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PRELIMINARY ASSESSMENT OF THE SUSCEPTIBILITY OF SELECTED ANIMAL WASTE TO STABILIZATION IN THE FENTON PROCESS

The stabilization of post-slaughter soft animal waste with Fenton's reagent has been studied. Crude waste was characterized by a high content of fat (581.8 g/kg d.m.) and proteins (264.5 g/kg d.m.), and the share of organic mass constituting 93.6% of d.m. The stabilization was investigated in two reaction variants using various doses of oxidant (100–1000 cm³/kg/d.m.) and Fe²⁺:H₂O₂ molar ratios (1:10, 2:10 and 4:10), for a period of 1 day. During the stabilization, an increase in the solubility of FeSO₄·7H₂O in waste was observed, probably due to the binding of Fe²⁺ ions in ferroorganic ligands. The dynamics of the process and the efficiency of the decomposition of organic compounds increased with increased doses of reagents. The biggest loss of organic mass was recorded for the stabilization variant without initial acidification of the reaction environment. The studies confirm the possibility of disregarding the preacidification step of stabilized waste without adversely affecting the oxidation efficiency of organic compounds. A high degree of reduction in protein and fat concentrations with a low organic mass loss are evidence of incomplete oxidation of these compounds.

1. INTRODUCTION

The agri-food industry is a sector of the economy that generates huge amounts of waste characterized by an increased content of organic fraction. This group includes wastes from the preparation and processing of animal food products. According to the literature [1], the meat processing industry consumes about 10⁹ m³ of water annually, of which a significant part is transformed into a wastewater stream with a load of organic compounds expressed in the COD parameter (chemical oxygen demand) of 4000 mg/dm³. In addition to the wastewater stream, meat processing also produces solid waste classified in the 02 02 group (in accordance with the current waste list). These wastes are generated both at the stage of slaughtering animals and during the processing of obtained meat

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raw materials. It is estimated that waste generated in the meat industry accounts for almost 30% of the input weight of animals. According to Sadecka [2], around 661 000 tonnes of waste from meat processing are generated annually in Poland. According to the National Waste Management Plan 2022, the total amount of waste from the preparation and processing of food products of animal origin generated in 2011–2013 ranged from 540 to 800 thousand tonnes. Detailed data on the amount of waste is provided in Table 1.

Table 1

Amount of waste from the 02 02 group generated in the years 2011–2013 according to the National Waste Management Plan 2022

Code	Type	Quantity [10 ³ t]		
		2011	2012	2013
02 02 02	waste animal tissue	18.5	23.1	11.6
02 02 03	raw materials and products unfit for consumption and processing	662.9	602.9	388.2
02 02 04	sludges from on-site effluent treatment	32.3	44.5	49.0
Total for the 02 02 group	waste from the preparation and processing of animal food products	803.7	768.4	544.7

Management of waste from the meat industry is regulated by the Regulation of the European Parliament and the Council [3], where the above-mentioned waste is defined as animal by-products (ABP). Within the meaning of the above-mentioned Regulation, ABP means products resulting from the slaughter of animals and the manufacturing of products from animal raw materials as well as the removal of fallen animals and outbreaks of infectious diseases. Due to threats to human and animal health and the environment, the ABP were divided into three categories.

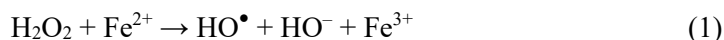
According to Regulation [3], after minimizing the risk to health and the environment, ABP can and should constitute industrial raw materials, e.g., in the pharmaceutical, feed, and leather industries. If it is not possible to eliminate the threats, they should be disposed of safely. Depending on the product category, ABP disposal methods may include incineration and co-incineration, pressure sterilization, transformation into biogas, silage, composting, and storage.

ABP such as waste animal tissue, bones and horns are the primary raw material to produce meat and meat-bone meal. Originally, meals were used as components to produce feed for farm animals. Due to the risk of the spread of bovine spongiform encephalopathy in the last three decades, the use of meal has been strictly limited [4, 5] and the Regulation [3] prohibits the feeding of terrestrial animals with processed animal protein from animals of the same species. Currently, meals are mainly used as an energy resource in combustion and co-incineration processes [4, 6]. Due to high investment and operating costs, the above solution is used for large processing plants.

Biological stabilization under aerobic or anaerobic conditions is another commonly used method of animal waste processing. The main restrictions on the use of biological methods are the duration of stabilization and the need to ensure sufficient quality of the input material. For composting, the most important parameters determining the efficiency of the process are the appropriate C:N:P ratio and the humidity of the input. The process requires the supply of oxygen as a substrate necessary for the biological decomposition of the organic fraction and cooling of the compost mass. A significant reduction in composting may be the provision of the required prism surface for several weeks maturing period of the compost mass [6]. In the case of methane fermentation of ABP, the main limitation is the high concentration of fats, which at the stage of hydrolysis are broken down into fatty acids. The concentration of acids causes a decrease in pH, which negatively affects the further stages of the fermentation process, especially the methanogenic phase [7]. For this reason, in practice, waste from slaughtering and processing of animals constitutes a few to a maximum of a dozen or so per cent of the feedstock material of the fermentation chamber [8]. Another possible solution is the initial disintegration of slaughter waste by physical, thermal, or chemical methods to partially hydrolyze fats before the actual anaerobic stabilization process [9].

Due to the above factors limiting the possibility of biological or thermal stabilization of waste with increased content of organic fraction, currently, new methods of stabilization are intensively sought. An alternative solution may be methods of chemical stabilization, allowing immediate elimination of hazards related to the uncontrolled decomposition of the organic fraction of waste. Regulation [3] considering the constant progress of science and technology allows the introduction of new technologies for the disposal of this type of waste.

One of the methods of chemical waste stabilization is the Fenton reaction (FR) belonging to the group of advanced oxidation processes (AOPs). Classical FR relies on the catalyzed decomposition of hydrogen peroxide (H_2O_2) into hydroxyl radicals (HO^\bullet) by reaction (1) [10]. The catalyst for breaking the double bond in the H_2O_2 peroxide group are transition metal ions, most often iron ions Fe^{2+} .



The oxidizing agent in FR is not only HO^\bullet radicals formed according to reaction (1) but also organic radicals (R^\bullet), organic peroxide radicals (ROO^\bullet) and hydroperoxide radicals (HO_2^\bullet), arising from the chain oxidation reactions of organic matter (RH) (2), (3) and the reaction between the formed Fe^{3+} ions and unreacted H_2O_2 (4). As a result, the combined oxidation mechanisms allow the decomposition of hardly biodegradable organic compounds into simple organic and inorganic compounds [11].





HO^\bullet radicals are characterized by a non-selective effect and the highest oxidizing potential (Eh) among all known oxidants. In an acidic environment, the Eh of the HO^\bullet radicals is 2.80 V and decreases with increasing pH, reaching 1.50 V in strongly alkaline conditions [12]. The value of Eh of radicals determines the reaction of FR, which is usually carried out at a pH in the range of 3–5 [11, 13]. The acidic medium is also justified due to keeping the Fe^{3+} ions formed in the reaction (1) in dissolved form. Literature data report that at $pH > 5$ Fe^{3+} ions are transformed into colloidal forms, which worsens the thermodynamic conditions of H_2O_2 dissociation to radicals in favour of oxygen, according to reaction (5) [14]. In turn, $pH < 2$ also adversely affects the efficiency of the processes of stabilizing the organic fraction. Under such conditions, H^+ ions become the main acceptor of HO^\bullet radicals according to reaction (6).



Concerning the mechanisms of AOPs, dissociation of H_2O_2 directly to oxygen means a loss of oxidizing potential. However, complete dissociation to radicals is difficult to achieve. In practice, H_2O_2 decomposition products are a mixture of oxygen and HO^\bullet radicals, and the percentage of individual products depends primarily on the pH value and the temperature of the reaction environment. Along with the increase in the value of both parameters, the share of radicals in dissociation products decreases, which translates into a decrease in the final efficiency of the oxidation process [11].

Until now, FR was most often used in remediation processes of soils contaminated with hardly biodegradable organic compounds. Removed compounds include polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pesticides, and herbicides [15–17]. Classical and modified FR has also found application in the treatment of industrial wastewater and the stabilization of municipal and similar sewage sludge with a high organic compound load [1, 6, 13, 18–20]. Barbusiński et al. [18] demonstrated the possibility of using FR as a method of fat destruction enabling the purification of industrial wastewater, achieving a COD reduction of 68%. Ebrahiem et al. [13] obtained a very high degree (95%) of the reduction in COD in the effluent from the cosmetics industry through FR-assisted UV radiation. Prazeres et al. [19] used FR, preceded by coagulation and sedimentation, to purify the whey, obtaining almost complete removal of organic compounds. Combined coagulation and FR processes have also been successfully used in the treatment of leachate from municipal waste landfills [20]. Numer-

ous authors underline the potential of FR as a preliminary method of wastewater treatment and stabilization of sewage sludge, increasing their susceptibility to biological degradation and facilitating drainage [18–21].

The purpose of this study was to determine the effectiveness of FR as a method of stabilizing post-slaughter waste with a high load of organic compounds, including proteins and fats. Until now, the Fenton process has not been used to stabilize this type of waste. As a rapid process to stabilize the organic fraction, FR can provide a promising alternative to widely used biological and thermal stabilization methods which, due to costs, duration and the need to ensure adequate technological conditions, are difficult to implement.

2. EXPERIMENTAL

Chemical reagents and analytical methods. As the oxidant, 30% H₂O₂ solution was used. The FR catalyst were Fe²⁺ iron ions dosed in the form of FeSO₄·7H₂O. The pH adjustment was carried out using 96% H₂SO₄. All reagents used in the oxidation process were substances with a purity level of p.a. In raw and stabilized waste, the concentration of proteins and fats, as well as hydration and the share of natural organic mass (NOM), were tested. The above indicators were determined using standard analytical procedures.

The protein content was calculated based on the amount of organic nitrogen determined using the Kjeldahl titration method. The samples were mineralized under the recommendations of the AOAC 981.10 procedure [22] using 96% H₂SO₄, 30% H₂O₂, K₂SO₄, and Se as mineralizing agents. The samples were then distilled to 4% H₃BO₃ and titrated with 0.2 M HCl. The content of organic nitrogen was converted into the concentration of proteins (g/kg d.m.) using the conversion factor recommended for meat products equal to 6.25 [22].

The fat content was determined by extraction with petroleum ether using the Soxhlet method. Extraction samples were acidified with HCl 1:2 to strongly acidic pH and evaporated on a water bath. Then the dried weight quantity was transferred quantitatively to the extraction thimble. The fat concentration was determined based on the weight difference between the extraction flask before extraction and after the process.

Hydration was determined as the difference in mass of raw waste and the same waste dried at 105 °C following the PN-EN 12880:2004 procedure. The share of NOM in raw and stabilized waste was determined based on roasting loss at 550 °C under PN-EN 15935:2013.

To determine FR dynamics and the degree of decomposition of organic compounds, temperature measurements were made directly after adding the oxidant, and after 1 day of stabilization. Measurements were made with the MT F3 meter with electrodes enabling measurement in semi-solid and solid waste.

Process flow. The raw slaughter waste was homogenized with a specialized Grindomix GM 200 knife device with a maximum rotational speed of 10 000 rpm. The tests were carried out on a laboratory scale on waste samples weighing 500 g. The initial waste temperature was equal to the normal temperature. The oxidation process was carried out in glass reactors protected by an opaque film to eliminate the possibility of photocatalytic decomposition of organic compounds and HO[•] radicals.

Stabilization was carried out in two different variants presented in Table 2. Variant 1 (series A, B and C) included acidifying the waste to pH 3 in the early stages of the process. In Variant 2 (series D, E and F), preacidification was omitted. For both variants, the oxidation process was carried out using 5 volumetric doses of oxidant (samples 1–5) equal to 100, 250, 500, 750, and 1000 cm³/kg d.m. The Fe²⁺:H₂O₂ quotient was 1:10 (series A and D), 2:10 (series B and E) and 4:10 (series C and F).

Table 2

Parameters of stabilization variants

Sample	H ₂ O ₂ dose [cm ³ /kg d.m.]	Variant 1 A, B, and C series			Variant 2 D, E, and F series		
		Preacidification	pH	Fe ²⁺ :H ₂ O ₂ molar ratio	Preacidification	pH	Fe ²⁺ :H ₂ O ₂ molar ratio
		1	100	yes	3.0	A – 1:10 B – 2:10 C – 4:10	no
2	250						
3	500						
4	750						
5	1000						

According to the procedure presented elsewhere [23], reagents in A, B and C series were dosed in the following order: H₂SO₄ – FeSO₄ – H₂O₂. During the addition of reagents, the reaction mixture was intensely mixed. The oxidant was dosed 0.5 h after the addition of iron salts to allow their hydrolysis. Hydrolysis of FeSO₄ as a strong acid salt resulted in acidification of the reaction environment. Due to the high hydration of waste, which is the main factor determining the rate of H₂O₂ dissociation and the dynamics of organic compounds oxidation, the adopted stabilization time was 1 day.

3. RESULTS AND DISCUSSION

The first stage of the tests involved determining the composition of stabilized waste. In sample 0 (homogenized raw waste), the concentration of proteins and fats, hydration, NOM, and pH were determined. The results of the analyses showed that the material under investigation was characterized by a very high concentration of fats (581.8 g/kg d.m.) and proteins (264.5 g/kg d.m.), which together constituted over 90% of NOM in

the waste. The hydration of the waste was 62.1% and the NOM content was 93.6% of dry matter (% d.m.). The waste was slightly acid (pH 6.0).

3.1. STABILIZATION OF STRONGLY ACIDIFIED WASTE (SERIES A, B, C)

Due to the hydrolysis of FeSO_4 , after the addition of iron salt, the determined pH of the waste further lowered to a value in the range from 2.0 to 2.8. According to the safety data sheet, the solubility of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in water at 20 °C is 400 g/dm³. Taking into account the hydration of waste undergoing stabilization (62.1%), it was estimated that the maximum dose of iron salts soluble in stabilized samples is approximately 180 g/kg. This value was determined on the assumption that all the liquid contained in the waste will be the solvent for the iron salts. Only for series A with $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ molar ratio equal 1:10 the doses of iron used were within the above solubility range. For the B and C series with $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ molar ratio equal 2:10 and 4:10, the iron doses exceeded the maximum stoichiometric solubility several times. For samples with the highest iron doses (5B and 3–5C), hydrolysis of FeSO_4 caused a change in the structure of the waste from amorphous to granular, with simultaneous separation of liquid.

During the addition of the oxidant, a sharp increase in the temperature of the stabilized waste was observed. The most dynamic temperature jumps occurred when due to hydrolysis of iron sulfate liquid was separated from raw waste. After 1 day of stabilization, a change in the structure of the waste from amorphous/granular to highly flocculent with a clear separation of the solid and liquid phases has been observed. The final concentration of proteins, fats, and the share of NOM in waste after 1-day stabilization for A, B and C series is presented in Figs. 1a–c.

The change in the structure of stabilized waste and its strong destabilization may indicate a rapid decomposition of organic compounds and the release of free and chemically bound water. As shown in Figs. 1a–c, the efficiency of removing organic compounds by oxidation with Fenton's reagent increased with increasing doses of reagents used. The best stabilization efficiency was obtained in the C series for the highest volume of oxidant (1000 cm³/kg d.m.) for which the degree of protein and fat removal was 54.7% and 50.5%, respectively, and the NOM content decreased by 23.0% d.m.

The results obtained in the A–C series show that the main factor limiting the degree of oxidation of organic compounds by FR is the concentration of Fe^{2+} ions. For each of the test series, the volumes of oxidant used were similar, while the concentration of the reaction catalyst changed. Comparing the obtained results, for the H_2O_2 dose of 500 cm³ in series A, B, and C, the reduction of proteins and fats was achieved by 14.3 and 17.2, 23.3 and 22.2, as well as 38.7% and 37.8%, respectively. It can be concluded that for the A and B series, the iron concentration was insufficient to catalyze the dissociation of the entire dose of oxidant to HO^\bullet radicals (reaction (1)). For the B and C series, despite the significant exceeding of stoichiometric levels of iron salts solubility, an in-

crease in the efficiency of oxidation of organic compounds was observed. These relationships indicate the increased solubility of Fe^{2+} ions in stabilized waste and their participation in catalyzing H_2O_2 dissociation to HO^\bullet radicals. The increase in solubility of iron salts was probably due to the formation of iron-organic ligands binding Fe^{2+} ions in ring structures [24]. Iron-binding compounds are, among others, organic acids [25]. It may be presumed that in the stabilized waste, Fe^{2+} chelators could be fatty acids, the products of hydrolysis of fats assisted by a high concentration of H^+ ions.

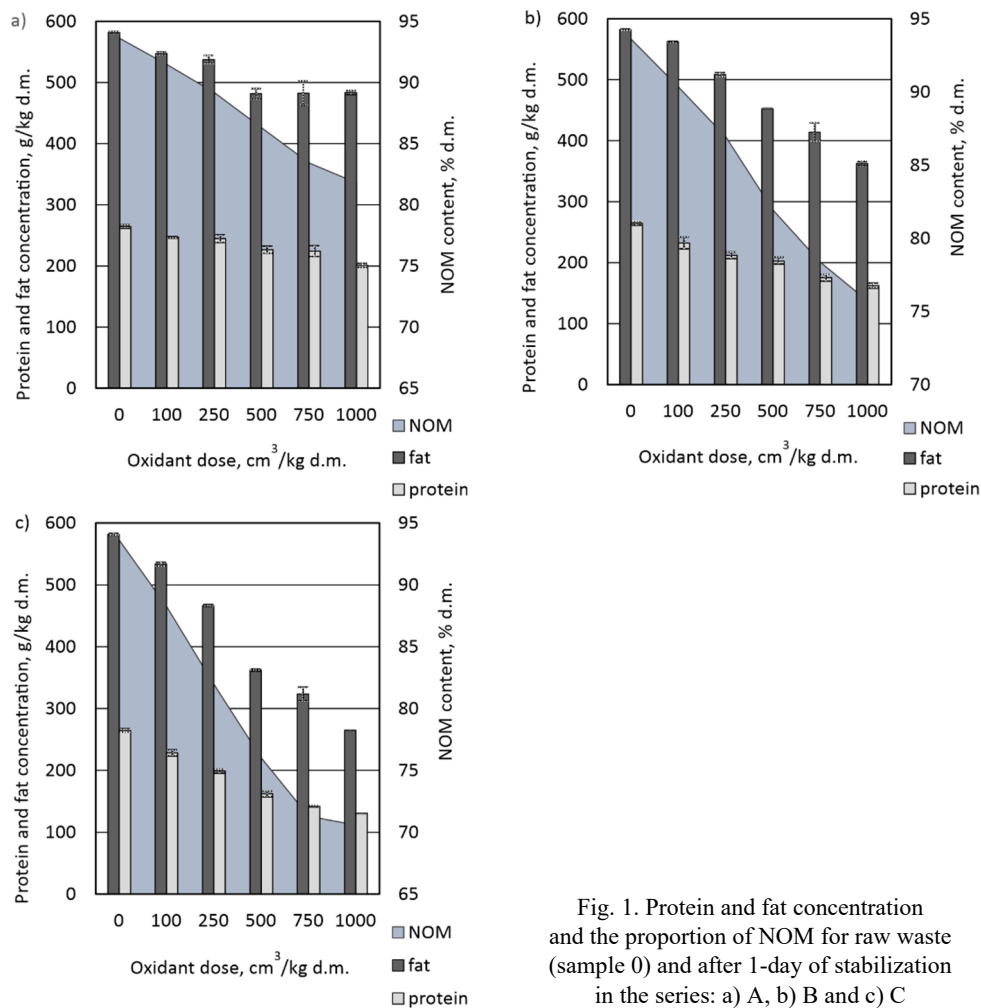


Fig. 1. Protein and fat concentration and the proportion of NOM for raw waste (sample 0) and after 1-day of stabilization in the series: a) A, b) B and c) C

Insufficient quantity of FR catalyst in series A and B probably caused partial dissociation of H_2O_2 directly into H_2O and O_2 following reaction (5) which resulted in a decrease in the final oxidation efficiency of organic compounds. This decomposition could

also be promoted by rapidly increasing temperature and decreasing pH of stabilized waste. The increase in temperature was the result of the accumulation of heat produced by the exothermic reaction of H_2O_2 dissociation and by the oxidation of NOM. The reduction in the pH of stabilized waste was caused by the discharge of intermediate acid degradation products of organic compounds. Accumulation of the above-mentioned products results in temporary or even long-lasting acidification of waste.

The total temperature increase over time reflects the dynamics of the dissociation and oxidation reactions involved. The final pH of waste can be the basis for determining the degree of degradation of organic compounds. The maximum waste temperature recorded immediately after the addition of the oxidant and pH of the waste after 1-day stabilization are summarized in Table 3.

Table 3

Temperature and pH of the waste for the A–C test series

Sample	H_2O_2 dose [cm ³ /kg d.m.]	Temperature [°C]				pH			
		Raw	A	B	C	Raw	A	B	C
1	100	20.0	35.0	38.2	48.0	3.0 ^a	1.9	2.0	1.9
2	250		70.9	86.1	70.0		1.8	1.9	2.2
3	500		93.0	90.7	92.7		2.3	2.2	2.2
4	750		95.0	90.4	94.8		2.2	2.7	2.1
5	1000		96.0	94.4	95.0		2.0	3.0	2.7

^aBefore $FeSO_4 \cdot 7H_2O$ addition.

Table 3 summarizes the maximum waste temperatures, recorded immediately after the addition of the oxidant. The provisional temperature increase was very rapid. The maximum temperatures were reached in several seconds after the addition of the oxidant. The dynamics of oxidation processes increased with the increase in the doses of reagents used. For the oxidant doses in the range from 500 to 1000 cm³/kg d.m., temperatures reached values higher than 90 °C. The most dynamic process took place for tests with the highest iron doses, when due to hydrolysis of iron salts, liquids were separated from raw waste. Addition of H_2O_2 caused their immediate dissociation leading to the boiling of the liquid phase of waste.

The decomposition of the NOM resulted in acidification of the reaction medium. As shown in Table 3, in samples 1A, 2A, 2B and 1C pH was lower than 2. Such a strongly acidic medium was considered to hurt Fenton's reaction [11, 13, 18]. This phenomenon was probably caused by the incomplete oxidation of organic compounds and the accumulation of acidic intermediate products of decomposition. Generally, the oxidation process resulted in partial or total decomposition of organic compounds. A measure of this total decomposition is the reduction of NOM expressed as a roasting loss. However, as shown in Figs. 1a–c, the loss of proteins and fats as the dominant groups of organic

compounds was not commensurate with the total reduction in the share of NOM. To assess the degree of complete oxidation of dominant groups of organic compounds present in the stabilized waste, i.e., proteins and fats, their final concentrations were calculated as a percentage of the total NOM of the waste (Fig. 2).

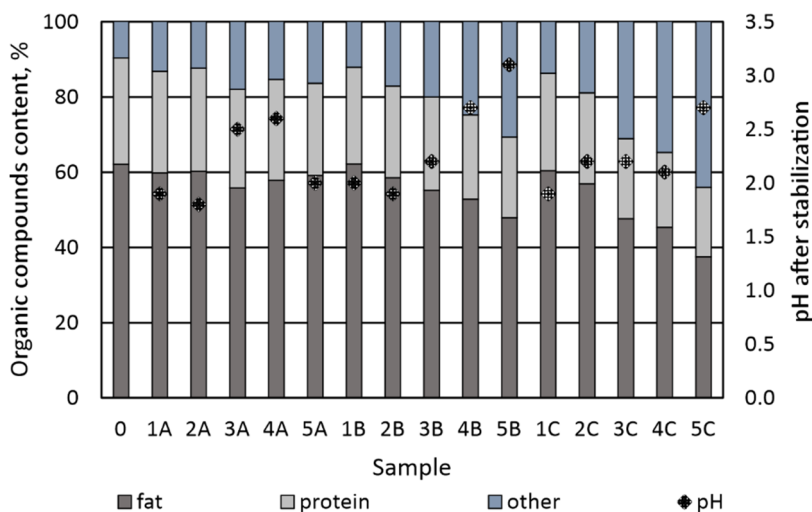


Fig. 2. Percentage of proteins, fats and other organic compounds as constituents of the total NOM for raw waste (sample 0) and waste after 1 day of stabilization in A–C test series

Proteins and fats were the dominant groups of organic compounds in raw waste and accounted for over 90% of total NOM. In samples after stabilization, their share decreased significantly in favour of other, unidentified organic compounds. These results prove that the doses of chemical reagents used to waste stabilization were insufficient for the complete oxidation of organic compounds. The decomposition of proteins and fats slowed down in intermediate stages with the formation of intermediate organic decomposition products. The share of intermediate organic decomposition products increased with increasing doses of chemical reagents, reaching the highest value of 44% for the 5C sample. Initially, the main compounds of indirect distribution were expected to be free fatty acids. However, no correlation between low pH values and a high proportion of intermediate NOM decomposition products was observed. It can be presumed that for samples with low doses of oxidant, the decomposition of some fats may have been limited to hydrolysis to long-chain fatty acids, which, when accumulated, led to a reduction in the waste pH. For tests with H_2O_2 doses in the range from 500 to 1000 cm^3/kg d.m., as a result of deeper fat decomposition to unstable short-chain fatty acids, the waste pH remained at the same level or increased.

3.2. STABILIZATION OF NON-ACIDIFIED WASTE

Barbusiński [24] reports that due to the spontaneous decrease in pH of stabilized waste during the processes of decomposition of organic compounds, it is possible to omit the stage of its initial acidification. Such a solution avoids a drastic reduction of pH in further process stages, which minimizes the risk of HO• radical consumption due to competitive reactions with H⁺ ions (6). As a result of the application of iron salts and the formation of intermediate acid products of NOM decomposition, the final pH of the waste after 1-day stabilization in A–C test series reached values in the range of 1.8–3.1. Exceeding the limit value of the reaction (pH < 2) could cause a reduction in the efficiency of oxidation of organic compounds. For this reason, a stabilization variant without the pre-acidification stage of the waste (D, E, F series) was chosen (Table 2). The stabilization procedure and parameters analyzed were the same as for the A–C test series.

In the second variant of stabilization after the addition of iron salts, the pH of stabilized wastes decreased to a value ranging from 4.0 to 2.7, reaching the values recommended for the operation of classical FR. After the addition of iron salts, the separation of liquid from raw waste with simultaneous changes in the structure of waste from amorphous to granular in series with the highest Fe²⁺ doses were observed (samples 3–5F). This phenomenon was similar to the course of the process in the series with preacidification. The pH values of the waste after stabilization and the obtained maximum instantaneous temperatures for the D–F test series are summarized in Table 4.

Table 4

Temperature and pH of the waste for the D–F test series

Sample	H ₂ O ₂ [cm ³ /kg d.m.]	Temperature [°C]				pH			
		Raw	D	E	F	Raw	D	E	F
1	100	20.0	24.8	35.8	37.0	6.0 ^a	3.4	3.2	2.6
2	250		72.2	65.0	69.0		2.9	2.3	2.2
3	500		88.6	95.0	~100		2.1	2.4	2.4
4	750		93.6	94.0	~100		2.0	2.5	2.7
5	1000		92.4	89.0	~100		2.0	2.4	2.7

^aBefore addition of Fe²⁺ salt.

As shown in Table 4, despite skipping the waste preacidification at the initial stage of the stabilization process, their final pH spontaneously decreased to a value in the range of 3.4–2.0. For the non-acidic samples, different dependencies can be observed than for the stabilization variant with preacidification, where the pH of the waste increased with the increase of the applied oxidant dose. The lowest pH of the waste after the 1-day stabilization was recorded for the test series with the lowest iron doses. For

none of the stabilization variants, pH did not exceed the limit value of 2 at which HO^\bullet radicals may be consumed by competitive reactions with H^+ ions (6).

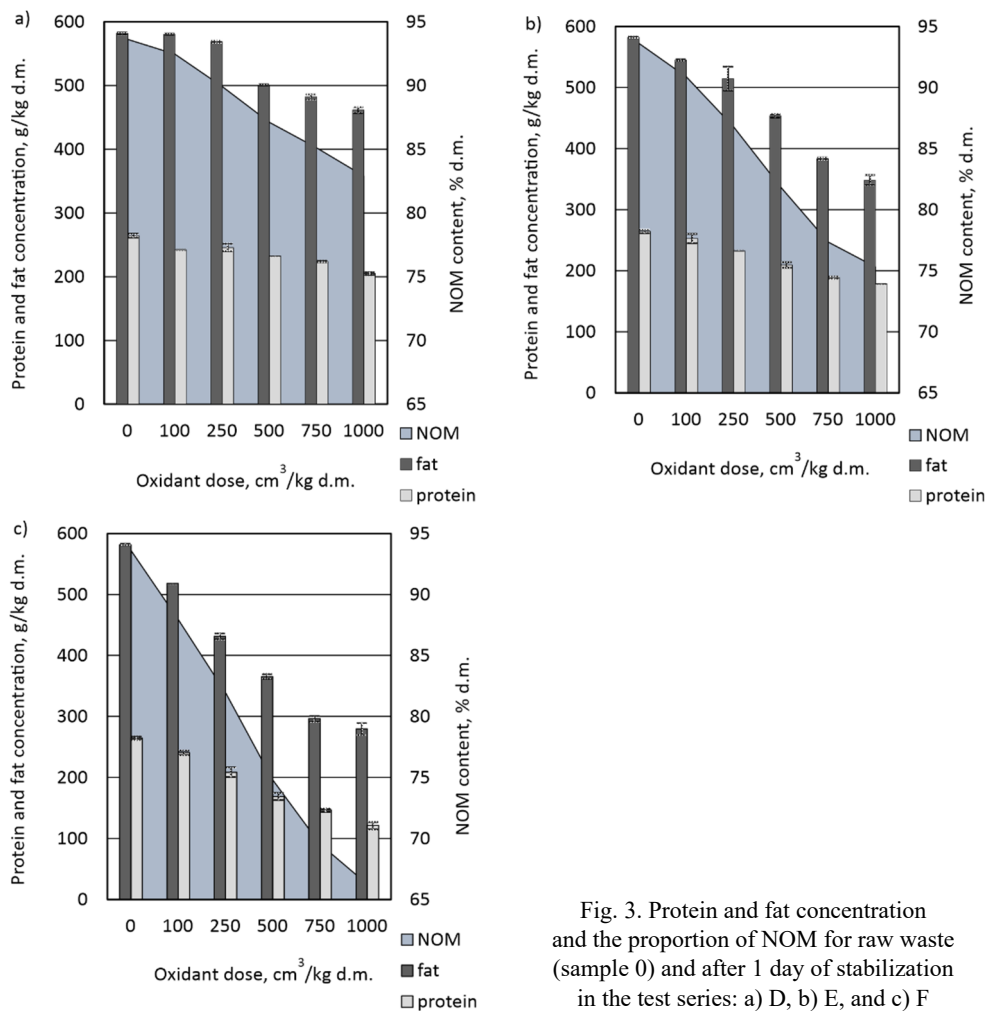


Fig. 3. Protein and fat concentration and the proportion of NOM for raw waste (sample 0) and after 1 day of stabilization in the test series: a) D, b) E, and c) F

The rate of H_2O_2 dissociation processes and oxidation of organic compounds increased with increasing doses of reagents applied. In the series without waste preacidification, the maximum temperatures achieved for the oxidant doses of 100 and 250 cm³/kg d.m. were lower than in the first stabilization variant for 5 out of 6 tests with values ranging from a few to several dozen degrees. The temperature increase was observed with a delay of several tens of seconds concerning the A–C test series probably due to the decrease in the H_2O_2 dissociation rate at higher pH. On the other hand, for the series (3–5F) with the highest Fe^{2+} ion concentration, the more rapid reaction was observed. Separation of

liquid from raw waste accelerated the dissociation of H_2O_2 . Maximum temperatures were reached before the complete mixing of the oxidant and stabilized waste, and the liquid contained in the waste was brought to a boil. The maximum temperatures recorded were higher than in the A–C test series. The lack of similar relationships in the 5E sample may indicate a decrease in the solubility of iron salts in a higher pH of waste, which in turn reduces the concentration of Fe^{2+} ions catalyzing H_2O_2 dissociation. Figures 3a–c show the efficiency of oxidation of organic compounds in the second stabilization variant.

The data presented in Figs. 3a–c confirm that the oxidation efficiency of organic compounds obtained in the D–F series was similar to the results obtained in the analogous A–C series and increased with the increase in the doses of FR reagents used. Comparing the efficiency of protein removal in the tests with and without preacidification, the greatest discrepancies were noted for test series with $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ molar ratio equal to 2:10. Protein reduction levels obtained in the series without preacidification were lower with values ranging from 2.5 to 7.8%. In the sample with the highest reagent doses, the final protein concentration was 130.4 g/kg d.m. which was a result better by 3.3% than for the first stabilization variant.

In the D series, the increase in the pH of stabilized waste resulted in the absence of a noticeable loss of fats for the oxidant volume of 100 and 250 cm^3/kg d.m. In the E series, the fat removal efficiency was higher than in the series with preacidification for 4 out of 5 doses of H_2O_2 used. For the F series, volumes of H_2O_2 ranging between 100 and 750 cm^3/kg d.m. resulted in maintaining or increasing the level of decomposition of fats from 2.7 to 6.0%. The exception was the highest volume of oxidant at which the final fat concentration was 14.5 g/kg d.m. higher than for the series with preacidification.

A measure of the total oxidation of organic compounds is the loss of NOM. In the test series D and E, differences in the final NOM share in waste relative to the corresponding series A and B were negligible and amounted to $\pm 1.5\%$. In the F series for each of the oxidation options, the final share of NOM was equal to or lower than in the C series. The lowest final NOM share of 66.2% d.m. was recorded for an oxidant volume of 1000 cm^3/kg d.m. (sample 5F). Based on the results presented, it can be stated that with increasing doses of reagents, the disparities between the oxidation efficiency of organic compounds obtained in the acidified and non-acidified wastes decreased probably caused by a gradual decrease in the pH of the stabilized waste resulting from the hydrolysis of FeSO_4 . The most optimal process conditions were obtained for the series with $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ molar ratio equal 4:10, which allowed one to increase the efficiency of organic fraction mineralization relative to the series with wastes preacidification. The waste pH of 2.7 ensured the maintenance of the high potential of HO^\bullet radicals, however, it did not cause favourable conditions for their consumption through competitive reactions with H^+ ions. To verify whether the increase in the pH of stabilized waste affected the degree of full mineralization of proteins and fats, the obtained results were converted into % shares in the total NOM and shown in Fig. 4.

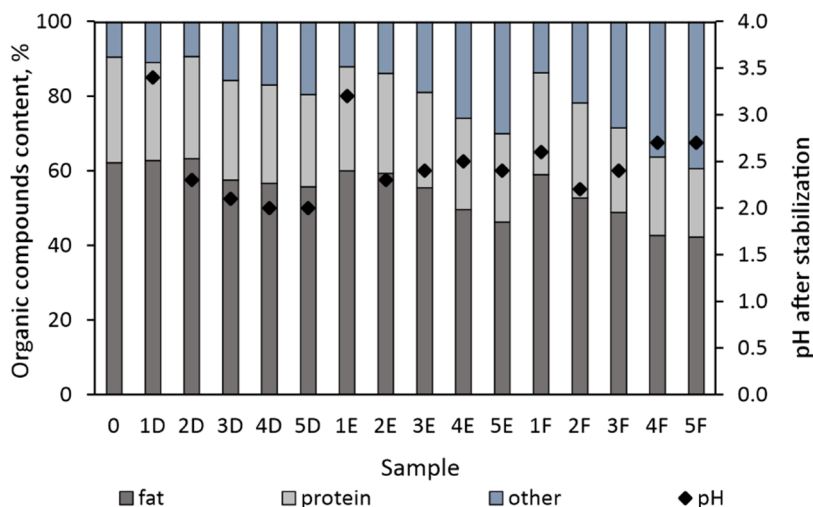


Fig. 4. Percentage of proteins, fats and other organic compounds as constituents of the total NOM for raw waste (sample 0) and waste after 1-day of stabilization in D–F test series

The test results presented in Fig. 4 showed a clear similarity to the results obtained for the A–C test series (Fig. 2). The share of intermediate decomposition products of organic compounds increased with increasing doses of chemical reagents, which were insufficient for complete mineralization of the organic fraction. The largest discrepancies were observed for the samples with the highest iron and oxidant doses, where the share of intermediate decomposition products was 4.5% lower than in the series with preacidification. For this variant, the lowest final NOM content was also noted, while the final fat concentration was higher. These data confirm that in this stabilization variant, more fat has been completely mineralized. At this stage of research, the causes of this phenomenon cannot be clearly identified. However, based on the results obtained and the literature reports, it is presumed that the key factor responsible for increasing the efficiency of organic fraction mineralization was the optimal pH of stabilized waste.

4. SUMMARY AND CONCLUSIONS

The effectiveness of the use of Fenton's reagent during the chemical stabilization of selected slaughterhouse wastes was investigated and discussed. The results confirm the potential of FR as a method of stabilizing waste with a high content of proteins and fats and allowed one to draw the following conclusions:

- The efficiency of decomposition of the organic compounds increased with the increase in the doses of chemical reagents applied. The amounts of reagents used were insufficient for complete oxidation of organic compounds, which resulted in inhibition of decomposition processes in intermediate stages. This is demonstrated by the high loss

of proteins and fats with a low degree of full mineralization of NOM. The most important factor limiting the NOM oxidation degree is the amount of FR catalyst, i.e., the concentration of Fe^{2+} ions in stabilized waste.

- The waste stabilization variants required the use of iron salt in amounts higher than those resulting from solubility. For the tests with the highest iron concentration, the separation of liquid from raw waste has been observed. Despite exceeding the stoichiometric level of solubility, an increase in the oxidation efficiency of organic compounds was noted. These relationships clearly show an increase in the solubility of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, probably due to the formation of ferro-organic ligands. Fe^{2+} ion chelators may have been fatty acids arising from the hydrolysis of fats.

- The results obtained for the non-acidified wastes were close to the efficiency of stabilization carried out in a strongly acid medium. For the highest doses of chemical reagents, there was an increase in total mineralization of NOM by 4.4% compared to classical FR. For none of the waste samples after stabilization, the reaction limit value ($\text{pH} < 2$) was also exceeded. The increase in the degree of NOM decomposition might be caused by lower losses of HO^\bullet radicals through competitive reactions with H^+ ions. The obtained results confirm the possibility of skipping the preacidification stage of the wastes without adversely affecting the achieved NOM oxidation efficiency. As a result of oxidation, the waste was strongly destabilized, which is an important advantage in the context of their susceptibility to more effective dewatering.

- In the best studied variant of stabilization the final NOM content was 66.2% d.m. This result, at the current stage of research, does not allow us to define wastes as stabilized. However, the short time of NOM stabilization with Fenton's reagent is a great advantage compared to long-term biological stabilization processes. For this reason, the chemical stabilization of post-slaughter wastes requires further research.

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