d.m.	40	38	38	39	36
P	% d.m.	7,55	7,22	5,6	7,07	6,55
Mg	% d.m.	1,03	0,53	1,34	1,44	0,98
Ca	% d.m.	25,43	61,76	40,99	78,85	56,3
Zn	mg/kg d.m.	353,7	209,9	503,3	612,1	623,8
Pb	mg/kg d.m.	136,0	29,99	88,08	135,7	101,23
Cu	mg/kg d.m.	54,42	35,99	50,33	90,47	68,4
Ni	mg/kg d.m.	40,82	29,99	12,58	66,34	49,25
K	% d.m.	-	11,2	29,5	25,3	21,4
Water content	%	63,3	66,7	68,21	66,84	63,45

Sludge nutrients (P, Mg, Ca, K)

Furthermore, nutrients content (P, Mg, Ca, K) of the analysed sludge after lime treatment was determined. Figure 1 shows nutrients content in the analysed sludge.

It was confirmed that all samples contained a high quantity of calcium. The highest value 78% d.m. was measured for sample no. 4, while the lowest value 25% d.m. was determined for the sample no 1. The measured values definitely exceeded levels maximum 10 % d.m., or in average 2-4 % d.m. given in the literature (Bień, 2007).

As mentioned before it is strictly connected with phosphate precipitation with lime.

The recorded amount of phosphorus and magnesium were also significant. As in the case of P, analyzed samples contained high level of calcium.

In general the average content of phosphorus in the sludge varied in the range of 0,6 and 9,2% d.m. (Rosik-Dulewska, 2000). The phosphorus content in examined samples changed in the range of 5,6 to 7,55% d.m. All above cited value are consistent with results achieved by Rosik-Dulewska (2000).

Apart from the high contains of calcium and phosphorus, the analyzed sludge samples have had also a high content of potassium, which can be considered as a valuable substitute of potassium – delivered by mineral fertilizers.

Magnesium concentration in the analyzed samples oscillated between 0,05 and 1,44 % d.m., with an average value 1,31 % d.m. In all samples taken into consideration, the magnesium level did not exceed the maximum value cited in the literature i.e.1,8 % (Bień, 2007).

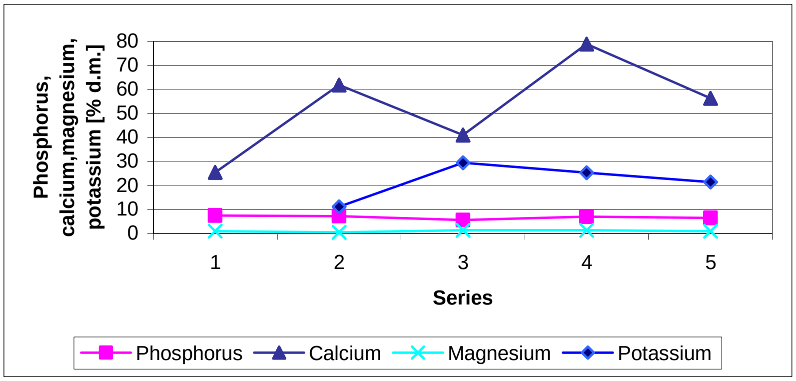

Fig.1. Nutrients content in series of measurement

Heavy metals concentration

Beside valuable nutrients, sewage sludge can contain various heavy metals. Figure 2 shows heavy metals concentration in the analyzed sludge.

As it is presented in the figure below, the lowest heavy metals concentration was recorded for sample no 2, while the highest for sample 4.

The zinc concentration usually did not exceed the value of 700 mg/kg d.m. (average value 500 mg/kg d.m.). In respect to permissible concentration of zinc in sludge to be used in agriculture the determined concentrations are definitively lower.

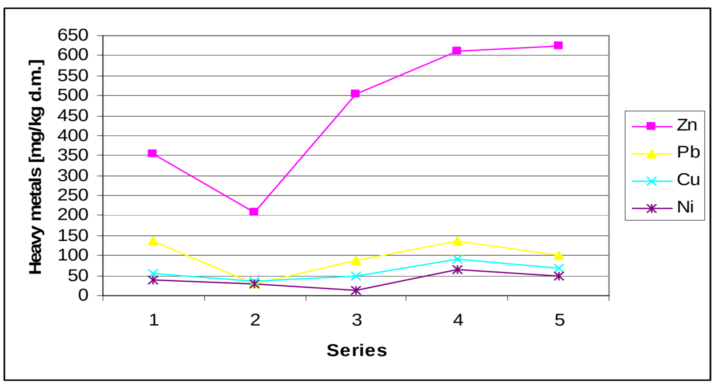

Fig. 2. Heavy metals content in series of measurement

The amount of nickel did also not exceed 70 mg/kg d.m. The concentration of this metal is much closer to the permissible (100 mg/kg d.m.) value allowed for soil application. The low concentration of nickel recorded was to some extend unexpected, mainly due to the fact that this metal is commonly used in edible oils processing as a catalyst. The literature shows (Rosik-Dulewska i in. 2006), that average degree of nickel reduction is about 1 %.

Copper concentration did also not exceed 100 mg/kg d.m. As concerned sludge agricultural and use, the maximum concentration of this metal should not be higher then 800 mg/kg d.m.

Finally, the concentration of lead was determined. In most case the recorded concentration was low and amounted to 206 mg/kg d.m (permissible – 1000 mg/kg d.m).

Example of application

Taking into account physical and chemical as well as nutrients and heavy metals content, the analyzed sludge can be used as a natural fertilize for the following purposes:

- plant cultivation: crops, sugar and folder beet, corn, rape, in edible plants, industrial crops, grass etc,
- fruit trees,
- bush nursery,
- pot plants (decorative).

The analysed sludge is reach in phosphorus, so it should be used in soils poor in phosphorus content. The recommended dosage – expressed as dry matter content is up to 3 tones /ha. Simultaneously, besides phosphorus (560kg P_2O_5**)** the soil will achieve about one ton of CaO and organic matter per hectare. The above figures were calculated for one cycle - a period of three years.

Before sludge application as fertilizer, the amount of nutrients in the soil should also be taken into consideration. Before addition of a new portion of sludge, it is necessary to calculate the required or permitted dose of phosphorus.

The investigated sludge should not be applied for the following purposes: edible potatoes production, vegetables cultivation, in the allotment area, and anywhere, where it is impossible to cover the soil after sludge application.

Summary

Based on carried out investigations, it was concluded that the analyzed industrial wastewater sludge after lime treatment can constitute as a valuable soil fertilizer. Taking into account the acid nature of most soil in our country (Poland), the high content of calcium and subsequent high pH value can positively affect the soil structure and acidity. Also high concentration of calcium assure required sanitary properties of the sludge and result in pathogens elimination.

As it was mentioned, the fertilization value of the sludge is determined by the concentration of the following compounds and elements: organic and mineral matter, nitrogen, phosphorus, microelements as well low levels of toxic substances. The analyzed sludge contained high levels of both organic matter (33 – 40 %) as well as nutrients (P: 5,6 – 7,55 % d.m., Mg: 0,53-1,44 %d.m., Ca:25,43- 78,8 % d.m.), which are necessary for appropriate plant growth. It should be stressed that heavy metals concentration are below permissible level for agriculture utilization. However, the analyses of Hg, Cr, Cd as well as pathogens should also be taken into account before the agriculture usage. Despite of the high calcium concentration, the analyzed sludge has had a tendency to generate mould if stored in anaerobic conditions.

In order to establish a proper sludge dosage as well as assess the influence of the previously used sludge, the soil quality should be taken into account.

The scope of the soil analyses should include: pH value, heavy metals as well as nutrients concentrations in the upper part of the soil. Discussing potential methods of the analyzed sludge utilization, the best solution appears to be the agriculture application, e.g. soil recultivation – degradated lands as well as areas, which are not covered by the soil.

The analyzed sludge can be temporally stored, if it is impossible to applied them directly. However, the sludge should undergo proper stabilization as well as dewatering. Another alternative is the process of involved co-combustion with other organic waste, however, some preparation steps have to been considered in order to achieve proper water content.

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