Original Research

The Use of Flotation in Fat Recovery and the Pretreatment of Wastewaters from Animal Fat Production

S. Żak^{1*}, Z. Pawlak^{1,2}

¹University of Technology and Agriculture, Department of Technology and Chemical Engineering, 85-326 Bydgoszcz, 3 Seminaryjna Street, Poland

²Utah Department of Health, Environmental Chemistry and Toxicology, Salt Lake City, 46 Medical Drive, UT 84113, USA

Received: March 17, 2005 Accepted: December 27, 2005

Abstract

This paper presents a method of fat recovery from wastewaters produced in the process of wet rendering. The solution may be used in protein recovery and for pretreatment of wastewaters. The essence of the method is based on dissolved air flotation (DAF) used to separate fats in the 1st stage and protein fractions in the 2nd stage of the process. Its special advantage is the possibility of the direct treatment of mixed wastewaters and silts produced by centrifuges. This method enables the recovery of fats and proteins in a non-rotten form, which permits their further utilization. A flotation system equipped with two separation chambers, pipe reactors, a water saturation station and a control system for optimizing the process were constructed in order to apply the method. The studied method was verified in a real scale installation by treating after-centrifugal wastewater in the volume up to 10.0 m³/day. Using the method, the fatty compounds recovery exceeds 85% and suspended proteins are separated from mixed processing wastewaters and after-centrifugal silts.

Keywords: wastewaters from animal fat processing, separation of fats and proteins, after-centrifugal wastewaters and silts, two-stage flotation, dissolved air flotation (DAF)

Introduction

The amount of the pollutant load and its contents in wastewater produced during the process of wet rendering of animal fats depends on the type of raw material, the way of separating a product and the effectiveness of the devices used to separate the final product [1]. The basic aim of the process of isolated animal fat recovery is the separation of three main phases: fats, proteins and water [2-4]. In the technological process a fatty tissue is ground then thermally melted and finally separated from water and cracklings by centrifuging [1, 3]. Raw, salted and

smoked types of fatback as well as leaf fat are raw materials of large and diversified contents of fat and protein substances. For example, the separated pork fats in a form of edible lard are rendered from the hypodermic fatty tissue and the leaf fat, rarely from the inner fatty tissue [2]. In order to produce long storage lard, the following raw materials are used: fatback, leaf lard, fine grease, groin fat, and jowl fat [1, 3], whereas salted and smoked fats [3] are additionally used for manufacturing short-time storage fats. Water separated in the process of centrifuging is the wastewater containing fats and proteins that easily decay. The decay is associated with the emission of hydrogen sulfide, which is a product of protein decomposition and a sulfate reduction [2]. Wastewater volumes in the form of

^{*}Corresponding author; e-mail: zak@atr.bydgoszcz.pl

gluey waters from wet rendering tallow and other types of fats are estimated at app. 0.35 m³/Mg of the final product [2]. The content of fats and proteins in the processing wastewater range widely and depend not only on the quality of the raw material and the time of rendering but also on the effectiveness of the centrifuges used to separate the product. The highest level of recovery is obtained by two-stage centrifuging with the use of the three-phase vertical centrifuges: a purifying one and a clarifying one [4]. The elimination of fats in the stage of pretreatment is especially significant for the further non-collision biological treatment of the processing wastewater [2, 5].

The proteins in the wastewater make a basic load of the suspended solids, COD, BOD and nitrogen. They occur as soluble or insoluble ones, forming suspensions or fat-protein emulsions [2-4]. These forms mainly result from denaturation, which takes place in the process of rendering, especially at high temperatures. Practically, these substances are not exposed to physical separation since there are no effective methods of their separation into a pure phase – particularly the separation from ballast fats. In well-known methods of the processing wastewater treatment, the total denatured and colloidal proteins are separated together with fats by coagulation with the use of iron salts (III) and aluminum salts (III) and by flocculation and then treated by flotation [6-12]. A soluble form of the proteins is a basic difficulty in the process of their removal [13-16]. High reduction of soluble proteins can be achieved by the use of phosphate salts, preferably in their condensed forms [17-19]. These are: sodium orthophosphates, tetrapoliphosphates, hexamethaphosphates, methaphosphates [19]. There are also well-known methods of protein separation with the use of the Colloidal Gas Aphrons (CGA) and non-ionic surfactants techniques [20-22].

A selective recovery of fats and proteins with the use of physical methods is not applied (or seldom applied) in practice and the organic load found in the processing wastewater is mostly transformed into biogas [23-26]. Similar methods are used for floats separated during wastewater chemical treatment [27]. The wastewater pretreated by physicochemical methods can be directed to further non-collision treatment by biological methods [2, 27]. It is also possible to use the pretreated wastewater in agriculture (as manure or field irrigation) after necessary requirements have been fulfilled, such as sanitary requirements, reduction of BOD and COD, etc. [28].

Experimental Procedures

The effectiveness of the method including the flotation unit was tested on the specially designed installation system for both the physical separation of fats and proteins and the pretreatment of effluents from wet rendering (Figure 1). The unit for separating the phases consisted of: two flotation cells I and II separating fats and proteins, a system saturating water with air – a saturation

station, pipe reactors for mixing streams of raw wastewater and air-saturated water, and a control system for optimizing the process. The installation for testing the method has been designed for the pretreatment of raw highly concentrated wastewater and after-centrifugal silts of total max. volume 10.0 m³/day. After dewatering the product with the use of a vertical centrifuge at 4000 rpm, hot and raw wastewater (SS1) was accumulated in the form of gluey waters in the tank of volume 2.0 m³ equipped with circulating and force pumps. It was transported from the tank by a pipeline to the chamber (1) of flotation cell I, volume 3.0 m³, equipped with an inner heating system (1.1). The contents of the chamber (1) of flotation cell I were averaged by the circulating system (1.2) with a circulating pump (1.3). Then, using air from a compressor (3), they were aerated using a Pfleiderer water system with a membrane duct diameter d=120 μm and the aerating disc diameter D=240 mm (1.4). Water was saturated under 400 kPa pressure in a tank (4) within 10.0-15.0 minutes. Then it was directed by a pressure valve (4.1) into a pipeline of the circulating system (1.2) and the pipe reactor (1.5). The after-centrifugal wastewater was mixed with saturated water in the volume ratio 4:1. The use of the circulating system permitted perfect averaging and mixing of the contents, inhibited fermentation and evenly distributed air-saturated water. After mixing the wastewater with the air-saturated water, the contents of the flotation chamber were left for 5.0 hours to separate phases. The mixture was additionally aerated by a fine bubble system with the air rate of 2.0 Nm³/h. To accelerate the wastewater degassing, the temperature was held within 50-55°C with the use of the system (1.1) during phase separation. After that period of time, the separation was made by directing the middle (Ib) and lower (Ic) phases into a flotation II chamber (2) with a force pump (1.6), and the phase of thickened fat was drained by the pipeline (1.7). Flotation cell II with a chamber (2)of volume 3.0 m³ was equipped with a circulating system (2.2) including a circulating pump (2.3) and an aerating system (Pfleiderer water system) (2.4) with membrane ducts of diameter d=120 µm and membrane disc diameter D=240 mm by using the air from the compressor (3). Water saturated in the tank (4) under 400 kPa air pressure within 10.0-15.0 minutes was supplied through the highpressure valve (4.2) into the circulating system (2.2) by the pipe reactor (2.5). The treated wastewater was mixed evenly with saturated water for 30.0 minutes. Then the mixture was circulated during the next 30 minutes and the 30% aqueous solution of hydrogen peroxide (d = 1.1110 g/mL) was added from station (5) to the pipe reactor inlet (2.5) in the amount of 400-450 mgH₂O₂ per 1.0 L of the wastewater. The contents of the flotation chamber were left for 5.0 hours to separate phases. The system (2.1) held the temperature of the contents within 50-55°C in order to accelerate the wastewater degassing during the phase separation. It was additionally intensified by fine bubble aeration with a rate of 3.0 Nm³/h. After that period of time, the separation was made by directing the

The Use of Flotation... 509

lower phase (II b) (SS2) to the general factory wastewater pumping station (6), and the upper phase (II a) – into the centrifuge (7) to separate proteins. Effective mixing in chambers (1) and (2) of flotation cells I and II was required to achieve high efficiency of the technological process and high homogeneity of the reagents. It was realized by installing pipe reactors (1.5) and (2.5) into the circulating systems and introducing the fine bubble aeration by using the systems (1.4) and (2.4). The aeration made a decrease in temperature. However, the process was continued so as not to reduce temperature below 50°C. In those circumstances particles of fats floated at total height of the flotation chamber. The fatty phase (Ia) separated on the surface was directed to the second rendering after the lower (I c) and middle (I b) phases had been drained, and directed into flotation cell II. Properly selected temperatures and proportions of the air-saturated water to raw wastewater prevented the formation of silts tending to settle at the bottom of the flotation chambers. This phenomenon was also eliminated by an inner circulation through pipe reactors. Moreover, it was found that it had an advantageous effect on the wastewater mixing, preferably on the rate of the flotation process and its effectiveness. The pretreated wastewater (SS2) was gravitationally drained into the factory pumping station (6) and directed to further full biological treatment.

To estimate the effectiveness of separation for the particular phases and the pretreatment process in averaged samples of raw wastewater (SS1) (point A in Fig. 1) after the fat (point B in Fig. 1) and protein flotation (SS2) (point C in Fig. 1), the following indicators were determined according to the applications given in standards for water and wastewater [29]: reaction/pH-value (PN-90/C-04540/01), chemical oxygen demand (COD) determined by dichromate method (PN-74/C-04578/03), biochemical oxygen demand (BOD_n) by dilution method (PN-EN 1899-1, 2002), ether extract (EE) (PN-86/C-04579/01) and total nitrogen (N) (PN-73/C-04576/12). The obtained results of the analyses for raw and pretreated wastewater are presented in Table 1. As hydrogen peroxide was used in the 2nd stage of flotation, the obtained COD values were corrected. The actual chemical oxygen demand was presented after correcting the value by subtracting the fraction induced by the residual oxidizer on the basis of the relation: $COD_r = COD_p - f \cdot d$ (COD_r) – actual, COD_p – determined in the after-reaction sample, d – concentration of H₂O₂ in a sample – determined iodometrically (titrant 0.05 M Na₂S₂O₃), f = 0.25 - a correction coefficient assumed on the basis of the data found in the paper [30]). The separated fatty phase was estimated on the basis of the analyses made in accordance with Polish Standards, respectively: taking and preparing samples for

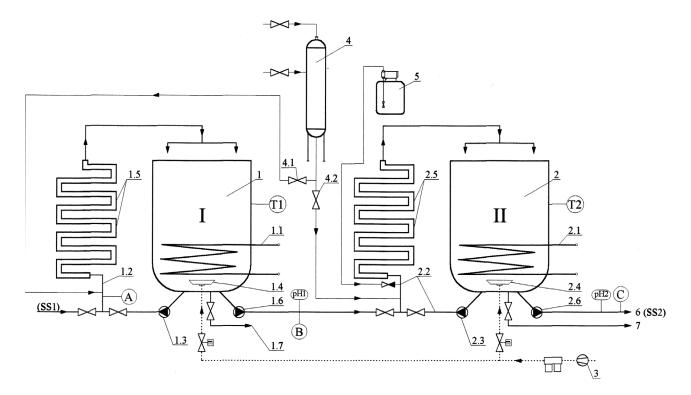


Fig. 1. Flow diagram of the installation for pretreating the processing wastewater from lard production, where: SS1 and SS2 are raw and pretreated wastewater, 1) chamber of flotator I, 1.1) inner heating system, 1.2) circulating-mixing system, 1.3) circulating pump, 1.4) aeration system, 1.5) pipe reactor, 1.6) force pump, 1.7) fatty phase drainage pipeline, 2) chamber of flotator II, 2.1) inner heating system, 2.2) inner mixing system, 2.3) circulating pump, 2.4) aerating system, 2.5) pipe reactor, 3) air compressor, 4) water saturation station, 4.1 and 4.2) pressure valves, 5) hydrogen peroxide dosing station, 6) SS2 to the factory wastewater pumping station, and 7) drainage pipeline for thickened proteins, T1 and T2 – temperature measurements, pH1 and pH2 – pH-meters.

analyses: PN-87/C-04288.02, PN-EN ISO 5555:2002 and PN-ISO 661:1995; determination of fat content PN-87/C-04288.04; determination of peroxide value PN-88/C-04288.10 and PN-ISO: 3960:1996; determination of acid value PN-88/C-04288.06 and PN-ISO 660:1998; determination of protein content PN-87/C-04288.14. In order to check the fatty fractions in the wastewater, fatty acids were analyzed using a gas chromatograph (GC) (Hewlett Packard HP-5890 series II, capillary column HP-1: length $1\!=\!30.0$ m, $(\phi\!=\!0.53$ mm, phase: Hypersil ODS Shandon) with detection by AED and ECD and a mass spectroscopy (MS 5972 series Mass Selective Detector – column: Pona $1\!=\!25.0$ m, $(\phi\!=\!0.33$ mm), extracting in the system liquid-liquid by means of chloroform and ether.

Necessary microbiological tests for raw (SS1) and pretreated (SS2) wastewater were carried out in accordance with the following techniques [31a-c]: Determination of Salmonella sp. (pre-incubation at 37°C for 18 h in Buffered Water, Inoculation on Tetrathionate Broth - incubation at 43°C for 24 h, Inoculation on Selenite Broth – incubation at 37°C for 18-20 h and acc. to the procedures: inoculation on - BPLS Agar - incubation at 37°C for 24 h, SS Agar – incubation at 37°C for 24 h, Bismuth Sulf. Agar – incubation at 37°C for 24 h, Pril Mannitol Agar - incubation at 37°C for 24 h). API 20 E (for Enterobacteriaceae) tests were also conducted to identify Salmonella genus [31a-c]. In order to establish the occurrence of intestinal parasite eggs as well as their abundances and viabilities, parasitological tests were carried out with the use of microscopic methods, based on morphological traits (enlarged 200 times with the use of the Vasilkova method). Sample preparation consisted of extracting with the 5% solution of NaOH, shaking and centrifuging. The next step was extraction with the saturated solution of sodium nitrate and the centrifuging of the flotation phase in which the microscopic analysis was made. The viability was determined with the use of a climatic chamber at 24-26°C and estimated every second day [32].

Results and Discussion

Full management and treatment of wastewater and silts after centrifuging from the animal fat production has not been well recognized yet. Most factories producing animal fats cope with the problem of their disposal [2]. Fat and protein recovery is a key issue as far as waste management is concerned. The problem becomes particularly important for fat separation. It is connected with the irreversible loss of the raw material, fast decay and protein degradation, which limits the effective separation of fats and makes their usage parameters worse. According to the state rules, the wastewater from the animal fat production belongs to the biodegradable category [28]. Analyses has shown that for all 21 series of measurements the wastewater contained neither bacteria of Salmonella sp. genus nor living parasite eggs (Ascaris sp., Trichuris sp. and Toxacara sp.), which satisfied the sanitary conditions allowing the use of wastewater in agriculture. A respective regulation requires the additional BOD₅ reduction in the wastewater (no less than 20%) and the reduction of total suspended solids content (no less than 50%) [28]. Besides, it requires a proper reaction (pH) and the lack of contents or even trace amounts of the following elements: As, Ba, Be, B, Zn, Sn, Cr(VI) and total Cr, Co, Cu, Mo, Ni, Pb, Se, Ag, Ra, Ti, V as well as some substances such as: free and total chlorine, free and bounded cyanides, fluorides, thiocyanates, surfactants and oil derivatives, etc. [28].

So far physical methods to separate fats (rarely proteins) have been used only to pretreat wastewater and the rest has been fully treated by biological methods [2]. This type of wastewater can also be used as a substrate for biogas production, which has become more and more popular [23-27]. To the basic disadvantages making the wastewater treatment difficult belong: significant variance of the contents, high temperature of raw wastewater (tending to drop during a long retention time) and the ability to decay fast after cooling to ambient temperature. Phases (fats and proteins) recovered from wastewater by wellknown methods are characterized by low quality and are not commonly applied. To solve the problem, it has been assumed that the pollutant elimination should be realized in the possibly shortest time after the process of centrifuging. This is important, considering the limitation of the decay processes inducing a partial fat hydrolysis and the destruction of protein substances. The processes lead to a fast growth of soluble COD and BOD and release ammonium nitrogen and hydrogen sulfide. This reduces the usage parameters of the separated phases and makes the pretreatment process less effective. Considerable fat volumes in the wastewater lower the effectiveness of aeration during the biological treatment in chambers with activated sludge due to reduced diffusivity and because of plastering and plugging holes in the aeration systems. High concentrations of fats in sludge result in foaming in separated fermentation chambers and disturb the work of the sludge dewatering appliances [2]. The fat load of the active sludge cannot exceed threshold values, otherwise the biological treatment processes are abruptly inhibited [5]. In raw wastewater directly after rendering, fats may occur as soluble, emulsified or suspended forms. The emulsified fats are a result of applying both very fine disintegration and high temperature of rendering [1]. Additionally, the presence of protein substances in the retained wastewater leads to a considerable hydrolysis and forms mono- and diglycerides of fatty acids 12:0, 14:0, 16:0, 16:1, 18:0; 18:1, 18:2, 18:3 and 20:1, known for their strong emulsifying properties [27].

The process of extracting fats from the raw material in the factory where the solution was tested belongs to the high temperature of fat rendering methods. It is continuous and includes the following operations: disintegration in a meat grinder of diameter 3-6 mm to destruct the structure of the fatty tissue, to reduce the time of rendering and to decrease heat demand; next come heating, fat rendering, decanting, separating by centrifuging, cooling and form-

ing. Most of these operations are often carried out at diverse temperatures and pressures. The direct steam heating of the raw material applies to fat rendering, and the water phase is separated mechanically by centrifuging.

The method aimed at recovering fats and proteins and at eliminating COD, BOD and nitrogen forms by the reduction of protein substances from the processing wastewater. The tested method was also used to work out the procedure of the wastewater pretreatment so that it could be used in agriculture for irrigation or as natural organic manure, in accordance with the respective regulations [28]. After a few hours of retention, the raw wastewater was characterized by a three-phase structure: the lower phase - containing thickened silts, the middle - waterprotein phase and the upper phase - containing mainly fats. The chromatographic analysis of fatty phase contents showed the existence of saturated fatty acids: 12:0, 14:0, 16:0, 18:0, monoenic: 16:1, 18:1, 20:1 and polyenic ones: 18:2, 18:3. The ratio of polyenic acids to the saturated ones was 0.19-0.23, which is in accordance with literature data [11, 28]. Fatty acids found in wastewater appeared in combinations of triacylglycerols with the irregular distribution of acid chains. The other types of wastewater, including the ones from washing the processing plant and floors as well as the after-disinfection wastes, were not directed into the tested installation.

The basic problem found during preliminary testing was to the maintain the temperature at 50-55°C, which is necessary for highly efficient separation. It was a result of the additional bottom-up aeration to intensify the process of the phase separation, which made the temperature drop below the assumed threshold value (50°C). Therefore, further results of the tests in the tables enclosed present the ones carried out with minimal-optimal aeration at 2.0 Nm³/h (with diameter of pores in aerating disc membranes d=120 µm and with the aeration disc diameter D=240 mm).

To estimate the effectiveness of the phase separation and thickening, the following individual separation phases were defined:

- a) in the 1st stage of the flotation (fat separation); Ia upper phase (fatty phase), Ib middle phase (protein phase) and Ic lower phase (wastewater phase);
- b) in the 2nd stage of the floatation (protein separation);
 IIa upper phase (protein phase), IIb lower phase (wastewater phase).

In order to make the data analysis and to assess the processing wastewater pretreatment system as well as to evaluate the level of phase recovery on the experimental installation, the effectiveness was defined by the following function: $\eta = 1 - [(X1-X2)/X1]$ (where: X1 – results of the analyses for samples taken at the inlet, X2 – results of the analyses for samples taken at the outlet) (Table 2). The effectiveness was interpreted as a ratio of fats and protein thickenings, which were to be recovered.

The second stage of flotation separation was additionally completed by introducing hydrogen peroxide in order to limit decay processes. The introduction was

followed by intensive foaming of the mixture and gas emissions of ammonium and hydrogen sulfide mainly. Hydrogen peroxide is characterized by bacteria- and fungicidal and by bacterio- and fungistatic properties, which significantly limits undesired processes or eliminates them totally [28]. It has been found that hydrogen peroxide, applied in the amount of 400-450 mgH₂O₂/L in the 2nd stage of the flotation, clearly inhibited both the decay processes and the characteristic "swelling" of the volume. Apart from that, the processes of hydrogen peroxide decomposition released molecular oxygen (H₂O₂) \rightarrow O₂ + 2H⁺ + 2e), forming gas micro-bubbles which intensified the flotation of the protein phase [30, 33]. The effect of producing micro-bubbles, which are advantageous for flotation, also results from the decomposition of the organic substrate forming carbon dioxide [30, 33, 34]. Hydrogen peroxide shows bacteriostatic properties, which increases the biological stability of the wastewater stream after flotation [30, 33, 34]. This concerns both the recovered proteins and the pretreated wastewater. The change in chemical compounds in the pollutant load caused by hydrogen peroxide in the 2nd stage of flotation may also induce reactions between the organic albumin substrate (A) and H₂O₂, such as: addition (e.g.: H₂O₂ + $A \rightarrow A \cdot H_2O_2$), substitution (e.g.: $H_2O_2 + 2AH \rightarrow AOOH$ + HA + $2H^+$ or $H_2O_2 + 2AX \rightarrow AOOA + 2HX$) as well as oxidation (e.g.: $H_2O_2 + A \rightarrow AO + H_2O$) [30]. Chemical changes which run in accordance with the schemes mentioned above lead mainly to the synthesis of forms more susceptible to biodegradation in the final stage of wastewater biological treatment.

The exemplary results of the analyses of the selected indicating parameters listed in Table 1 (including 21 measurement series for raw and pretreated wastewater) show characteristic dispersion of the indicator values. The applied method of separation with the assumed constant parameters of: circulation flow, aeration, temperature and the period of the individual operations, permitted better analytical values in the 1st stage of flotation (thickening of fat and protein phases), respectively in phase Ib with reference to raw wastewater (Tables 1 and 2): chemical oxygen demand (COD) 3-18%, 5-day biochemical oxygen demand (BOD_c) 43-106% and total nitrogen (N) 6-26%.

It should be emphasized that the research was conducted at low temperatures outside – in the winter (December, January and February), which had a significant effect on the quality of the raw material used in the process of rendering. Additionally, the time from the moment of separating fat from the primary animal material to the second processing in the factory where the tests were carried out, did not exceed 12 hours and the raw material was stored at temperatures lower than 5°C.

As a result of applying the method, the increase in fatty compounds in phase Ia (in reactor I) exceeded 70% of the phase weight and fats recovery amounted to 85% (Table 2). The two-parameter values differed and depended on the type of the raw material used for rendering fats.

Table 1. A list of selected analytical parameters for raw and pretreated wastewater from the individual phases of separation - drained from the tested installation.

Item	Parameter	Type of wastewater or phase ^{a)}	Unit	Range of occurence	Effectivenes of elimination ^{b)}
1		raw wastewater		6.0 – 6.4	
2		phase Ia		6.7 - 7.1	
3		phase Ib	рН	6.1 - 6.5	
4	reaction	phase Ic		6.1 – 6.4	
5		phase IIa		6.4 - 6.9	
6		phase IIb		6.2 - 6.6	
7		raw wastewater		6920.8 - 44704.1	
8		phase Ib		7321.2 – 56402.3	$\eta_{\rm lb} = 0.06 - 0.26$
9	total nitrogen (N)	phase Ic	mgN/L	1920.8 - 14704.1	
10		phase IIa		10288.7 - 51055.0	$\eta_{IIa} = 0.14 - 0.49$
11		phase IIb		970.0 – 2724.8	
12		raw wastewater		49770.6 - 95482.3	
13	chemical oxygen	phase Ib		58588.6 - 98302.1	$\eta_{1b} = 0.03 - 0.18$
14	demand (COD)	phase Ic	mgO_2/L	26220.1 - 53832.2	
15	demand (COD)	phase IIac)		64299.4 – 99220.0	$\eta_{IIa} = 0.04 - 0.29$
16		phase IIbc)		2977.4 – 11304.6	
17		raw wastewater		13108.2 - 32028.6	
18	biochemical oxygen	phase Ib		18802.0 - 66114.2	$\eta_{\rm Ib} = 0.43 - 1.06$
19	demand (BOD ₅)	phase Ic	mgO_2/L	15108.2 - 19028.6	
20	demand (BOD ₅)	phase IIa		52776.7 - 80488.3	$\eta_{IIa} = 1.51 - 3.03$
21		phase IIb		1367.6 – 4878.3	

^{a)} pretreated I - after first stage of fat separation (a, b and c - phases: upper one - fatty phase, middle one - protein phase and lower one); II - after second separation of the protein suspensions and colloids (a and b - phases: upper one - protein phase and lower one); ^{b)} the effectiveness of thickening for 1st stage was defined as: $(\eta_I = 1 - [(A-B)/A] \text{ (where: } A \text{ - the results of analyses for wastewater samples taken at point A, B - the results of analyses for wastewater samples taken at point B); the effectiveness of thickening for 1st stage was defined as: <math>(\eta_{II} = 1 - [(B-C)/A] \text{ (where: } B \text{ - the results of analyses for wastewater samples taken at point B, C - the results of analyses for wastewater samples taken at point C in Fig. 1); ^{c)} COD presented as the corrected COD_r = COD_p - f·d.$

Table 2. Balance of: COD, CODr, BOD5 and N ratios after two-stage flotation*.

Item	Ratio ^{a)}	Type of wastewater or a phase	Stated value of the ratio ^{a)}	
1	BOD /COD	raw wastewater	0.26 - 0.34	
2	BOD _s /COD	phase Ib	0.32 - 0.67	
3		phase Ic	0.35 - 0.58	
4	BOD /COD	phase IIa ^{a)}	0.81 - 0.82	
5	BOD ₅ /COD _r	phase IIb ^{a)}	0.43 - 0.46	
6	COD/N	raw wastewater	2.14 – 7.19	
7		phase Ib	1.74 - 8.00	
8		phase Ic	3.66 - 13.65	
9	COD/N	phase IIa ^{a)}	1.94 – 6.25	
10		phase IIb ^{a)}	3.07 – 4.15	
11		raw wastewater	0.72 - 1.89	
12		phase Ib	1.17 - 2.57	
13	BOD ₅ /N	phase Ic	1.29 – 7.86	
14		phase IIa	1.58 - 5.13	
15		phase IIb	1.41 – 1.79	

^{*} results were calculated for 21 series of measurements; a) $COD_r = COD_p - f \cdot d$ (f = 0.25)

After defatting in the 1st stage of flotation, the 2nd stage was characterized by constant parameters of circulation flow, aeration, temperature, individual oxidizer doses (450 mgH₂O₂/L) and the periods of the particular operations. The evident enlargement of the selected ana-

lytical values (increase in concentration of the suspended protein phase mainly) with reference to the raw wastewater in the 2nd stage of flotation in phase IIa was as follows (Tables 1 and 2): chemical oxygen demand (COD including coefficient f = 0.25) 4-29%, 5-day biological

The Use of Flotation... 513

Table 3. Exemplary parameters of	the separated fatty phase (Ia	ι)*.
----------------------------------	-------------------------------	------

Item	Fat recovery ^{a)} [%]	Fat content ^{b)} [%]	Protein content ^{b)} [%]	Acid value ^{b)} [mgKOH/g]	Peroxide value ^{b)} [meq/kg]
1	90.2	73.8	1.7	9.5	2.4
2	91.4	77.4	1.3	8.4	2.6
3	92.2	76.8	1.4	12.1	2.2
4	85.6	82.3	0.6	10.5	3.7
5	86.6	78.1	2.2	14.2	3.5
6	87.0	79.3	2.3	12.1	3.8
7	88.3	79.4	2.1	11.9	4.1
8	89.6	78.0	1.6	14.7	5.4
9	84.6	74.5	1.1	16.3	5.8

^{*} for samples from different batches of the raw material tested in winter months: December-February: 1-3) unsalted raw leaf fat; 4) jowl fats, 5-7) leaf fat, 8-9) poultry fat, ^{a)} measured with the reference to the contents in raw wastewater, ^{b)} measured in phase Ia

Table 4. Exemplary parameters of fatty phase (Ia) separated under different conditions of the environment*.

Item	Type of raw material - fat	Month	Storage time ^{a,b)} [h]	Temperature of the environment ^{c)} [°C]	Acid value ^{d)} [mgKOH/g]	Peroxide value ^{d)} [meq/kg]
1	leaf fat	April	10	15-20	10.4	3.8
2	leaf fat	July	6	25-30	29.9	4.2
3	leaf fat	August	18	25-30	42.8	7.8
4	leaf fat	October	12	15-18	7.8	12.9
5	fatback	July	14	25-30	26.3	23.0
6	fatback	August	14	25-30	48,6	10.9
7	poultry fat	March	12	10-15	10.4	3.1
8	poultry fat	May	12	15-20	17.8	9.9
9	poultry fat	July	8	25-30	29.8	13.6
10	poultry fat	September	14	15-20	14.7	8.2
11	poultry fat	November	8	10-15	7.8	6.4

^{*} accordingly to the seasons of gaining and processing raw material, a) measured from the moment of primary output (animal partition) up to the secondary rendering, b) time with tolerance \pm 0.5 h, c) temperature of raw material storage (including its transport), d) measured in phase Ia

oxygen demand (BOD₅) 151-303%, and total nitrogen (N) 14-49%. It was found that the flotation process aided with hydrogen peroxide changed the COD(BOD₅)/N ratio (and COD_r) in phase Ib with reference to IIa. Total nitrogen increased twice in the 2nd stage, COD – about 20-60% and BOD₅ – three times, considering a full range of the determined analytical values. The relatively lower COD concentration in relation to BOD₅ is a result of a higher fraction of soluble COD with reference to total COD, compared to total BOD₅ and the distribution of the amounts of soluble compounds in relation to the insoluble ones. It is related to a significant contribution of this parameter in the total suspended proteins concentrated in phase IIa.

The fats separated in phase Ia were characterized by parameters presented in Table 3. The fat found in the phase had the acid value no higher than 20.0 mgKOH/g and the peroxide value lower than 6.0 meq/kg (meq/kg – in accordance with PN-ISO 3960:1996, a peroxide value defined in miliequivalents of active oxygen in 1.0 kg of fat), which classified the material after its re-ren-

dering for the further use, e.g. as a fodder supplement. The quality of the fatty material recovered with the use of the discussed method is an essential problem in seasons characterized by high temperatures, especially in the summer. It is connected with worse parameters of the recovered fatty phase (Ia), and particularly with a higher acid number which is the result of both the decay processes taking place in the raw material. and the hydrolysis of triglycerides forming free acids. Table 4 presents exemplary parameters of the fatty phase (Ia) recovered in different periods of the year.

The wastewaters pretreated using the discussed method can be directed to further full non-collision biological treatment [2, 6]. Their further application in agriculture, as manure or field irrigation, can also be taken into account after the respective regulations have been fulfilled [28].

Conclusion

The method with the designed system for the

two-stage flotation permits the recovery of fats and proteins of advantageous usage parameters from after-centrifugal processing wastewaters. Another benefit of the method is the possibility of pretreating the wastewaters to make their further non-collision biological treatment possible, e.g. by using the method of activated sludge. Full elimination of fat and protein suspensions is a crucial benefit, which, considering favorable sanitary parameters and trace amounts of toxic elements and substances, makes the wastewater pretreated by the discussed method usable in agriculture.

References

- 1. NIEWIADOMSKI H. Edible fat processing, Scientific Publishers WNT: Warsaw, pp 110-118, 1993 (in Polish).
- RÜFFER, H., ROSENWINKEL, K.H. Taschenbuch der industrieabwasserreinigung, Oldenbourg Verlag: München Wien, pp 115-134, 1991.
- NIEWIADOMSKI H., SZCZEPAŃSKA H. By-products Fatty Wastes. The use and effect on environment, Scientific Publishers PWN: Warsaw, pp 214-223, 1989 (in Polish).
- CAVEY A., EYARS R., HILL S., SIMPSON A., KUBICKI M., NIEWIADOMSKA U., ORZESZKO G., SARNAC-KA A. Environment Protection in Fat Processing, General Guide. Publishing House of FAPA, the work edited by Kubicki M., Warsaw, pp 56-73, 1998 (in Polish).
- ŻAK S., KARKOCHA W. The method of separating and treatment of fatty acids in wastewaters, Pol. Pat. Apll., No. P. 358413, 2002.
- KRAUSE A. Pflanzliche und tierische fette in ihrer wirkung auf mikroorganismen in biologischen klänlagen, Fette-Seifen-Anstrichmittel, 84. Jahrg., 1. Sonderheft, pp 536-543, 1982.
- AGUILAR M. I., SÁEZ J., LLORÉNS M., SOLER A., OR-TUÑO J. F., MESEGUER V., FUENTES A. Improvement of coagulation–flocculation process using anionic polyacrylamide as coagulant aid. Chemosphere 58, 47, 2005.
- 7. HALLIDAY. P. J., BESZEDITS. S. Proteins from food processing wastewaters. Eng. Digest. **30**, 24, **1984**.
- 8. JOHNS M. R. Developments in wastewater treatment in the meat processing industry: a review. Biores. Technol. **54**, 203, **1995**.
- ŻAK S. The method of wastewater defatting. Pol. Pat. Apll., No. P. 351059, 2002; The method of defatting and deproteinizing. Pol. Pat. Apll., No. P. 363662, 2003; The method of treating wastewaters from protein-fat pollutants. Pol. Pat. Apll., No. P. 363663, 2003; The method of eliminating fats and proteins from wastewaters. Pol. Pat. Apll., No. P. 363664, 2003.9.
- 10. SCHULZ P., DOBIAS B. Gewinnung von proteinen aus abwässern durch flotation. Wissensch. Umwelt. 4, 246, 1982.
- 11. ŻAK S., ZABŁOCKI L., MERDA J. Fatty wastewater treatment plant. Pol. Pat. Apll., No. P. 350875, **2001**.
- 12. ŻAK S. Processing of organic waste from vegetable and animal fat production. Pol. J. Chem. Technol., 7, 74, 2005.

 ZIEMLAŃSKI Ś., BUDZYŃSKA-TOPOLEWSKA J. Food fats and systemic lipides, Scientific Publishers WNT: Warsaw, pp 89-94, 1991 (in Polish).

- BREMMELL K. E., JAMESON G. J., FARRUGIA T. R. Agglomeration of fats and proteins. Chem. Eng. Aust. 19, 23, 1994.
- FRIEDMAN M., ZAHNLEY J. C., MASTERS P. M. Relationship between in vitro digestibility of casein and its content of lysinoalanine d-amino acids. J. Food Sci. 46, 127, 1981.
- 16. LI ANG CHEN, CARBONELLI R. G., SERAD G.A. Recovery of proteins and other biological compounds from food processing wastewaters using fibrous materials and polyelectrolytes. Water Res. 34, 510, 2000.
- 17. PELROY G. A., SPINELLI J. Availability of amino acids in sarcoplasmic fish proteins complexed with sodium hexametaphosphate. J. Food Sci. **36**, 144, **1971**.
- 18. SPINELLI J., KOURY B. Phosphate complexes of soluble fish proteins. J. Agr. Food Chem. **18**, 284, **1970**.
- SCHULTS G. W., RUSSELL D. R., WIERBICKI E. Effect of condensed phosphates on pH, swelling and water-holding capacity of beef. J. Food Sci. 32, 860, 1972.
- JARUDILOKKUL S., RUNGPHETCHARAT K., BOON-AMNUAYVITAYA V. Protein separation by colloidal gas aphrons using nonionic surfactant. Sep. Purif. Technol. 35, 23, 2004.
- OSTERMAIER K., DOBIAŠ B. The separation of proteins from their mixtures using flotation. Colloid. Surface. 14, 199, 1985.
- RUBIO J., SOUZA M.L., SMITH R. W. Overview of flotation as a wastewater treatment technique. Minerals Eng. 15, 139, 2002.
- 23. ROVIROSA N., SÁNCHEZ E., BENÍTEZ F., TRAVIESO L., PELLÓN A. An integrated system for agricultural wastewater treatment. Water Sci. Technol. 32, 165, 1995.
- 24. ANGENENT L. T., KARIM K., AL-DAHHAN M. H., WRENN B. A., DOMÍGUEZ-ESPINOSA R. Production of bioenergy and biochemicals from industrial and agricultural wastewater. Trends Biotechnol. 22, 477, 2004.
- 25. BORJA R., GONZÁLEZ E., RAPOSO F., MILLÁN F., MARTÍN A. Performance evaluation of a mesophilic anaerobic fluidized-bed reactor treating wastewater derived from the production of proteins from extracted sunflower flour. Biores. Technol. 76, 45, 2001.
- 26. TAGAWA T., TAKAHASHI H., SEKIGUCHI Y., OHASHI A., HARADA H. Pilot-plant study on anaerobic treatment of a lipid- and protein-rich food industrial wastewater by a thermophilic multi-staged UASB reactor. Water Sci. Technol. 45, 225, 2002.
- ŻAK S., ZABŁOCKI L. The use of flotation to pretreat wastewater from animal fat rendering. Pol. J. Chem. Technol., 7, 94, 2005.
- 28. Regulation of the Environment Minister of 8th July 2004 on terms necessary to fulfill when introducing wastewaters into natural water or ground, as well as on substances particularly toxic for natural water environment (the Polish Journal of Laws, 2004, No. 168, Item 1763) (in Polish).

The Use of Flotation... 515

 HERMANOWICZ W., DOJLIDO J., DOŻAŃSKA W., KOZIOROWSKI B., ZERBE J. Physico-chemical analysis of water and sewage, Scientific Publishers Arkady: Warsaw 1999 (in Polish).

- 30. TALINLI I., ANDERSON G.K. Interference of hydrogen peroxide on the standard COD test. Water Res. **26**, 107, **1992**.
- a) American Public Health Association, American Water Works Association and Water Pollution Control Federation – Standard Methods for the Examination of Water and Wastewater, 14-th Ed.: Washington 1975; b) Association of Official Analytical Chemists, Bacteriological Analytical
- Manual, 6-th Ed.: Washington **1989**; c) International Organization for Standarization, Microbiology-General guidance on methods for the detection of *Salmonella* and *Shigella*. Ref. method ISO 3565-1975(E), Ref. method ISO 6579-1981(E), Ref. method ISO 6785-1985.
- 32. Guidelines for sanitary assessment of wastewaters designated for farming, Scientific Publishers IMW: Lublin 1993.
- 33. http://www.h2o2.com/applications/industrialwastewater
- 34. STEINER N., GEC R. Plant experience using hydrogen peroxide for enhanced fat flotation and BOD removal. Environ. Prog. 11, 261, 1992.