THE LABORATORY EXPERIMENTS ON REDUCTION OF ORGANIC POLLUTANTS LOAD IN WASTEWATER GENERATED IN FISH PROCESSING INDUSTRY

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ABSTRACT
The way of reduction of pollutants discharge to municipal sewer system with industrial wastewater has been proposed. Coagulation process has been applied for protein and fat recovery from fish processing wastewater. Post-coagulation sludge was added to fish hydrolyzates production. Technology of the process has been modified and the sulphuric acid was replaced by phosphoric acid. In this way the concentration of absorbable iron in the fish silage has been reduced to the desired level.

KEYWORDS
wastewater treatment, fish processing wastewater, post-coagulation sludge, fish silage.

INTRODUCTION

In fish processing plants a huge amount of wastewater is generated. The main components of this wastewater are proteins and fats, substances of nutritious value, and the load of these pollutants may be extremely high depending on the production type.
In table 1 the content of particular pollutants in wastewater from production of various fish products are presented.

Table 1. Characteristics of wastewater from fish processing [1]

Sector	Pollutants [g/dm^3]			
	BOD_5	COD	Fat	Protein
Canned fish production	4-20	5-22	5-11	4-6
Fish meal production	3-50	4-60	1-20	1-10
Fish defrozing	0.3-1	0.5-1,2	0.5-1	0.2

As it can be seen from table 1 the big loses of protein and fat are observed in fish processing sector. The annual discharge of protein and fat with wastewater from fish processing sector in Poland is presented in table 2.

Table 2. Protein and fat annual discharge with wastewater from fish processing industry in Poland [2]

Products	Production [t]	Discharge to wastewater	
		Protein [t]	Fat [t]
Canned fish	37580	1236	1495
Pickles	26711	684	8
Salted fish	23612	899	85
Smoked fish	32233	322	129
Fish meal	7543	1946	1267
	total	**5087**	**2984**

Such huge amount of organic pollutants in wastewater makes problems with its treatment when they are combined with municipal wastewater. And more such tremendous losses of valuable substances should be avoided. One of the possibility is to recover them during wastewater treatment [3-5]. The aim of this research was to recover proteins and fats from wastewater in form useful for animal feed production.

Wastewater from fish processing can be treated in different ways: mechanically, chemically or biologically [6]. Chemical treatment it is a coagulation process in which the added chemicals (coagulants) form flocks to which dispersed pollutants easily attach [7]. These material is separated from wastewater by sedimentation. As coagulants usually aluminum or iron salts are used. Post-coagulation sediment from fish processing wastewater consist of coagulant (in form of aluminum or ferric hydroxide) and separated pollutants e.g. proteins, fats and other colloids. However, the main component in these sludge is water. Post-coagulation sludge containing nutritious substances can be used as an additive to animal feed production.

There are two possibilities: dry feed – e.g. fish meal and liquid feed – e.g. fish silage (protein hydrolyzates) [8]. In this research the utilization of sludge for fish silage production has been investigated.

Fish silage is produced in a way presented on these scheme [9]:

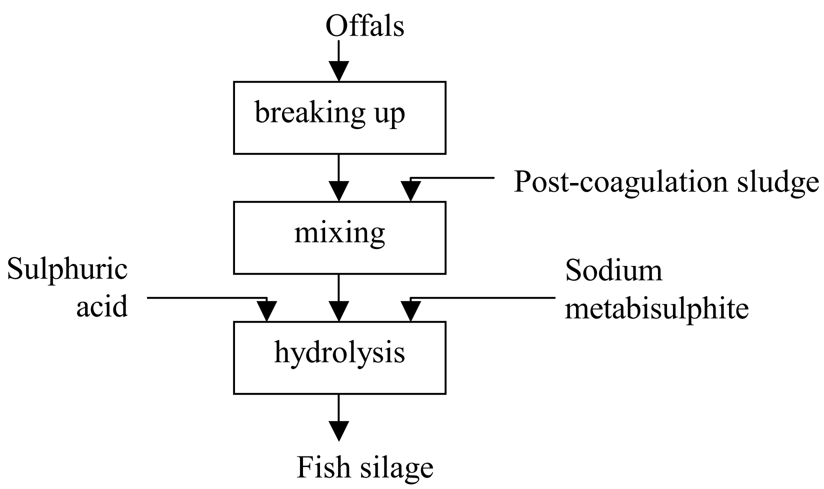

Figure 1. Scheme of fish hydrolyzates production

Fish silage is usually produced from fish offal (heads, intestines, skin, etc.) or waste fish. The enzymes present in fish viscera decompose these tissues and the liquid protein hydrolyzate is the final product [10-12]. To avoid bacteria growth a pH about 2 is required and a relevant amount of organic and inorganic acid is added, usually it is sulphuric acid. The idea was to supply a certain amount of post-coagulation sludge for silage production [13].

EXPERIMENTAL

In our experiments the coagulation of fish processing wastewater was performed with using ferric sulfate. The sludge generated in this process has been added for silage production. The sludge characteristics is presented in table 3.

The total amount of iron in wastewater during coagulation depends mainly on the amount of coagulant added. However, as it can be seen from table 3 about 90% of the iron present in raw wastewater and added as a coagulant is transferred to the post-coagulation sludge. In the sludge its concentration was about 2.6 g/dm^3 (about 0.26 %) which is about 2.6% of dry matter of the sludge (table 4).

Table 3. Iron concentration in wastewater and in post-coagulation sludge

Process	Iron in raw wastewater [mg/dm^3]	Iron added for coagulation process [mg/dm^3]	Iron in wastewater after coagulation [mg/dm^3]	Iron transferred to post-coagulation sludge [%]
1	17.0	175.0	16.1	91.6
2	19.3	175.0	20.2	89.6
3	23.1	100.0	13.7	88.9
4	23.4	50.0	5.1	93.0

Table 4. Characteristics of post-coagulation sludge

Parameters	[%]	[mg/dm^3]
Water	89.7	-
Fat	6.2	-
Protein	2.7	-
Ash	0.7	-
Total iron	0.26	2599.7
Iron absorbable	0.03	269.5

When the post-coagulation sludge is added to hydrolyzates production, then the iron hydroxide is converted into ferric sulfate, which is well soluble in water. Too high content of soluble iron compounds which are easily absorbable should be avoided, as the excessive amount of the iron in the diet is harmful [14]. It leads to some disease like hemochromatosis or siderosis. Thus, the aim of our research was to find a method of decreasing the absorbable iron content of fish silage.

The iron absorption is enhanced when soluble monomeric complexes are formed (in the presence of e.g. proteins, amino acids, ascorbic acid, EDTA, citric acid etc.) [14]. The iron absorption is inhibited in the presence of carbonates, oxalates and phosphates. Probably they participate in macromolecular polymers formation, which are not absorbable from alimentary canal.

Thus in our investigations sulphuric acid used in hydrolysates production has been replaced by phosphoric acid. Such change should be effective in diminishing the iron absorption as the iron phosphates are non soluble in water. In the first series of experiments the hydrolyzates were produced only from fish, without sludge. The characteristics of hydrolizates produced from fish is presented in tables 5 and 6.

Table 5. Characteristics of hydrolizates produced with using sulfuric acid or phosphoric acid

Process	Hydrolysis mixture	Protein [%]	Fat [%]	Water [%]	Ash [%]
1	Fish + 1 % H_2SO_4	14.1	6.6	76.1	2.7
2	Fish + 1 % H_3PO_4	14.0	6.2	77.0	3.0
3	Fish + 1 % H_2SO_4 + Fe*	14.2	6.4	76.8	3.1
4	Fish + 1 % H_3PO_4 + Fe*	14.2	6.2	75.2	3.8
5	Fish + 2 % H_3PO_4 + Fe*	13.9	6.5	74.1	4.2

* - samples enriched with iron - 200 mgFe/dm^3

Table 6. Iron content in fish hydrolyzates

Process	Hydrolysis mixture	Total iron [mgFe/kg]	Absorbable iron [mgFe/kg]
1	Fish + 1 % H_2SO_4	251.6	86.3
2	Fish + 1 % H_3PO_4	250.2	30.5
3	Fish + 1 % H_2SO_4 + Fe*	426.6	257.4
4	Fish + 1 % H_3PO_4 + Fe*	451.4	123.9
5	Fish + 2 % H_3PO_4 + Fe*	436.3	2.5

* - samples enriched with iron - 200 mgFe/dm^3

As it can be seen from table 5, the hydrolyzates properties were similar in the case of both acids. The only difference was observed for absorbable iron content (table 6). When phosphoric acid was used the concentration of absorbable iron was much lower (30.5 mgFe/kg) then it was when sulphuric acid was applied (86.3 mgFe/kg). However, the decrease of absorbable iron was lower than it should be, if consider the stoichiometry. The amount of phosphoric acid used was about 20 times higher than that, required for complete iron precipitation in form of $FePO_4$. However, further addition of phosphoric acid (2 % process 5, table 6) results in very effective decrease of absorbable iron content (2.5 mgFe/kg).
In the next series the hydrolyzates were produced from fish or fish viscera with the addition of 20 % of post-coagulation sludge. The characteristic of hydrolyzates is presented in table 7.

Table 7. Characteristics of hydrolyzates produced with using sulfuric acid or phosphoric acid

Process	Hydrolysis mixture	Protein [%]	Fat [%]	Water [%]	Ash [%]
1	Fish + 1 % H_2SO_4	14.1	6.2	76.4	2.6
2	Fish + 1 % H_3PO_4	14.3	6.3	76.9	2.9
3	Fish + sludge + 1 % H_2SO_4	12.2	6.3	77.4	3.1
4	Fish + sludge + 1 % H_3PO_4	10.9	6.3	78.0	4.2
5	Viscera + 1 % H_2SO_4	12.4	17.5	66.1	3.0
6	Viscera + 1 % H_3PO_4	12.6	17.8	67.7	3.3
7	Viscera + sludge + 1 % H_2SO_4	9.7	15.7	71.5	2.2
8	Viscera + sludge + 1 % H_3PO_4	9.5	14.9	72.4	2.9

As it can be seen, the sludge addition decreases protein content in silage by about 2÷3 %. Other parameters has changed not much. The only difference was again observed for iron content (fig. 2).

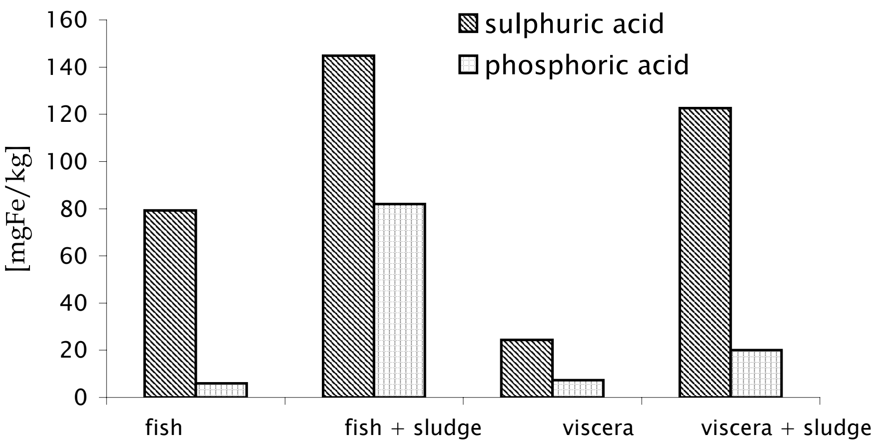

Figure 2. Concentration of absorbable iron in fish hydrolysates obtained with sulfuric or phosphoric acid

As it can be seen from fig. 2 the content of absorbable iron was higher if hydrolyzates were produced with the addition of post-coagulation sludge. Very effective reduction of the soluble iron concentration has been achieved when phosphoric acid was used instead of sulphuric acid.

CONCLUSIONS

In the described method the load of pollutants discharged to municipal sewer system with industrial wastewater could be reduced to a great extent.

The results obtained in these investigations show that it is possible to recover nutritious substances (protein and fat) from fish processing wastewater by coagulation. Post-coagulation sludge can be used as a supplementary material for fish hydrolyzates production. This liquid feed is usually used for fur animal or young pigs feeding. Too high content of absorbable iron can be reduced by phosphoric acid use in hydrolysis process instead of sulfuric acid.

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