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TREATMENT OF MEAT INDUSTRY WASTEWATER USING COAGULATION AND FENTON'S REAGENT

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The aim of the paper was to study meat industry wastewater treatment efficiency during chemical processes. The research was carried out in two steps. The first step was the coagulation process and the second step was the Fenton reaction. It was found that wastewater treatment with the use of Fenton's reagent achieved a higher degree of removal of the pollutants determined as COD, TOC and TN in comparison to the coagulation of PIX113. The most profitable dose of the Fenton's reagent was 0.6/1.8 Fe^{2+}/H_2O_2 g/dm^3. The degree of COD removal from the wastewater with the use of the Fenton's reagent was higher by 10% on average compared to PIX 113. TOC and TN removal efficiency, using the Fenton's reagent was higher by 13% and 40.5% respectively when compared to the coagulation process.

Keywords: meat industry wastewater, coagulation process, Fenton process, PIX 113, PAX XL 19

1. INTRODUCTION

Meat industry plants make a significant environmental impact by discharging effluents into the receiving water which contains a high concentration of biodegradable organic matter. Slaughterhouses also generate a large volume of effluents. The consumption of water per slaughtered animal varies, depending on the animal and the processes employed in each industry, and ranges from 1 to 8.3m^3.

The meat industry wastewater composition is strong compared to the domestic wastewater. This wastewater is high in dissolved and suspended

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organic matter, in particular, proteins and fats are high in organic nitrogen and fats and many of them contain a significant amount of pathogens [1-2-5].
Table 1 presents the qualitative characteristics of wastewater generated in the meat industry.

Table.1. Pollution concentration in raw wastewater (for a wastewater treatment plant whose daily flow is bellow 2000 m^3) [3,6,13]

Pollution indices	Concentration of pollution in raw wastewater [mg/dm^3]		Permissible standards [mg/dm^3]	
	Range	Mean value	Sewage system	Natural receiver
pH	6-10	-	6-9,5	6,5-9
COD	1600-8000	4800	1000	125
BOD_5	1200-5000	3100	700	25
Total nitrogen	50-400	225	50	30
Total phosphate	15-100	58	15	5
Total suspension	100-2000	1050	350	50
Ether extract	1000-1500	1250	100	50

The slaughterhouse and meat industry wastewater is strong and unpleasant, as it comprises urine, blood washed from carcasses, floors, utensils, and undigested food from the paunches of the slaughtered animals.

The quantity of wastewater will depend very much on the slaughterhouse dosing, operation practices and the cleaning methods employed.

The wastewater generation rates are usually expressed as a volume per unit of product or per animal slaughtered, and there is a reasonable degree of consistency between some of the values reported from reliable sources for different animal types [2-4].

The average amount of water produced in a meat plant is 150 m^3 / d, which corresponds to the size of a population equivalent (PE) of BOD_5 by 9500 [2,6].
Although the meat industry wastewater (as well as other food industries) does not contain toxic substances, it does include enormous amounts of organic substances which flow directly into water bodies which, in turn, have an adverse impact [10-12].

The composition, characteristics and presence of blood in the meat industry wastewater support the belief that wastewater can be efficiently treated by advanced oxidation processes (AOPs) such as white Fenton’s reagent [5].

The effects of pollutant degradation with the application of the Fenton reaction cause the oxidation and coagulation of organic pollutants in wastewater with a high concentration of blood (including the removal of putrescible substances).

Additional potential effects of the Fenton reaction may include an improvement in the sanitary properties of wastewater from the meat industry, through the removal of pathogenic organisms and parasites. [1,5,8].

Another advantage of the Fenton's reagent is the removal of odours and elimination of the red color.

The research compared the effectiveness of wastewater treatment by coagulation with the Fenton's reagent.

2. MATERIAL AND METHOD

2.1. Material

The wastewater came from the meat-processing plant near Częstochowa, whose activity covers the slaughtering and processing of pigs. The values of the basic and eutrophic pollution indicators were high and differed significantly during the whole production cycle. The wastewater had a red and brown colour and smelled bad. It was also characterised by a tendency to rot and foaming.

The characteristics of the raw wastewater are presented in Table 2.

Table 2 Characteristics of wastewater from a meat industry plant near Czestochowa

Pollution indices	Concentration of pollution in raw wastewater	Permissible standards-natural receiver mg/dm^3 [14]
COD, mg O_2/dm^3	2454	125
pH	7.4	6.5 – 9
Total nitrogen, mgN /dm^3	539	30
TOC, mg C/dm^3	826	30

2.2. Analytical methods

The parameters of the raw wastewater samples were determined in accordance with the Polish Standards and these were: COD (chemical oxygen demand), total nitrogen (TN), total organic carbons (TOC) and pH value [7]. The same characteristics were determined for wastewater samples collected after the coagulation process and the Fenton reactions.

The COD results determinations were obtained by means of the test method with the use of the HACH-DR 4000 spectrophotometer.The pH value was determined with the Cole Parmer pH-meter. TOC and TN were analysed using Kiper TOC 10C Analyzer PX-120 (AS40-Dione autosampler).

The coagulants used included PIX 113 [$Fe_2(SO_4)_3$, ~ 11.8% total Fe] and PAX XL 19 [Al_2O_3 , ~ 12,5% Al^{3+}] purchased in KEMIPOL S.A., Police (PL).

2.3. Methodology

The methods used in the studies were based on chemical processes. The research was carried out in two steps.

The first step – The coagulation process

In this study, a jar test was used. The general test procedure consisted in introducing 0.4 dm^3 of raw wastewater samples into calibrated jar test beakers (0.5 dm^3). The first coagulant test was based on aluminum (PAX XL 19) and the second one on iron (PIX 113). Coagulant doses ranged from 0.20 to 1.0 g/dm^3.
Parameters of coagulation:

– rapid mixing – destabilisation (at 350 rpm, 120 s)
– slow mixing - coagulation (at 30 rpm, 30 mins)
– sedimentation- (30 mins)

The stages of the wastewater coagulation testing process are shown in Fig.1.

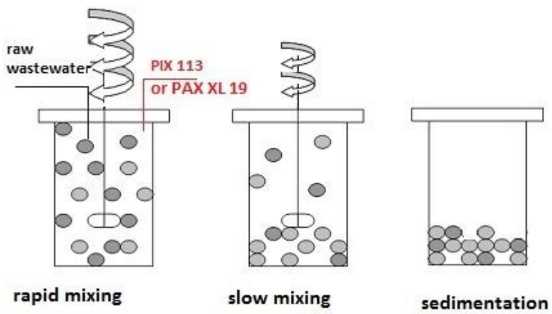


Fig.1 Steps of wastewater testing by the use of jar test

The second stage - The Fenton reaction

This stage of the study was also conducted with the use of a jar test.
The parameters of the Fenton reaction are as follows:
-acidification to pH 3.5 or 5
- rapid mixing (addition of $FeSO_4$, time - 5 mins)
- rapid mixing (addition of H_2O^2, time - 5 mins)
-slow mixing (reaction time- 3 hours)
-neutralisation to pH 7
-slow mixing (30 mins)

-sedimentation (4 hours)
-Fe^{2+}/H_2O_2 ratio-1:3
-H_2O_2 dose 0.6-3.0 g/dm^3

The stages of wastewater testing by means of the Fenton reaction are presented in Fig.2

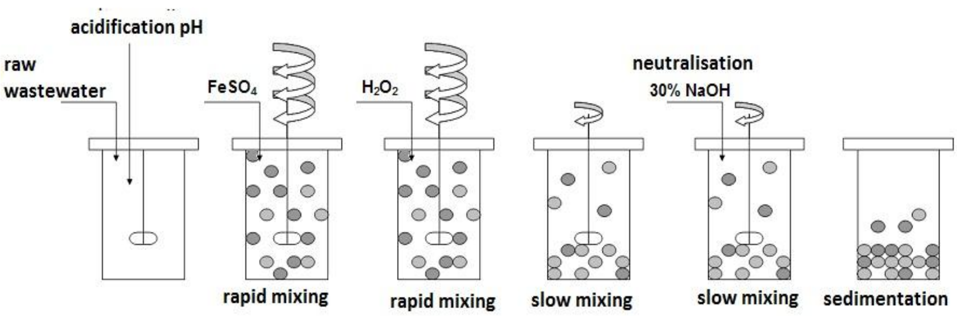


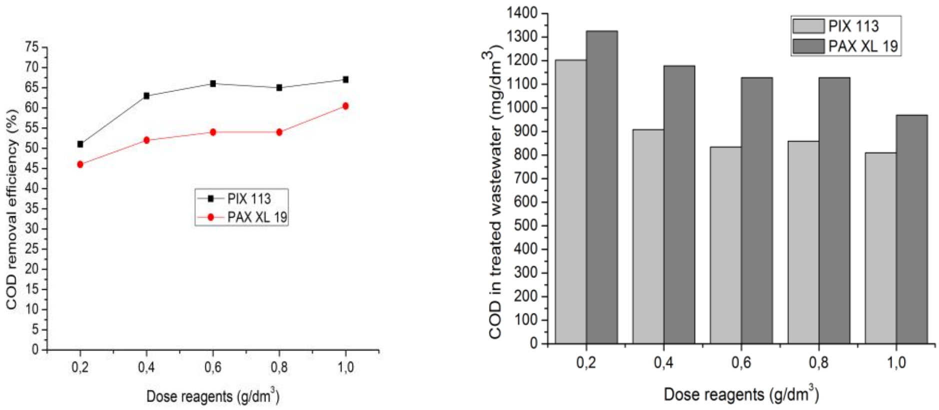
Fig.2. Steps of wastewater testing by the use of jar test

3. RESULTS AND DISCUSSION

3.1 Treatment of meat industry wastewater in coagulation process

The study attempted to determine the effectiveness of the coagulation process in the treatment of wastewater generated during slaughtering. Two types of coagulants (PAX XL 19 and PIX 113) were used. COD raw wastewater amounted to 2454 mg/dm^3. The use of PIX 113 in all doses tested led to a greater degree of COD removal from the treated wastewater when compared to PAX XL 19. Using both coagulants, COD removal efficiency increases when the doses used increase as well. The treatment of wastewater using the smallest dose of coagulants at 0.2 g/dm^3 led to the removal of COD at 51% (PIX 113) and at 46% (PAX XL 19). Effluents of COD amounted to 1202 mg/dm^3 (PIX 113) and 1325 mg/dm^3 (PAX XL 19). The highest degrees of COD removal at 67% (PIX 113) and 60.5% (PAX XL 19) were recorded in case of using 1.0 g/dm^3 of coagulants. It was observed that increasing the doses of PIX 113 above 0.4 g/dm^3 did not increase the efficiency of the COD removal . Using PAX XL 19 in doses ranging from 0.4 to 0.8 g/dm^3, the COD removal rate was identical and equal to 54%. It was ascertained that the removal of COD was 9% higher on average with the use of PIX 113 than when PAX XL 19 was used.

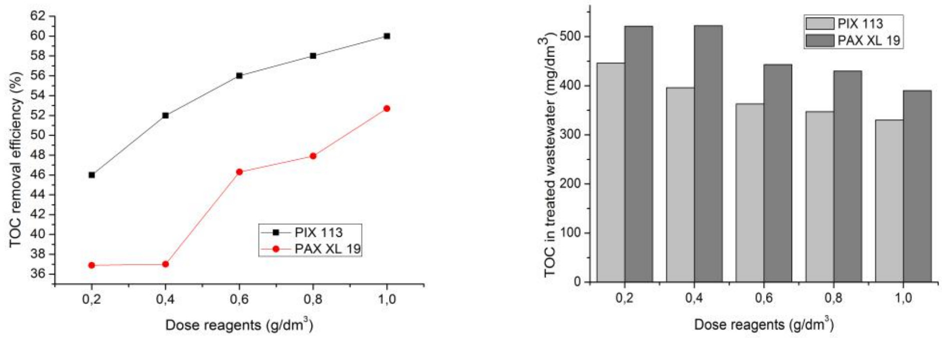
Fig. 3a presents the changes in the degree of COD removal after using both coagulants. COD effluents, depending on the doses used in both coagulants, are presented in Fig.3b.



a) b)

Fig.3. COD removal efficiency from wastewater (a) and COD treated wastewater (b) at different doses coagulants

TOC in the raw wastewater amounted to 826 mg/dm^3. The coagulation process contributed significantly to the removal of organic pollutants. Just as in the case of removal of TOC, better results were achieved owing to the use of PIX 113. A conclusion was drawn that increasing the doses of both coagulants contributed to an increase in the TOC removal efficiency from wastewater. At a dose of 1.0 g/dm^3 for both coagulants, the highest degree of TOC removal was reported. The degree of TOC removal for PIX 113 and PAX XL 19 was 60% and 52.7% respectively. TOC effluents amounted to 330 mg/dm^3 (PIX 113) and 390 mg/dm^3 (PAX XL19). Conducting the process of coagulation with PAX XL 19 at doses of 0.2 g/dm^3 and 0.4 g/dm^3 resulted in the removal of TOC in the effluents to the same level of 521 mg/dm^3. It was found that a 10% higher degree of removal of TOC, was achieved on average,with the useof PIX 113 rather than PAX XL 19. It was observed that at a dose of 0.4 g/dm^3 of PIX 113, the TOC removal efficiency amounted to 52% and was 15% higher in comparison to PAX XL 19 (at the same dose). Figure 4a summarises the changes in the extent of TOC removal, depending on the type of the coagulant (and the doses). TOC effluents after the coagulation process are presented in Fig. 4b.

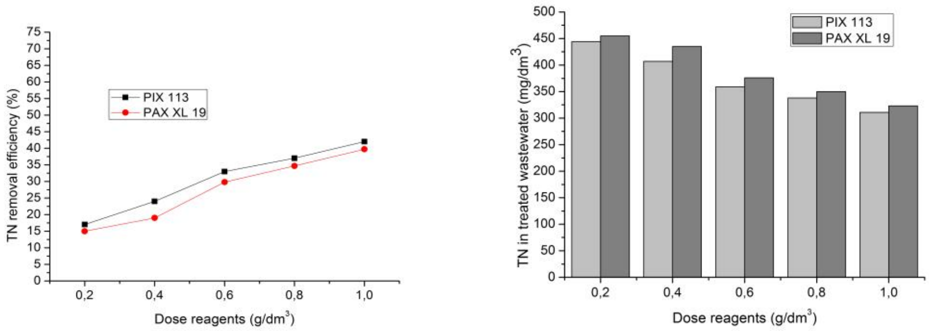


a) b)

Fig.4. TOC removal efficiency from wastewater (a) and TOC treated wastewater (b) at different doses coagulants

The use of coagulation also resulted in the removal of TN from the wastewater. The TN in the raw wastewater was 539 mg/dm^3. A similar TN removal efficiency was obtained by using both coagulants. The highest degree of TN removal with both coagulants was observed by using the highest dose (1,0 g/dm ^{3}). This is analogous to the situation with the COD removal and TOC removal.

The TN removal efficiency reached the value of 42% (PIX 113) and 39.7% (PAX XL 19). These changes are presented in Fig. 5a and 5b.



a) b)

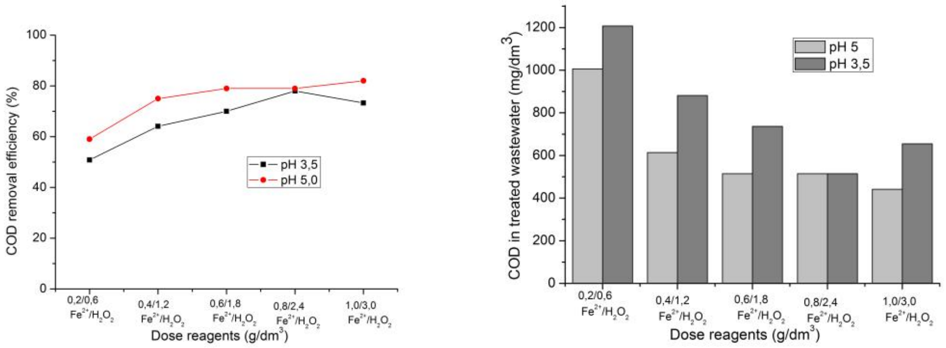
Fig.5. TN removal efficiency from wastewater (a) and TN treated wastewater (b) at different doses coagulants

It was concluded that the coagulation process of the meat industry wastewater should preferably be carried out with PIX 113.

Owing to the use of PIX 113, the degree of COD and TOC removal was 10% higher on average, and in the case of TN- 3% higher than in the situation when PAX XL 19 was used.

3.2. Treatment of the meat industry wastewater using the Fenton reaction

The study attempted to determine the impact of the initial pH of the effluent on the efficiency of conducting the Fenton reaction. Raw wastewater (pH 7.4) was adjusted to pH 3.5 and pH 5. It was found that all the tested doses in Fenton reaction had better results when the pH was adjusted to the value of 5. The degree of COD removal for the wastewater with pH value of 5 was 8% higher on average in comparison to the wastewater with a pH value of 3.5. Only in the case of the Fenton's reagent dose of 0.8/1.6 Fe^{2+}/H_2O_2 g/dm^3 in both cases, was the COD removal efficiency at the level of 78% and the COD in the treated wastewater amounted to 515 mg/dm^3. Increasing the dose to 1.0/3.0 Fe^{2+}/H_2O_2 g/dm^3 in the case of water acidified to pH 5 resulted in further decrease in COD in the treated wastewater up to 441.7 mg/dm^3. For the wastewater with the pH value of 3.5, an increase in the COD in the treated wastewater to 655 mg/dm^3 was observed. These changes are presented in Fig.6a and 6b.

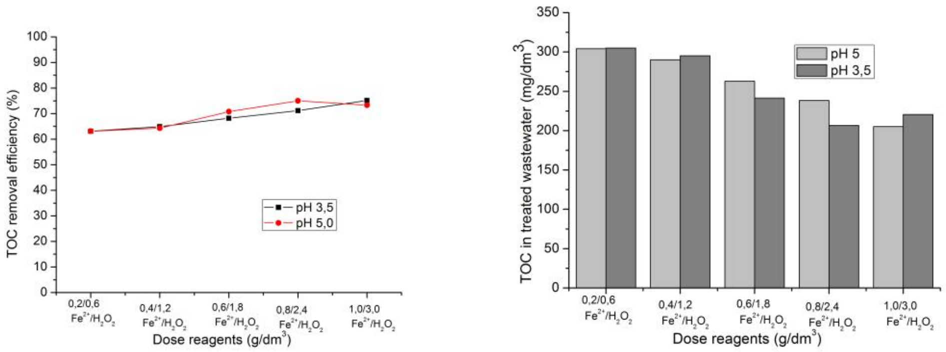


a) b)

Fig.6. COD removal efficiency from wastewater (a) and COD treated wastewater (b) at different doses and intial pH wastewater

Changing the initial pH of the wastewater undergoing treatment using Fenton's reagent did not affect significantly the changes in the degree of removal from wastewater TC and TOC.

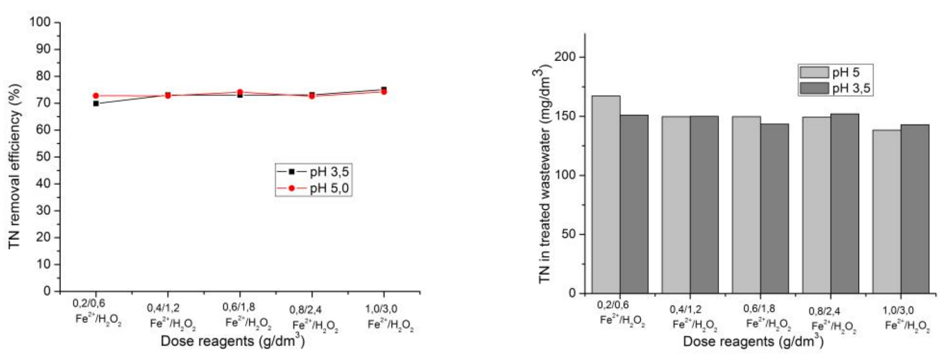
The most effective dose of Fenton reagent for wastewater previously acidified to pH 3.5 and pH 5 was 1.0/3.0 Fe^{2+}/ H_2O_2 g/dm^3. COD values in effluent were 205.1 mg/dm^3 (pH 3.5) and 220.5 mg/dm^3 (pH 5). The same low degree of TOC removal was recorded at dose 0.2 /0.6 Fe^{2+}/ H_2O_2 g/ dm^3 and value of the of effluent TOC was 304 mg/dm^3.These changes are presented in Figure 7a and 7b.



a) b)

Fig.7. TOC removal efficiency from wastewater (a) and TOC treated wastewater (b) at different doses and intial pH wastewater

In the case of TN removal efficiency by means of the Fenton process, maintaining the wastewater at varying pHs gave similar results. It was found that in the case of wastewater with a pH of 3.5 the same results with doses of the reagent at 0.2 Fe^{2+}/ H_2O_2 g/dm^3 ,0.4 Fe^{2+}/ H_2O_2 g/dm^3 and 0.6 Fe^{2+}/ H_2O_2 g/dm^3 were achieved. The degree of TN removal was 73% and the TN in the wastewater maintained the level of 149.9 mg/dm^3. These changes are presented in Figures 8a and 8b.



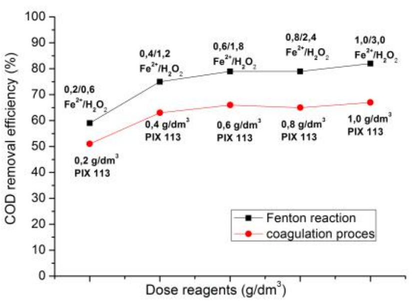
a) b)

Fig.8. TN removal efficiency from wastewater (a) and TN treated wastewater (b) at different doses and intial pH wastewater

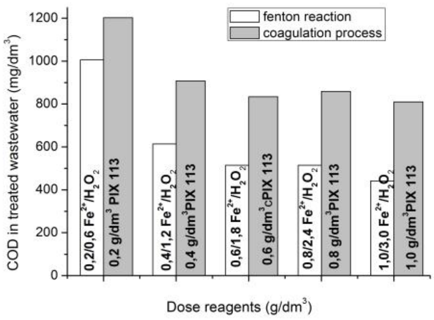
3.3. Comparison of the effectiveness of the treatment of meat industry wastewater, using the coagulation process and the Fenton reaction

It was concluded that wastewater treatment by means of the Fenton's reagent caused a higher degree of removal of pollutants determined as COD, TOC and TN in comparison to the coagulation of PIX113.

The comparison of efficiency of the COD removal at the most profitable designated doses of reagents (i.e. PIX 113 at 0.6 g/dm^3 and Fenton's reagent at 0.6/1.8 Fe^{2+}/H_2O_2 g/dm^3) led to a conclusion that it was preferable to carry out the chemical processes on wastewater using the Fenton reaction. The COD in effluents, owing to coagulation and the Fenton's reagent amounted to 515 mg/dm^3 and 834 mg/dm^3 respectively. The degree of COD removal from wastewater using the Fenton's reagent was higher by 10% on average when compared to PIX 113. These changes are presented in Fig.9a and 9b.



a)

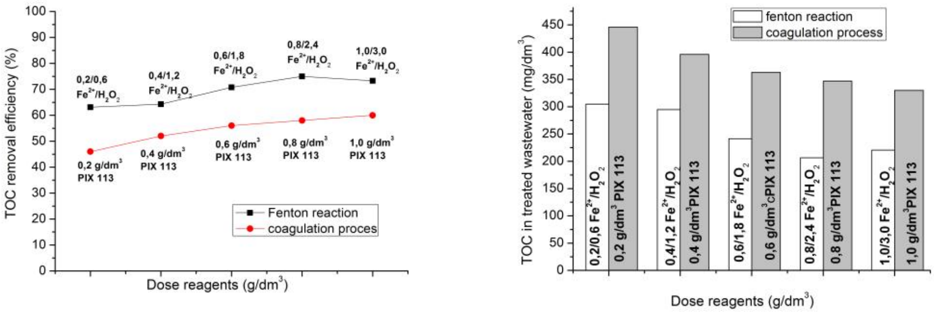


b)

Fig.9. COD removal efficiency from wastewater (a) and COD treated wastewater (b) after Fenton and coagulation process

The degree of TOC removal from wastewater using the Fenton's reagent was 13% higher on average in comparison to the coagulation process. The biggest differences in the efficiency of the two reagents were reported when applying their smallest doses (0.2 g/dm^3 PIX 133 and 0.2/0.6 Fe^{2+}/ H_2O_2 g/dm^3). The degree of TOC removal was 63.1% (Fenton process) and 46% (coagulation process).

The TOC concentration in the treated wastewater using the Fenton reaction and the coagulation process were at the level of 220.5 mg /dm^3 and 330 mg/dm^3 respectively. The results are shown in Figure 10 a and 10 b.

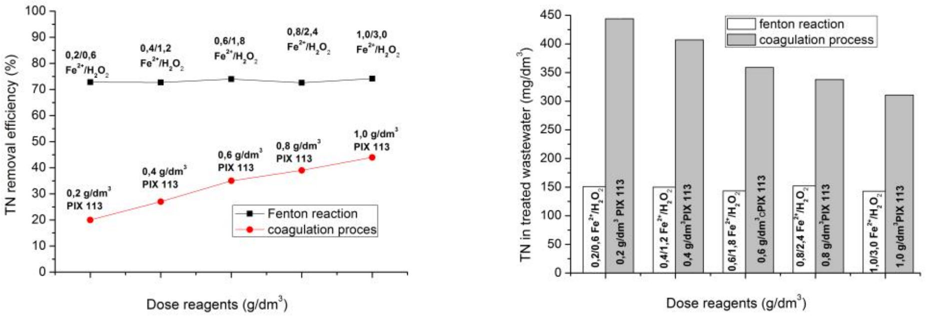


a) b)

Fig.10 TOC removal efficiency from wastewater (a) and TOC in treated wastewater (b) after Fenton reaction and coagulation process

Research shows significant differences in the TN removal from wastewater, in connection with the process of coagulation and the Fenton reaction. It turned out that in the case of all the tested doses of the Fenton's reagent, the TN removal rate was 40.5% higher on average.

The concentration of TN in the treated wastewater in the case of the Fenton reaction and the coagulation process was at the level of 143.5 mg /dm^3 (74%) and 359 mg/dm^3 (36%) respectively. The obtained results are shown in Figure 11a and 11b.



a) b)

Fig.11. TN removal efficiency from wastewater (a) and TN treated wastewater (b)after Fenton and coagulation process

The research has shown that despite the high degree of removal of the impurities in the two chemical processes of meat industry wastewater, it is not possible to discharge them into a natural receiver. For both processes, the effluent COD values were nearly 7-fold (coagulation process) and 4-fold (Fenton reaction) in excess of the permissible standards. The TOC values after coagulation and the Fenton reaction were in excess by 12- and 8-fold respectively. The value of total nitrogen in the treated wastewater was in excess by nearly 5-fold (Fenton's reagent) and 12-fold (coagulation process).

It is suggested that these processes be combined with other unit processes such as the biological process or the pressure membrane techniques.

Table.3. Comparison of effluent quality in both chemical processes (the best process conditions)

	PIX 113 dose – 0.6 g/dm^3	Fenton reaction pH = 5 dose-0.6/1.8 Fe^{2+}/H_2O_2 g/dm^3	Permissible standards- natural receiver [13]
TOC, mg/dm^3	363	241.4	125
COD, mg/dm^3	834	515	30
TN, mg/dm^3	359	143.5	30
pH	7.0	7.0	6.5 - 9

4. CONCLUSION

Research on the comparison of the effectiveness of treatment of meat industry wastewater with the use of the coagulation process and the Fenton's reagent allows the following conclusions to be drawn:

- owing to the use of PIX 113, the degree of COD and TOC removal was on average 10% higher, and in the case of TN, 3% higher than in the situation when PAX XL 19 was used;
- the most profitable dose of the Fenton's reagent was 0.6/1.8 Fe^{2+}/H_2O_2 g/dm^3;
- it was concluded that wastewater treatment with the use of the Fenton's reagent was effective to a greater extent in the removal of pollutants determined as COD, TOC and TN than the coagulation of PIX113;
- the degree of COD removal from wastewater using the Fenton's reagent was higher by 10% on average when compared to PIX 113;
- TOC and TN removal efficiency with the use of the Fenton's reagent was higher by 13% and 40.5% respectively when compared to the coagulation process;
- for both processes, the effluent COD value was nearly 7-fold (coagulation process) and 4 - fold (Fenton reaction) in excess of the permissible standards;
- The TOC value after the coagulation and Fenton reaction was in excess of 12 and 8-fold respectively. The value of total nitrogen in the treated wastewater exceeded permissible standards nearly 5-fold (Fenton's reagent) and 12-fold (coagulation);

– due to the poor quality of effluents after using the chemical processes, they cannot be discharged into natural water without an additional treatment process.

ACKNOWLEDGEMENT

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13. Rozporządzenie Ministra Środowiska z dnia 28 stycznia 2009 roku zmieniające rozporządzenie w sprawie warunków, jakie należy spełnić przy wprowadzaniu ścieków do wód lub do ziemi, oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego (Dz.U.09.27.169).

OCZYSZCZANIE ŚCIEKÓW ZAKŁADÓW MIĘSNYCH W PROCESIE KOAGULACJI I Z ZASTOSOWANIEM ODCZYNNIKA FENTONA

Streszczenie

W badaniach porównano efektywności oczyszczania ścieków powstających podczas uboju i przetwórstwa mięsa w procesie koagulacji oraz w procesie utleniania z zastosowaniem odczynnika Fentona. W procesie koagulacji wykorzystano dwa rodzaje koagulantów (PIX 113 i PAX XL 19). Stwierdzono, że stopień usunięcia ChZT przy użyciu PIX 113 był średnio o 9% wyższy w porównaniu do PAX XL 19.
Stosując wyznaczoną jako najkorzystniejszą dawkę PIX 113 wynoszącą 0,6 g/dm^3 ścieki po procesie koagulacji charakteryzowały się wartością ChZT, OWO i CA odpowiednio na poziomie 836 mg/dm^3, 363 mg/dm^3 i 359 mg/dm^3.

Porównując efektywność usunięcia zanieczyszczeń z oczyszczanych ścieków stwierdzono, że korzystniej prowadzić chemiczny proces ich oczyszczania z zastosowanie odczynnika Fentona. Jako najkorzystniejszą dawkę odczynnika Fentona wyznaczono 0,6/1,8 Fe^{2+}/H_2O_2 g/dm^3. Wartość ChZT ścieków oczyszczonych na drodze koagulacji oraz z zastosowaniem odczynnika Fentona wynosiła odpowiednio 515 mg/dm^3 i 834 mg/dm^3. Stopień usunięcia OWO ze ścieków z zastosowaniem odczynnika Fentona był średnio o 13% wyższy w porównaniu do procesu koagulacji.

Stężenie OWO ścieków oczyszczonych w przypadku reakcji Fentona było na poziomie 241,4 mg/dm^3 a po procesie koagulacji 363 mg /dm^3.

Przeprowadzone badania pokazały również że pomimo wysokiego stopnia usunięcia zanieczyszczeń ścieki oczyszczone w obu procesach chemicznych nie mogą być odprowadzone do odbiornika naturalnego. Po obu procesach wartość ChZT ścieków oczyszczonych była prawie 7-krotnie (proces koagulacji) i 4- krotnie (reakcja Fentona) przekroczona w stosunku do dopuszczalnych wartości. Wartość OWO po procesie koagulacji i Fentona została przekroczona odpowiednio 12 i 8-krotnie. Prawie 5-krotnie (odczynnik Fentona) i 12-krotnie (proces koagulacji) w ściekach oczyszczonych została przekroczona wartość azotu całkowitego.

Z uwagi na to sugeruje się łączenie tych procesów z innym procesami jednostkowymi np. procesem biologicznym lub ciśnieniowymi technikami membranowymi.