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Original Research

Combined Wastewater Treatment from Manganese Phosphate Coating: Coagulation-Ozonation-Fenton Reaction-Sorption

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Abstract

Wastewater arising from manganese phosphate coating contains plenty of biogenic compounds, heavy metals such as nickel, iron, manganese, and therefore also constitutes a serious threat to the environment. The combined method of removing pollutants from wastewater from manganese phosphate coating consisting of coagulation, ozonation and Fenton reaction allowed to reduce biogenic pollutants and remove heavy metals. Coagulation was performed with iron(III) chloride and Flopam AN 934 SHU flocculant. The Fenton reaction was performed in two combinations with and without the addition of iron(III) salt. Ozonation was carried out in a column with an ozone generator, and wastewater was treated in the following sequence: coagulation-ozonation-Fenton reaction. The results of experiments demonstrated that the use of combined methods of coagulation, ozonation and Fenton reaction have brought the expected outturns. As a result of using the Fenton reaction, the content of nitrates(V) was lowered from 13.0 mg/l to 0.012 mg/l. Physico-chemical analyses of wastewater were performed using UV-VIS molecular spectrophotometry.

Keywords: industrial wastewater, wastewater treatment, phosphating wastewater treatment, fenton reaction, sewage ozonation, coagulation processc, manganese phosphate coating

Introduction

The industry is a manufacturer of one of the most toxic wastewaters in the economy. The fast-growing metallurgical economy produces two million tons of wastewater on a daily basis [1]. The main components most often wastewater from phosphate process include heavy metals such as Cd, Cr, Cu, Ni, Pb, Zn [2] and substances such as detergents or oils [2, 3]. Most of the produced extraneous substances from galvanic production often have teratogenic, mutagenic or carcinogenic properties in relation to the human body [4-6]. It is therefore very important that toxic and harmful substances from wastewater are removed before discharging them into sewage systems or directly into the environment.

The methods of industrial wastewater treatment include precipitation techniques with the use of calcium compounds [7, 8], coagulation methods with the use of aluminum and iron compounds [9, 10], treatment with

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the use of membrane methods [11], adsorption processes using zeolites or biomass [12], processes using nanofiltration or reverse osmosis [13, 14], electrodialysis [15-17], photocatalytic methods [18], ultrafiltration [19], purification with the use of activated carbon [20-22] as well as techniques of advanced oxidation with the use of ozone, hydrogen peroxide, UV radiation and Fenton's reagents [23,24]. Beside chemical methods, we should also list physical methods in wastewater treatment, such as sedimentation [25] or processes related to the equalization of wastewater flow, which mainly consist of buffering by introducing equalizing devices or such retaining the flowing wastewater [26]. Physical treatment of wastewater involves methods consisting in the separation of floating solid particles, which could prejudice further treatment [27-32].

One important branch is the automotive industry, which involves the production of car and truck construction elements as well as the manufacture of material handling equipment such as elevator components, conveyor belts, and cranes. These devices operate under extreme conditions, often in a humid environment, and therefore require protection against corrosion. One of the methods for protecting such elements against corrosion is the manganese phosphate coating process, which is the source of wastewater containing orthophosphates, nitrates(V), manganese, nickel, chlorides, sulphates(VI), sodium cations; potassium and even titanium and zirconium compounds, as well as nitrogen compounds such as nitro compounds, including nitroguanidine [33-34]. Due to the high content of these compounds and their chemical diversity, such sewage is particularly burdensome and difficult to treat.

In this regard, the aim of this paper is to develop a method that would allow for pretreatment of wastewater generated in the manganese phosphate coating process. Real wastewater samples have been characterized and treated using such processes as coagulation, sorption with the use of activated carbon and zeolite, ozonation and the Fenton reaction. Sewage treatment efficiency was assessed on the basis of 16 parameters determined in the sewage before and after treatment. It is the first such paper to have discussed the application of ozonation and the Fenton method for wastewater treatment from manganese phosphate coating. To this day, these methods have mainly been used for treatment of sewage containing organic compounds, including dyes [35-40]. Due to the content of iron and manganese phosphate compounds in the sewage, the use of oxidation methods allowed to reduce the total amount of these substances, which can be easily separated from the sewage with a filter press.

Material and Methods

In this paper, we used wastewater from manganese phosphate coating from Mayr Polska based at Hetmańska 1 Street, 63-500 Ostrzeszów. Also used was raw sewage collected directly from the washings buffer tank, in which acidic sewage is mixed after digestion in hydrochloric acid and alkaline acid after degreasing in a solution of potassium and sodium hydroxide.

Preparation of Sewage Samples

The wastewater sample treated with coagulation and the raw wastewater sample were collected during 8.0 h in the total amount of 2.5 dm^3. The samples prepared in this way were poured and an average sample was obtained. Wastewater samples were collected in accordance with the Polish Standard for wastewater sampling [41]. Next, they were subjected to a physico-chemical analysis, carried out in accordance with the methodology of Polish and European Standards, and further treatment in the case of raw sewage.

Parameters such as pH, electrical conductivity as well as temperature were determined using multifunction meter CX-601 (ELMETRON, Poland). Turbidity was measured using a 2100Q turbidity meter (HACH, USA). The content of biogenic compounds: nitrate nitrogen (III) N-NO$_2$, nitrate(V) NO$_3$, ammonium nitrogen N-NH$_4$ and orthophosphates(V) PO$_4$ was determined by colorimetric method using the Macherey-Nagel cuvette tests by means of a PF-12 photometer (Macherey-Nagel, Germany). Metals such as Fe, Mn, Cr were established utilizing the spectrophotometric method with a UV-VIS spectrophotometer (METASH, China). Chlorides, hardness, alkalinity were calculated by means of titration methods. All devices were calibrated before use as stated by the manufacturer's instructions.

Coagulation

Wastewater from manganese phosphate coating with the composition presented in Table 2 was subjected to neutralization. Coagulation, neutralization with limewash and flocculation were carried out in an automatic system under industrial conditions in three separate reaction tanks with mechanical mixers, each with a capacity of 0.369 m^3. The process took place next to the manganese phosphate coating process in Mayr (Mayr Polska, Hetmańska 1 str., 63-500 Ostrzeszów, Poland). Iron(III) chloride solution with a concentration of 40% (m/m) stabilized with hydrochloric acid was used as a coagulant. A calcium hydroxide suspension prepared in a 1.2 m^3 tank was used as a neutralizing agent. A suspension of 4% concentration was used in a dose determined depending on the sewage feed, until a pH of 10.1 was obtained in the neutralization chamber. FLOPAM AN 934 SHU in the form of a solution with a concentration of 80 g/m^3 was used as a flocculant.

The diagram of the manganese phosphate coating wastewater neutralizer used by Mayr Polska is shown in Fig. 1.

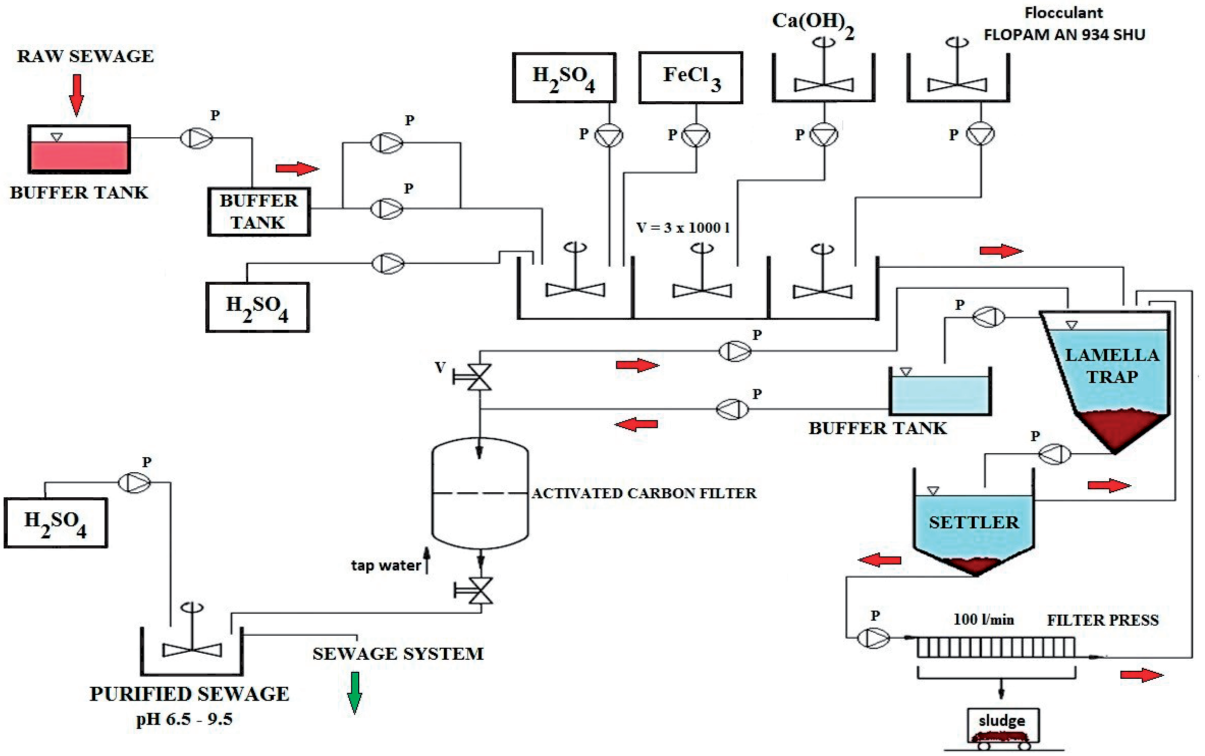

Fig. 1. Manganese phosphate coating sewage treatment plant.

Ozonation

Ozonation was performed in the barbotage ozone column at the Department of Environmental Technology, Faculty of Chemistry, University of Gdańsk (Gdańsk, Poland). The process was carried out with the use of 3 dm^3 of raw sewage and 3 dm^3 of treated sewage during 1 hour. The unreacted ozone was collected in a washer containing 150 ml of 5% (w/m) KI solution and analyzed. During ozonation in 21ºC, samples for physico-chemical analysis were taken at 10-minute intervals.

Fenton Reaction

For this purpose, a solution of $FeCl_3$ with a concentration of 30% (m/m) in the amount of 0.1 ml and 35% (m/m) solution of H_2O_2 in varying amounts from 1 to 3 ml were added to a sample of 500 ml. Also, sulfuric acid (VI) 95% (m/m) in the amount of 0.05 ml was introduced into the measuring system. The reaction was carried out for 30 minutes in 21ºC. The test samples were taken at regular intervals.

Cleaning on Mixed Bed of Activated Charcoal-Zeolite

Wastewater sorption was carried out in the activated carbon-zeolite structure in a dual-column sorption system. The process schema is shown in Fig. 2; it involved the use of activated coconut charcoal with granulation of 0.6-2.36 mm (30 – 8 mesh) (Sigma-Aldrich) and granulated zeolite (Sigma-Aldrich). In order to purify the wastewater, a sewage sample of variable volume was passed through a column packed with activated carbon and zeolite in the amount of 100.0 g each.

Results and Discussion

The study involved the use of raw wastewater from manganese phosphate coating. Wastewater samples were prepared in accordance with the methodologies of Polish and European standards as listed in Tables 2, 3.

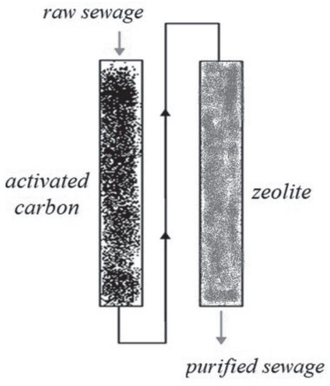

Fig. 2. Wastewater treatment system in the activated carbon-zeolite structure.

The study was conducted to compare the efficiency of electroplating wastewater treatment from manganese phosphate coating by coagulation using iron(III) chloride as a coagulant and waste sulfuric(VI) acid, calcium hydroxide as a precipitant and flocculation with the use of FLOPAM AN 934 SHU flocculant solution with a concentration of 80 g/m^3. These methods were compared with ozonation and purification with the Fenton reaction. The method of cleaning with sorption was also used.

Characteristics of Wastewater from Manganese Phosphate Coating

Characterization of wastewater from unit processes, unmixed with one another, was prepared on the basis of 120 samples collected between January and June of 2020, and shown in Table 1.

Wastewater from manganese phosphate coating is characterized by a variable composition (Table 1). It is most often determined by the daily or weekly production, which is closely related to the use of water for rinsing of the obtained coatings. Manganese phosphate coating involves the production of several types of wastewater, which are most often collected in the same tank where all washings from the technological process are kept. This type of sewage includes diluted sewage, which is represented by acid-alkaline washings (Table 1). This wastewater is produced in the amount of about 2.5-3.0 m^3 within eight hours. Such washings are formed at the stage of rinsing of galvanized elements such as:

- after the step of washing in strongly alkaline baths. Washing bath pH>11.0, sodium and potassium hydroxide concentration converted to KOH: 0.5 mol, temp. >80°C. These washings are produced during rinsing and degreasing of metal elements undergoing further treatment. Aqueous washing liquids contain the remains of NaOH, KOH, phosphates, surfactants, detergents and emulsifying agent,
- after digestion in hydrochloric acid. These washings contain chromium Cr^{6+}, nickel Ni^{2+}, large amounts of iron Fe^{2+} from the etched metal,
- after galvanization in a phosphating bath (bath composition: H_3PO_4, Mn^{2+} compounds, Ni^{2+} compounds, nitrates(V), sometimes chlorates and nitro compounds) [33-34].

Another type of sewage is concentrated wastewater from surface activation processes just prior to phosphating; surface passivation as well as wastewater from the hydrochloric acid vapor scrubber.

This type of sewage includes wastewater from the periodic replacement of the process baths with new ones, e.g. wastewater from activation of the metal surface. Depending on the type of activating agent, it contains large amounts of inorganic acids or

Table 1. Typical composition of washings from unit manganese phosphate coating processes. Data averaged on the basis of 6-month studies, i.e. 120 trials.

Parameter	Unit	Type of absorption washer			
		Alkaline washer	Washer after digestion with HCl	Washer after phosphate coating	Washer after passivation
pH	-	10.4±0.2	3.06±1	3.2±0.5	3.85±0.5
Conductivity	µS/cm	636±50	861±110	961±150	115±44
Ammonium nitrogen	mg/l	3.35±0.4	0.102±0.03	0.096±0.01	0.025±0.005
Nitrate NO_3^-	mg/l	5.0±0.5	4.0±0.34	106.0±7.0	15.0±2.5
Nitrite NO_2^-	mg/l	<0.02	<0.02	<0.02	< 0.02
Phosphate PO_4^{3-}	mg/l	14.2± 0.5	7.96±3	118.2±30	20.05±5
Chlorides	mg/l	24±4.0	438±60	32±7	27±5
Fluorides	mg/l	0.017±0.002	0.023±0.002	0.016±0.005	0.256±0.1
Sulphureous	mg/l	25±2.0	22±4.0	21±4.0	26±1.0
Alkalinity	mg/l $CaCO_3$	180±10	-	-	-
Na	mg/l	345±60	25±5.0	78±9	122±30
K	mg/l	325±70	33±6.0	122±10	24±8.0
Zr	mg/l	0.022±0.01	0.019±0.005	0.011±0.002	0.961±0.2
Fe	mg/l	0.58±0.07	35.5±11	6.4±2.2	0.54±0.1
Mn	mg/l	3.0±0.2	14.0±1	160.0±20	15.0±1.7
Cr	mg/l	0.039±0.001	0.005±0.001	0.026±0.006	0.008±0.002

Table 2. Physico-chemical composition of demineralized water and tap water. Data averaged on the basis of 6-month studies, i.e. 120 trials.

No.	Parameter	Unit	Demineralized water	Tap water	Analytical method
1	pH	-	6.8-7.1 (25°C)	7.2-7.5 (25°C)	PN-EN ISO 10523:2012
2	Conductivity	µS/cm	maximum 5.0 (25 °C)	Maximum 350 (25°C)	PN-EN 27888:1999
3	Ammonium nitrogen	mg/l	0	Maximum 0.035	PC-C-04576-4
4	Chlorides	mg/l	0	Maximum 45	PN-ISO 9297:1994
5	Sulphureous	mg/l	0	Maximum 25	PN-79-C-04566.10
6	Total Fe	mg/l	0	Maximum 0.025	PN-EN ISO11885:2009
7	Cr(VI)	µg/l	0	<1.0	PN-77/C04604/08
8	Total Cr	mg/l	0	0.0	PN-77/C04604/08
9	Hardness	mmol/l	0	Maximum 1.50	PN-EN ISO 11885:2009
10	Mn	mg/l	0	Maximum 0.025	PN-EN ISO 11885:2009
11	NO_3^-	mg/l	0	Maximum 0.6	PN-EN ISO 13395:2001
12	NO_2^-	mg/l	0	Maximum 0.05	PN-EN ISO 13395:2001
13	PO_4^{3-}	mg/l	0	Maximum 0.25	PN-EN ISO 15681:2009

phosphorus compounds. Such wastewater may also contain manganese compounds (including: manganese hydrogen phosphate $MnHPO_4$) [33]. Another type of sewage is wastewater and washings from the passivation of metal surfaces. Depending on the agent used, the wastewater may contain manganese, titanium, chromium, zirconium and nitric acid compounds. Due to the highly toxic, carcinogenic nature, chromium(VI) compounds are no longer used in the passivation stage of conversion coatings. Wastewaters from the manganese phosphate coating line go to one tank, where they enter into a partial reaction with one another. Next, they are pneumatically transported to the feeding tank before the neutralization process. From there, they reach the coagulation chamber, where iron(III) chloride is dosed together with sulfuric(VI) acid as a pH correcting substance. The next stage is the neutralization chamber, where the limewash solution is dosed, and from there it goes through the overflow to the flocculation chamber. Each reaction chamber is equipped with a mechanically driven agitator. The chambers are equipped with level and pH meters. The next stage of treatment is the transfer of sewage containing sludge floc to a settling tank with lamellar filling, where the flowing solid particles are separated from the sewage by gravity. The sludge is partially thickened and the surplus is pumped to the conical settling tank from where it is sent to the filter press, where the already treated sewage is completely separated from the sludge (Fig. 1) [33-34]. A schematic record of the reactions that take place during wastewater treatment can be divided into two stages, i.e. pH up to 9.5 and pH above 10:

Reactions taking place at a pH>9.5:

$$3Ca(OH)_2 + 2\ FeCl_3 \rightarrow 2Fe(OH)_3\downarrow + 3CaCl_2 \quad (1)$$

$$Ca(OH)_2 + FeCl_2 \rightarrow Fe(OH)_2\downarrow + CaCl_2 \quad (2)$$

$$5\ Ca(OH)_2 + 3\ H_3PO_4 \rightarrow Ca_5(PO_4)_3OH\downarrow + 9\ H_2O \quad (3)$$

$$Ca(OH)_2 + 2\ HNO_3 \rightarrow Ca(NO_3)_2 + 2\ H_2O \quad (4)$$

$$Ca(OH)_2 + H_2ZrF_6 \rightarrow CaZrF_6\downarrow + 2\ H_2O \quad (5)$$

$$2\ Ca(OH)_2 + 2\ Mn(NO_3)_2 + O_2 \rightarrow 2\ MnO_2 \cdot H_2O\downarrow + 2\ Ca(NO_3)_2 \quad (6)$$

Reactions taking place at a pH > 10.0:

$$Ca(OH)_2 + Ni(NO_3)_2 \rightarrow Ni(OH)_2\downarrow + Ca(NO_3)_2$$

Manganese phosphate coating for rinsing of phosphate steel elements involves the use of demineralized water produced on site using ion exchange with an ion exchange resin and tap water.

The typical composition of tap water and demineralized water is shown in Table 2.

The washings stored in the buffer tank form the so-called raw sewage. A typical composition of raw sewage from manganese phosphate coating, which comprises a mixture of washings from degreasing, etching, phosphating and passivation processes, is presented in Table 3.

Table 3. Composition of raw sewage from manganese phosphate coating.

No.	Parameter	Result	Analytical method	Legal limit[*]
1	pH	5.9±0.5 (21.8ºC)	PN-EN ISO 10523:2012	6.5-9.5
2	Conductivity	486±33 µS/cm (21.8ºC)	PN-EN 27888:1999	1500 µS/cm
3	Ammonium nitrogen	1.16±0.2 mg/l	Test Merck Nr 1.14752	200 mg/l
4	Total Phosphorus	30.5±3.0 mg/l	Test Merck Nr 1.14729	20 mg/l
5	ChZT-Cr	68±10 mg/l	PN-ISO 15705:2005	2000 mg/l
6	BZT$_5$	28±5 mg/l	PN-EN 1899-1:2002	1500 mg/l
8	Chlorides	70±10 mg/l	Test Merck Nr 1.14897	1000 mg/l
9	Sulphureous	25±2 mg/l	Test Merck Nr 1.00617	500 mg/l
10	Total Fe	6.63±1.0 mg/l	PN-EN ISO 11885:2009	10 mg/l
11	Mo	<0.004 mg/l	PN-EN ISO 11885:2009	1.0 mg/l
12	Cr(VI)	<0.010 mg/l	PN-77/C04604/08	0.1 mg/l
13	Total Cr	0.043±0.008 mg/l	PN-EN ISO 11885:2009	0.5 mg/l
14	Hardness	59.1±5 mg/l CaCO$_3$	PN-EN ISO 11885:2009	-
15	Zn	0.203±0.06 mg/l	PN-EN ISO 11885	5.0 mg/l
16	Cd	<0.0005 mg/l	PN-EN ISO 11885:2009	0.4 mg/l
17	Mn	31.7±7 mg/l	PN-EN ISO 11885:2009	-
18	Ni	0.963±0.2 mg/l	PN-EN ISO 11885:2009	0.5 mg/l
19	Co	0.0042±0.002 mg/l	PN-EN ISO 11885:2009	1.0 mg/l
20	K	33.2±6 mg/l	PN-EN ISO 11885:2009	80 mg/l
21	Na	22.2±7.0 mg/l	PN-EN ISO 11885:2009	800 mg/l
22	NO$_3^-$	26.3±5.0 mg/l	PN-EN ISO 13395:2001	-
23	NO$_2^-$	8.51±1.5 mg/l	PN-EN ISO 13395:2001	200 mg/l
24	F$^-$	1.04±0.3 mg/l	PN-78/C-04588/03	25.0 mg/l
25	Volatile phenols	0.017±0.004 mg/l	PN-ISO 6439:1994	0.1 mg/l
26	TOC	23.3±3 mg/l	PN-EN 1484:1999	1000 mg/l
27	Total PAHs (Polycyclic aromatic hydrocarbons)	<0.006 µg/l	PN-EN ISO 17993:2005	0.2 mg/l
28	Ether extract	15.0±4 mg/l	PN-86/C-04573.01	100 mg/l
29	BTX	<1.0 µg/l	PN-ISO 11423-1:2002	1.0 mg/l
30	Anionic detergents ASPC	0.73±0.2 mg/l	PN-EN 7875-2:2002	15 mg/l
31	Nonionic detergents NSPC	1.86±0.25 mg/l	PN-EN ISO 7875-2:2002	20 mg/l
32	Si	4.09±0.5 mg/l	PN-EN ISO 11885:2009	-
33	γ- hexachlorocyclohexane	<0.001 µg/l	PN-EN ISO 6468:2002	0.0
34	Alachlor	<0.001 ng/l	PN-EN ISO 6468:2002	0.0
35	Heptachlor	<0.0002 µg/l	PN-EN ISO 6468:2002	0.0
36	Aldrin	<0.001 µg/l	PN-EN ISO 6468:2002	0.0
37	Heptachlor-endo-epoxide isomer A	<0.0002 ng/l	PN-EN ISO 6468:2002	-
38	Heptachlor-endo-epoxide isomer B	<0.0002 ng/l	PN-EN ISO 6468:2002	-
39	Dieldrin	<0.001 µg/l	PN-EN ISO 6468:2002	0.0
40	Endrin	<0.001 µg/l	PN-EN ISO 6468:2002	0.0

Table 3. Continued.

41	Methoxychlor	<0.001 μg/l	PN-EN ISO 6468:2002	0.0
42	Hexachlorobenzene	<0.001 μg/l	PN-EN ISO 6468:2002	2.0 mg/l
43	Zr	0.416±0.12 mg/l	PN-EN ISO 11885:2009	-
44	PO_4^{3-}	38.1±7 mg/l	PN-EN ISO 15681:2009	20.5 mg/l
45	Ca	21.7±4 mg/l	PN-EN ISO 11885:2009	-
46	Mg	1.19±0.3 mg/l	PN-EN ISO 11885:2009	-
47	Hg	<0.00001 mg/l	PN-EN ISO 11885:2009	0.06 mg/l

*legal limit for wastewater discharged into the sewage system based on Polish standards [42]

Effectiveness of Wastewater Treatment with the Use of Coagulation

The effectiveness of coagulation was analyzed on raw sewage for 36 months by performing a total of 750 unit analyses. In order to increase the treatment efficiency in the coagulation process with a 40% (m/m) solution of iron(III) chloride, a waste 30% (m/m) solution of sulfuric acid was used. Sulfuric acid is used in the process of cleaning the manganese phosphate coating bath from iron(III) phosphate(V) deposits, which is formed as a by-product in the above-mentioned process. Sulfuric acid does not react with iron(III) phosphate, but dissolves it, so it can be easily filtered from the working liquid. The sulfuric acid used in this way contains large amounts of iron(III), which allowed to reduce the consumption of iron(III) chloride. Thus, the costly disposal of the abovementioned sulfuric acid was abandoned. This combination permitted the reduction of high pollution values. In order to increase the efficiency of wastewater treatment, a combined flocculation process was used. The results of wastewater treatment by coagulation with flocculation are presented in Table 4.

During the analysis of the obtained results and their comparison with the typical composition of raw sewage (Table 2), it should be indicated that coagulation allowed to obtain a high reduction of biogenic compounds, i.e. orthophosphates, nitrates and heavy metals such as iron and manganese (Table 5, 6). As a result of wastewater treatment by coagulation with iron(III) chloride together with waste sulfuric(VI) acid, nitrates(V) were reduced by approx. 62%, phosphates(V) by approx. 78.5%, iron by approx. 53%, manganese by approx. 40%.

The total results of 750 tests of physico-chemical analyses of treated wastewater samples using coagulation with iron(III) chloride and waste sulfuric acid(VI) carried out from January 2017 until December 2019 are shown in Table 5.

Coagulation with iron(III) chloride allows to reduce the pollutants contained in the sewage. The high efficiency of pollution reduction means that this method is readily used by the industry. One of the by-products of this process is residue of precipitated hydroxides that must be separated from the liquid portion. It is this process that is most often used in hydraulic systems, e.g. in the form of a filter press. The amount of separated sludge formed is on average 48-54 kg/day.

Table 4. Results of wastewater treatment by coagulation with iron(III) chloride. Data averaged on the basis of 6-month studies, i.e. 120 trials.

No.	Parameter	Unit	Raw sewage	Treated wastewater	Average pollution reduction	Reduction [%]	Legal limit*
1	pH	-	9.3±0.5	7.8±1.1	-	-	6.5 – 9.5
2	Conductivity	μS/cm	428±50	425±23	-	-	max. 1500 μS/cm
3	Chlorides	mg/l	95±7	72±9	23	24.2	max. 1000 mg/l
4	Nitrates	mg/l	13±3	5±1	8	61.6	-
5	Nitrites	mg/l	0.04±0.02	0.04±0.01	-	-	max. 10 mg/l
6	Phosphates	mg/l	18.5±4	2.0±0.4	16.5	78.4	max. 25 mg/l
7	Mn	mg/l	7.6±3	4.5±1.5	3.1	40.8	-
8	Fe	mg/l	1.30±0.25	0.61±0.1	0.69	53.08	max. 10 mg/l

*legal limit for wastewater discharged into the sewage system based on Polish standards[41]

Table 5. Results of wastewater treatment by coagulation with iron(III) chloride. Monthly averages from 3-year studies.

	unit	January	February	March	April	May	June	July	August	September	October	November	December	annual average
2017														
temperature	°C	21.2 ± 1	22.8 ± 1	24.4 ± 2	25.3 ± 3	25.3 ± 2	28.3 ± 1.2	29.6 ± 4	30.3 ± 5	28.7 ± 4	26.6 ± 2	26.2 ± 1	25.4 ± 1	26.3
pH	-	5.17 ± 0.2	6.30 ± 0.1	6.61 ± 0.05	6.27 ± 0.1	6.13 ± 0.1	9.42 ± 0.5	8.38 ± 0.4	7.44 ± 0.2	6.60 ± 0.2	5.54 ± 0.1	6.17 ± 0.1	6.15 ± 0.2	6.73
conductivity	µS/cm	4387 ± 540	2746 ± 170	3265 ± 230	3319 ± 345	3330 ± 270	1644 ± 120	1350 ± 135	2178 ± 450	1795 ± 220	2627 ± 250	2282 ± 330	2633 ± 400	2600
chlorides	mg/l	724 ± 55	415 ± 40	497 ± 20	649 ± 54	546 ± 35	122 ± 19	173 ± 20	221 ± 22	169 ± 15	255 ± 50	254 ± 40	345 ± 40	356
nitrates	mg/l	11.2 ± 0.5	9.75 ± 0.2	10.0 ± 0.9	17.0 ± 1	11.5 ±1.2	10.2 ±0.5	13.8 ± 0.4	11.6 ± 0.6	8.9 ± 0.5	15.0 ± 0.2	14.6 ± 0.4	12.4 ± 0.3	12.1
nitrites	mg/l	0.08 ± 0.02	0.12 ± 0.05	0.10 ± 0.02	0.048 ± 0.01	0.046	0.029 ±0.01	0.074 ±0.01	0.030 ± 0.01	0.021 ± 0.02	0.015 ±0.005	0.016 ±0.007	0.013 ±0.004	0.051 ± 0.008
ammonium ion	mg/l	1.21 ± 0.3	4.69 ± 0.5	1.43 ± 0.5	1.06 ± 0.11	1.53 ± 0.2	1.44 ± 0.1	1.33 ± 0.2	1.20 ± 0.3	1.63 ± 0.2	1.66 ± 0.2	1.63 ± 0.25	1.61 ± 0.11	1.72
orthophosphates	mg/l	0.66 ± 0.2	1.20 ± 0.3	1.70 ± 0.1	1.57 ± 0.2	1.76 ± 0.1	2.54 ± 0.2	3.73 ± 0.3	6.93 ± 0.6	1.67 ± 0.07	3.48 ± 0.9	5.11 ± 0.7	2.15 ± 0.06	2.70
sulphureous	mg/l	977.8 ± 9	713.9 ± 20	998.0 ± 55	776.3 ± 50	750.7 ± 65	604.9 ± 40	487.8 ± 45	677.1 ± 60	867.0 ± 45	961.5 ± 120	779.4 ± 55	760.3 ± 60	779.2
Fe	mg/l	0.76 ± 0.4	0.35 ± 0.1	0.40 ± 0.11	5.11 ± 1.1	12.08 ± 2	0.36 ± 0.1	0.31 ±0.1	0.34 ± 0.15	0.50 ± 0.25	0.81 ± 0.4	0.88 ± 0.35	1.04 ± 0.2	1.94
Mn	mg/l	3.51 ± 0.1	3.09 ± 0.8	3.4 ± 0.9	1.90 ± 0.6	1.5 ± 0.6	2.92 ± 0.9	2.51 ± 0.3	3.04 ± 1	1.88 ± 0.7	1.22 ± 0.24	3.41 ± 0.7	0.90 ± 0.4	2.44
K	mg/l	18.75 ± 0.5	15.9 ± 1	25.9 ± 2	20.6 ± 1	15.3 ± 2	16.0 ± 3	13.2 ±2	16.9 ± 1.1	18.9 ± 1.3	15.7 ± 1.7	18.3 ± 0.8	21.8 ± 0.6	17.96
2018														
temperature	°C	26.0 ± 2	25.7 ± 5	25.4 ±6	26.7 ± 3	29.4 ± 3	29.8 ± 5	31.0 ± 4	29.7 ± 3	22.6 ± 2	22.0 ± 3	23.0 ± 6	23.1 ± 4	26.2
pH	-	5.70 ± 1.2	7.02 ± 0.6	8.01 ± 0.6	9.53 ± 0.8	10.36 ± 1.1	8.29 ± 0.9	9.15 ± 0.9	7.59 ± 0.6	7.32 ± 0.6	7.78 ± 1.1	8.05 ± 1.3	8.33 ± 0.4	8.09
conductivity	µS/cm	2313 ± 130	2379 ± 220	1983 ± 150	2725 ± 446	3979 ± 400	1962 ± 430	1791 ± 90	1675 ± 180	1621 ± 75	1411 ± 140	1555 ± 320	1896 ± 190	2107.6
chlorides	mg/l	238 ± 44	362 ± 89	193 ± 70	416 ± 55	348 ± 60	233 ± 22	260 ± 48	212 ± 33	207 ± 44	202 ± 35	229 ± 15	204 ± 20	258.7
nitrates	mg/l	12.8 ± 1.1	13.2 ± 1	11.6 ± 2.2	11.7 ± 1.7	17.8 ± 0.6	16.7 ± 0.9	14.9 ± 0.7	13.0 ± 0.9	13.1 ± 2.2	11.5 ± 2.6	12.2 ± 1.5	10.5 ± 1.8	13.3
nitrites	mg/l	0.026 ± 0.01	0.019 ± 0.005	0.088 ± 0.02	0.054 ± 0.02	0.063 ±0.01	0.129 ±0.01	0.063 ±0.02	0.213 ±0.03	0.145 ±0.04	0.186 ±0.013	0.129 ±0.02	0.435 ±0.1	0.13
ammonium ion	mg/l	1.87 ± 0.4	1.87 ± 0.4	2.01 ± 0.5	2.74 ± 0.2	2.83 ± 0.7	2.96 ± 0.8	3.15 ± 0.8	2.92 ± 1	2.61 ± 0.6	2.80 ± 0.4	2.91 ± 0.8	3.28 ± 1.1	1.87
orthophosphates	mg/l	2.58 ± 1.1	1.91	2.61	1.92	1.34	3.68	1.43	2.88	1.84	2.05	2.01	1.21	2.11
sulphureous	mg/l	910.5 ± 230	707.0 ± 120	427.0 ± 50	121.2 ±55	351.8 ± 54	555.7 ± 40	398.4 ± 30	502.9 ± 25	448.8 ± 60	287.5 ± 45	343.3 ± 120	480.8 ± 55	910.5
Fe	mg/l	0.870 ± 0.11	0.18 ± 0.2	0.719 ± 0.2	0.139 ± 0.04	0.117 ± 0.1	0.472 ± 0.1	0.298 ± 0.1	0.32 ± 0.05	0.34 ± 0.9	0.31 ± 0.12	0.21 ± 0.04	2.06 ± 0.8	0.870
Mn	mg/l	3.19 ± 0.2	1.74 ± 0.8	0.79 ±0.35	0.45 ± 0.2	0.50 ± 0.1	1.49 ±0.2	1.27 ±0.3	1.41 ±0.11	1.09 ± 0.4	0.84 ± 0.4	2.16 ± 0.8	3.43 ±0.6	3.19
K	mg/l	22.0 ± 5	18.3 ± 4	17.7 ± 6	21.8 ± 3	30.3 ± 8	20.9 ± 4.8	19.9 ± 5	19.1 ± 3	19.4 ± 3.3	19.8 ± 0.9	18.0 ± 2.6	20.9 ± 2.5	22.0
2019														
temperature	°C	24.5 ± 3	25.2 ± 2.5	26.9 ± 3	27.0 ± 4	29.6 ± 5	29.8 ± 5	32.2 ± 2	31.5 ± 3	24.3 ± 5	23.6 ± 3	22.6 ± 2.5	21.6 ± 3	26.6
pH	-	6.60 ± 1.1	6.90 ± 1.9	7.50 ± 0.6	9.20 ± 1.9	9.30 ± 1.3	7.50 ± 1.1	9.20 ± 0.6	8.20 ± 0.5	7.90 ± 0.5	7.10 ± 0.6	8.60 ± 0.7	8.40 ± 0.6	8.03
conductivity	µS/cm	1225 ± 50	1296 ± 130	1449 ± 70	1563 ± 60	1775 ± 140	1225 ± 200	1412 ± 235	1633 ± 55	1425 ± 40	1711 ± 70	900 ±67	1563 ±	1431.4
chlorides	mg/l	211 ± 30	252 ± 44	205 ± 40	332 ± 20	274 ± 28	241 ± 35	233 ± 40	256 ± 55	266 ± 30	296 ± 40	211 ± 20	205 ± 25	248.5
nitrates	mg/l	13.0 ± 2.4	2.9 ± 2.2	12.3 ± 1.9	7.5 ± 3.4	16.3 ± 2.2	14.2 ± 3	12.3 ± 2.8	11.0 ± 1.1	10.3 ± 2.7	11.6 ± 3	12.9 ± 3.9	10.5 ± 5	11.2
nitrites	mg/l	0.022 ± 0.04	0.015 ± 0.01	0.08 ± 0.01	0.123 ± 0.04	0.123 ± 0.2	0.112 ± 0.01	0.078 ± 0.03	0.121 ± 0.01	0.088 ± 0.03	0.098 ± 0.04	0.22 ± 0.03	0.036 ± 0.04	0.082
ammonium ion	mg/l	0.030 ± 0.015	0.025 ± 0.01	0.077 ± 0.04	0.036 ± 0.01	0.055 ± 0.02	0.098 ± 0.02	0.074 ± 0.03	0.125 ± 0.06	0.174 ± 0.02	0.196 ± 0.03	0.177 ± 0.09	0.363 ± 0.07	0.12
orthophosphates	mg/l	1.22 ± 0.5	1.36 ± 0.4	1.96 ± 0.3	1.74 ± 0.4	2.20 ± 0.6	2.30 ± 0.3	2.90 ± 0.4	3.05 ± 0.5	2.70 ± 0.6	2.44 ± 0.9	2.93 ± 0.2	2.80 ± 0.7	2.30
sulphureous	mg/l	3.30 ± 1.3	2.30 ± 0.9	2.80 ± 1.1	2.50 ± 0.9	2.30 ± 0.8	2.70 ± 0.7	2.99 ± 0.9	2.90 ± 0.5	3.50 ± 0.4	2.20 ± 0.8	2.90 ± 0.2	2.70 ± 0.6	2.8
Fe	mg/l	2.452 ± 1.1	2.103 ± 0.09	1.50 ± 1	1.06 ± 0.04	0.82 ± 0.09	0.66 ± 0.05	1.16 ± 0.03	0.33 ± 0.04	0.19 ± 0.02	3.0 ± 0.1	1.20 ± 0.2	0.711 ± 0.4	1.26
Mn	mg/l	2.770 ± 1.3	2.69 ± 1.4	3.770 ± 1.5	1.250 ± 0.9	3.360 ± 2.2	2.450 ± 0.1	1.220 ± 0.7	3.19 ± 0.3	3.38 ± 1.3	3.55 ± 1.8	3.29 ± 1.0	3.20 ± 1.2	2.84
K	mg/l	0.96 ± 0.5	1.50 ± 1.0	0.70 ± 0.9	0.90 ± 0.8	0.90 ± 0.7	1.22 ± 0.6	1.78 ± 0.3	1.26 ± 0.5	2.30 ± 0.3	1.50 ± 0.7	1.70 ± 0.6	2.20 ± 1.1	1.4

The average degree of pollution reduction by coagulation is shown in Table 6.

Effectiveness of Wastewater Treatment with the Use of Ozonation

The ozonation process showed that the ozone produced in the amount of 0.00235 mol/dm^3 reacted differently with ozonated sewage samples (treated and raw sewage). Carried out for 60 minutes, it resulted in the raw sewage's lack of initial reaction with the generated ozone; the generated ozone began to react with the sewage only from the 40th minute.

The wastewater treated with coagulation and subjected to ozonation behaved differently than the raw sewage sample. Within 0-20 minutes, the ozone passed through the column reacted with the wastewater sample. Only after 20 minutes, its content in the KI washer

Table 6. Average degree of pollution reduction with iron(III) chloride and waste sulfuric(VI) acid.

	Average annual reduction [%]			
Year	Orthophosphate	Nitrates	Fe	Mn
2017	92.9±5	54.0±4.5	70.7±4	92.3±4
2018	94.4±4	49.5±4	86.8±5	90±2.5
2019	93.4±4	57.5±5	81±5	91.04±3

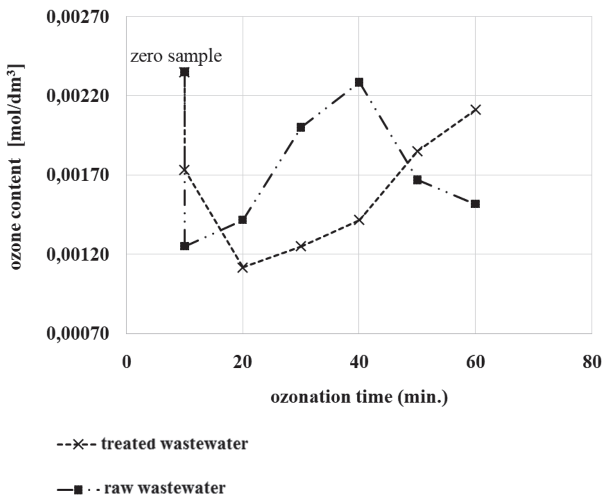

Fig. 3. Reaction of ozone with raw sewage and treated sewage by coagulation.

increased proportionally, which proves that ozonation is complete. Ozone reaction with the wastewater dose is shown in Fig. 3.

During ozonation, 5 ml of samples were taken for UV-VIS spectrophotometric measurements. As a result of ozonation, the orthophosphate content was reduced by 28% for raw sewage and by 45% for treated sewage. The content of nitrates(V) was reduced by 60% for raw sewage and by 20% for sewage treated with coagulation.

However, the content of nitrates in raw sewage during ozonation initially decreased to the value of 4-6 mg/l within 20-30 min. of the process. Within 30 minutes, this value increased to 19 mg/l, which proves the oxidation of all nitrogen compounds contained in the wastewater to the form of nitrates(V), which then decreased to the value of 5.2 mg/l. The results of analyses are presented in Fig. 4.

In addition to parameters such as the content of biogenic compounds, a turbidity analysis per standard unit of formazin was also performed for wastewater samples. As a result of ozonation, different results were obtained on samples treated with coagulation and on the raw sewage sample. Initially, the turbidity of the sample was 31.5 NTU, and that of the treated sewage was 29.5 NTU. With conducting ozonation, the turbidity of treated sewage was reduced to 21.6 NTU, and the turbidity of raw sewage increased to 51.6 NTU. Raw sewage contains large amounts of dissolved iron(II) and manganese(II) compounds (Table 1), which is easily oxidized to iron(III) and manganese(IV) compounds in colloidal formunder the influence of ozone, hence the observed increase in turbidity (Fig. 5).

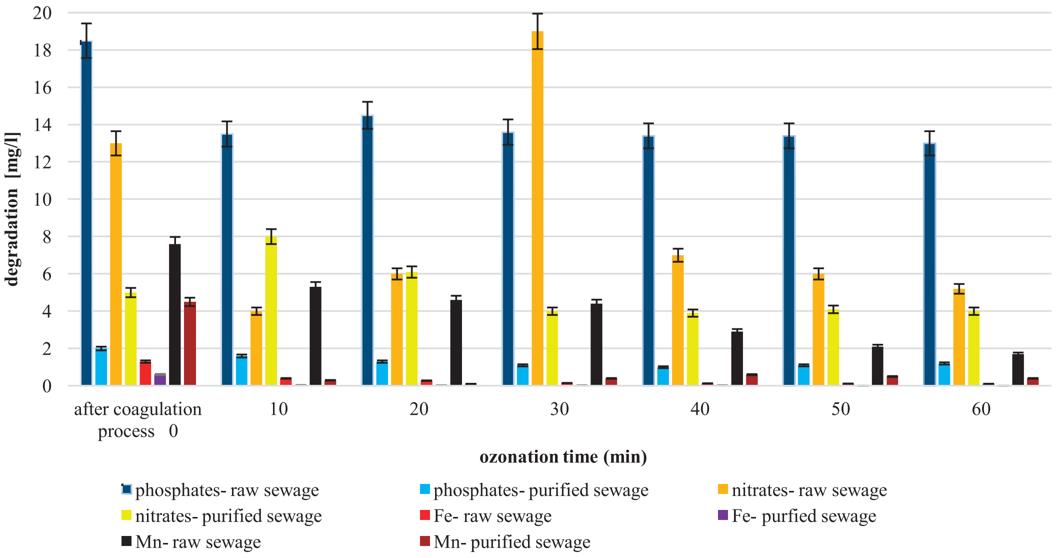

Fig. 4. Results for treated and raw sewage during ozonation.

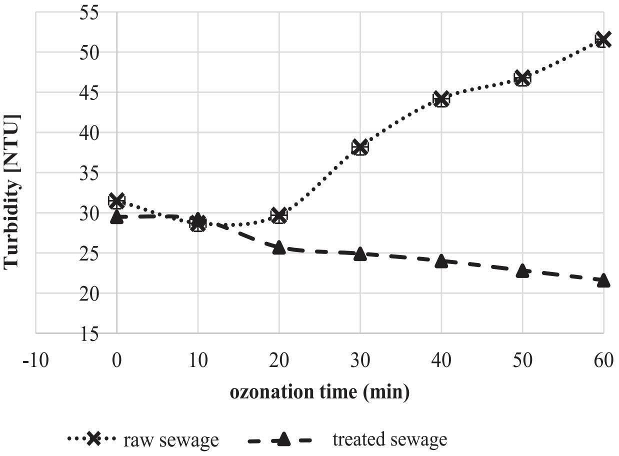

Fig. 5. Results of turbidity measurement of raw and treated sewage samples.

The sewage treated with coagulation contains minor amounts of suspended solids which are decomposed into a soluble form under the influence of ozone, hence the decrease in the value of the turbidity parameter (Fig. 5).

Table 7. Average degree of reduction of nitrates(V) using the Fenton reaction.

Dose of H_2O_2 (ml)	**2**	**3**
Reaction time (min.)	Concentration of nitrates (mg/l)	
0	13.00	13.00
1	2.20	3.90
5	0.089	0.075
10	0.075	0.037
20	0.041	0.014
30	0.031	0.012

Fenton Reaction

The Fenton reaction was carried out in two variants with and without the addition of $FeCl_3$ solution, which is dictated by the iron content in raw sewage in the amount of 1.63 mg/l. The Fenton process was carried out for 30 minutes in 5 variants in pH 4.0-5.0: without the addition of iron with a dose of H_2O_2: 1, 2, 3 ml and

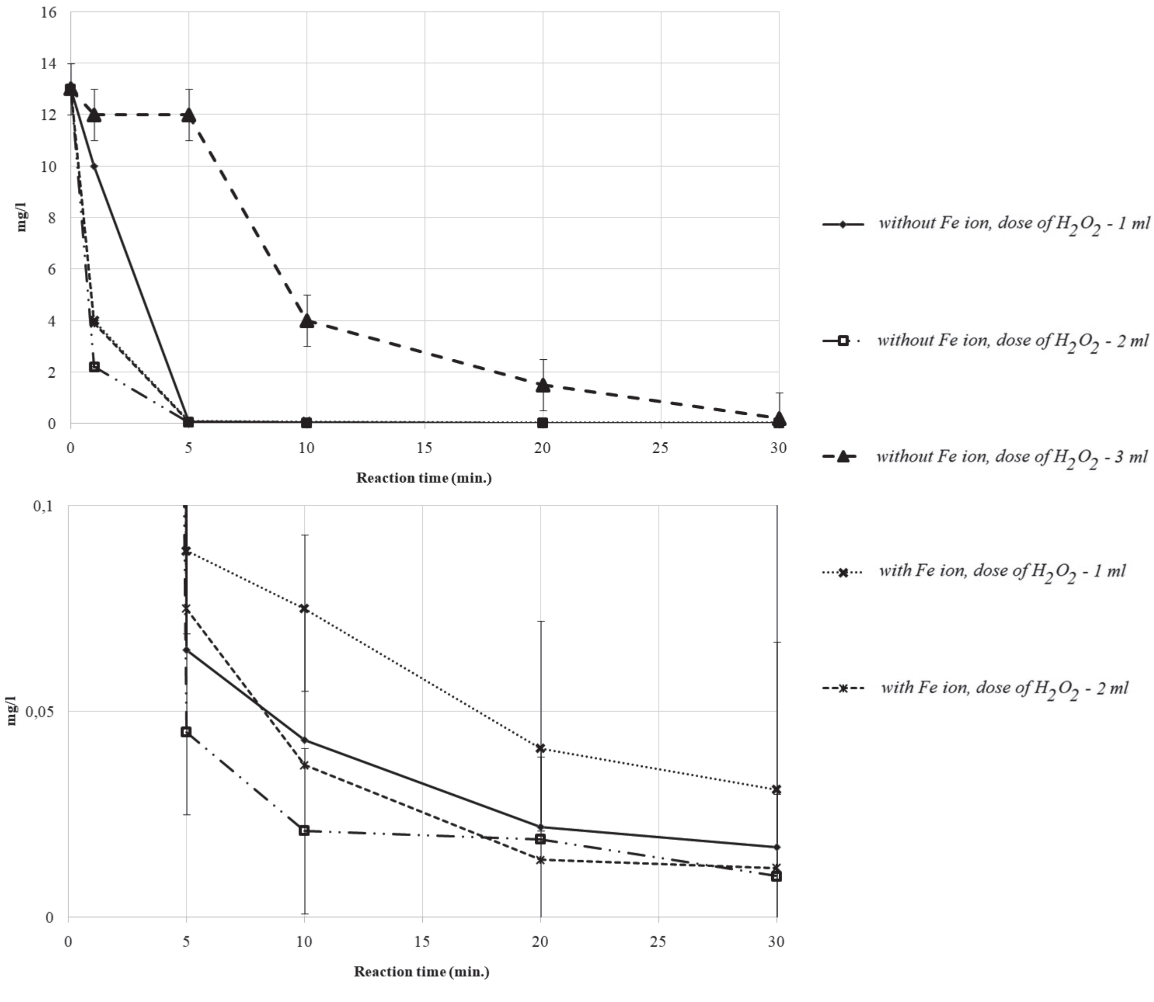

Fig. 6. Reduction of nitrate(V) content using the Fenton method.

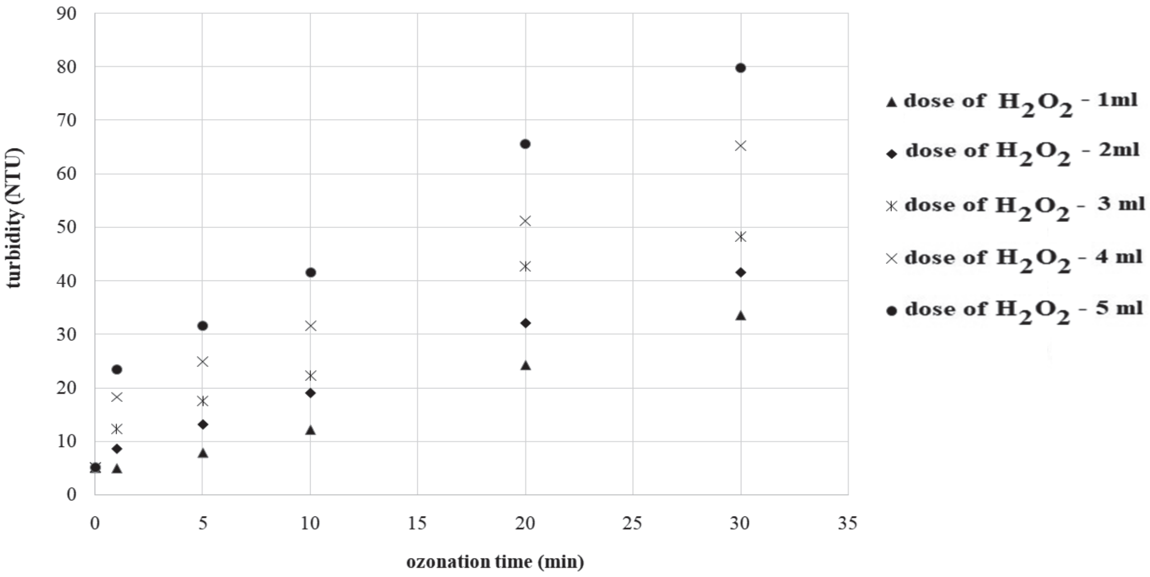

Fig. 7. Determination of turbidity in raw sewage samples depending on the dose of hydrogen peroxide.

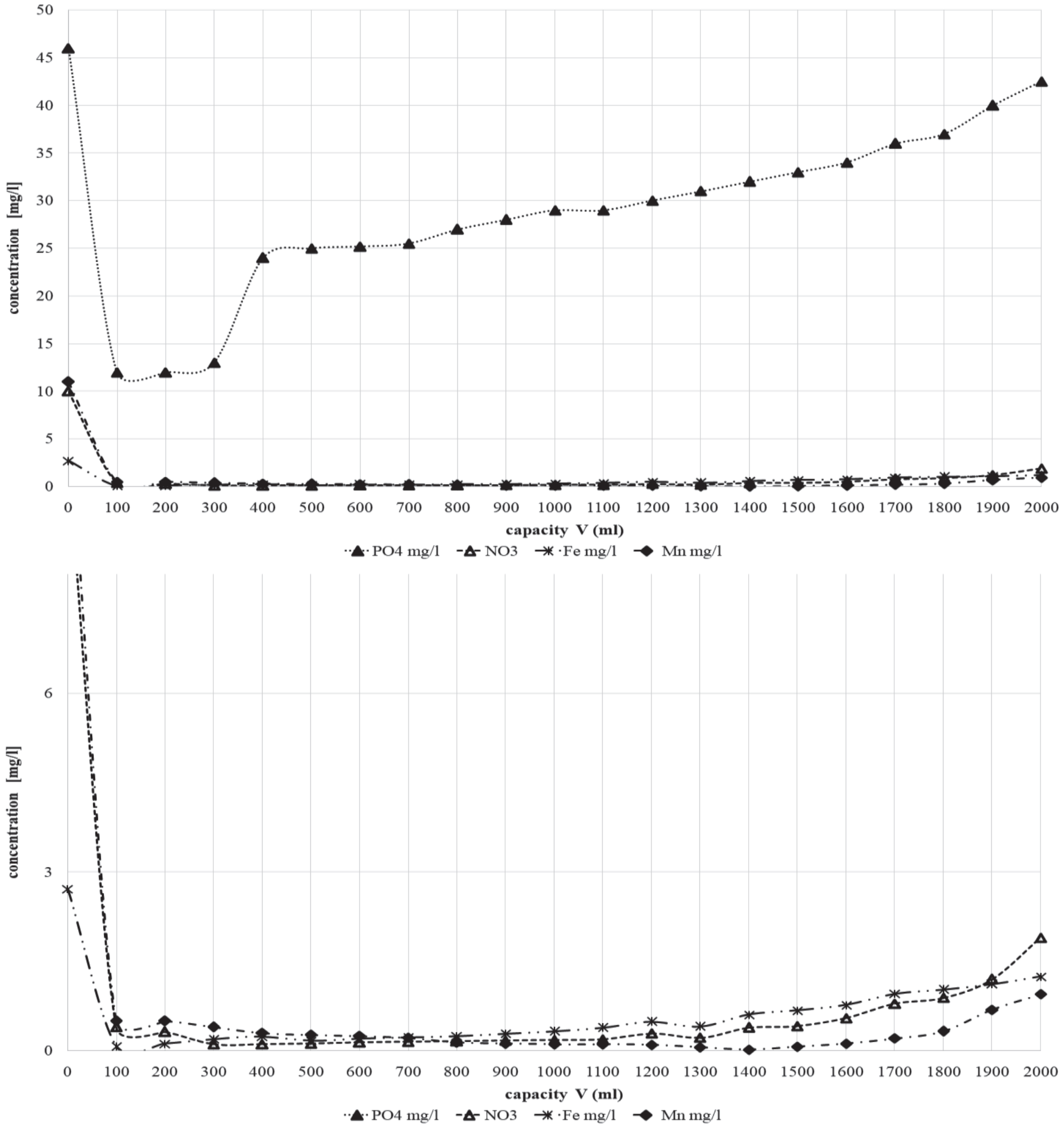

Fig. 8. Wastewater sorption using the activated carbon-zeolite system.

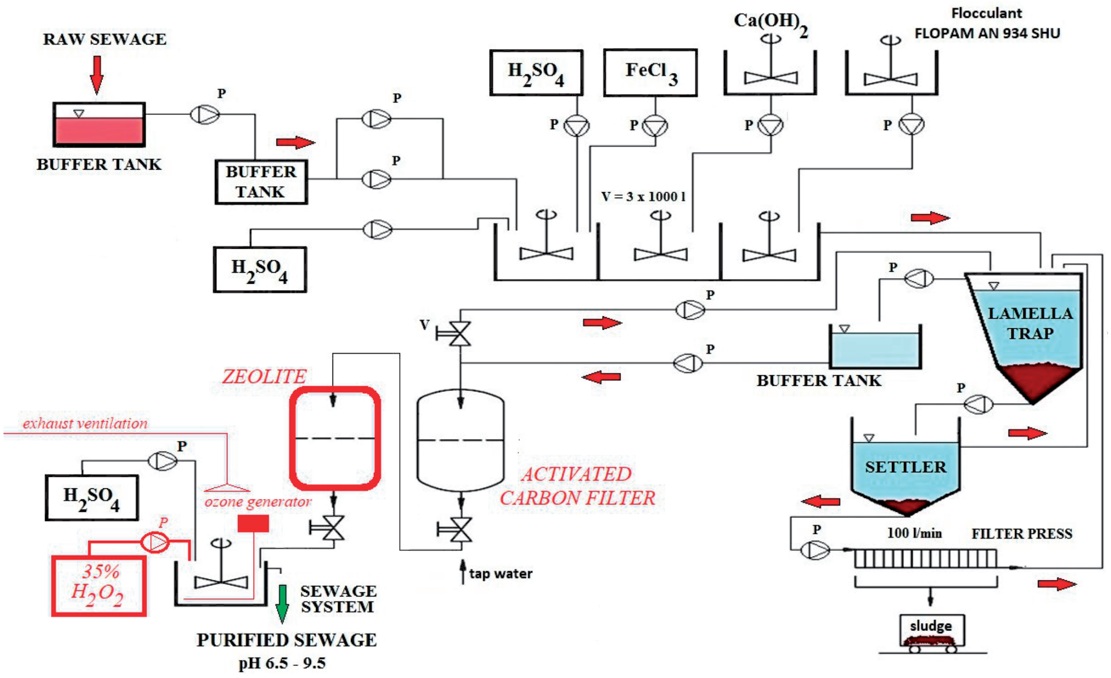

Fig. 9. A proposal for a new manganese phosphate coating wastewater treatment system.

with the addition of solution of iron chloride in the amount of 0.1 ml and a dose of H_2O_2 in the amount of 1 and 2 ml. Samples of 5 ml were taken every 5 minutes. The results of measurements of wastewater treatment using the Fenton method are shown in Fig. 6.

Conducting the Fenton process allowed to reduce the content of nitrates(V) in raw sewage from 13 mg/l to the value of 0.031 mg/l at the dose of H_2O_2 2 ml/500 ml of the sewage sample and to the value of 0.012 mg/l at the dose of 3 ml within 30 minutes without addition iron compound. Out of all five tests, the most favorable involved the addition of 2-3 ml hydrogen peroxide without iron(III) compound (Fig. 6). The results of the efficiency of wastewater treatment with the Fenton reaction in the system are presented in Table 7.

Nitrates(V) contained in the wastewater originate from the process baths containing nitrates, which are a process accelerator in the case of manganese phosphate coating. One of such compounds is manganese(II) nitrate(V), potassium nitrate(V). Nitrate(V) and also nitrite(III) and ammonia compounds decomposition proceeds according to two proposed chemical reactions:

$$2\ KNO_3 + 3\ H_2O_2 + H_2SO_4 \rightarrow 4\ H_2O + K_2SO_4 + 3\ O_2 + 2\ NO\uparrow \tag{7}$$

$$2\ KNO_2 + 2\ H_2O_2 + 2\ H_2SO_4 \rightarrow (NH_4)_2SO_4 + K_2SO_4 + 5\ O_2 \tag{8}$$

$$2\ NH_3 + 3\ H_2O_2 \rightarrow 6\ H_2O + N_2\uparrow \tag{9}$$

During the Fenton process, the turbidity of the sewage/hydrogen peroxide mixture was also measured. For this purpose, five samples of raw sewage were prepared with a volume of 500 ml and a variable dose of 1-5 ml H_2O_2. Depending on the dose of hydrogen peroxide, the turbidity of the solution increases in direct proportion to the amount of oxidizing agent used, due to precipitation of manganese and iron oxides and hydroxides. The results are shown in Fig. 7.

Sorption on Activated Carbon and Zeolite

On the basis of the obtained test results, it can be concluded that passing the sewage through the system with activated carbon-zeolite effectively reduces iron, manganese and nitrates(V) (Fig. 8). However, this method does not give favorable effects in the case of reduction of phosphates(V).

When analyzing the obtained results, it should be indicated that in the case of wastewater from manganese phosphate coating, this technique may be useful in the treatment of technological washers and recycling of water in a closed cycle, which will reduce the cost of phosphating. It can also be helpful in cleaning sewage already treated by coagulation.

Based on the conducted sorption of wastewater with the use of activated carbon and zeolite (Fig. 8), it can be concluded that this process does not bring much results in the reduction of orthophosphates. It can be stated that the sorption capacity is low in relation to orthophosphates. The bed breakthrough took place after 200 ml of raw sewage had been passed through. Sorption has been used to remove contaminants such as nitrates, iron and manganese. After passing 2,000 ml of raw sewage through a system containing 100 g of filling, the iron concentration was reduced from

2.70 mg/l to 1.25 mg/l, the manganese concentration from 11.0 mg/l to 0.95 mg/l, and the nitrate concentration from 10 mg/l up to 1.9 mg/l (Fig. 8).

Wastewater treatment in the activated carbon-zeolite system allowed the reduction of nitrates(V) by 81%, iron by an average of 54% and manganese by an average of 91.4%. This method is useful in cleaning washers and returning water in a closed system due to the rapid breakthrough of the bed in a setting of phosphate content. In the case of other parameters, the technical use of a bed with a mixed filling of activated carbon-zeolite would reduce the amount of tap water used.

Based on the obtained results of research on raw sewage from manganese phosphate coating, a new sewage treatment system was proposed using several methods; it is demonstrated in Fig. 9. It proposes the installation of a pressure filter with a zeolite bed assembled just before the filter filled with activated carbon. Another new element is the installation of a tank with a hydrogen peroxide solution with an automatic dosing pump that would feed a certain amount of H_2O_2 during the discharge of sewage to the municipal sewage system. Such a solution will effectively reduce the removed nitrates(V), thus decreasing the burden of nitrogen compounds in the municipal sewage treatment plant.

A new optional solution is also the installation of an ozone generator with a feeding nozzle, which would additionally oxidize the residual nitrates(V) removed in the sewage. A major element in the structure is the installation of an air extraction system which will remove the residual unreacted ozone; this would allow safe operation of the entire installation due to the toxicity of the generated ozone (Fig. 9).

Conclusions

The treatment of wastewater from manganese phosphate coating by coagulation using iron(III) chloride and waste sulfuric(VI) acid contaminated with iron(III) phosphate allowed to reduce the content of phosphates by 93.6%, nitrate(V) by 53.6%, iron by 79.5% and manganese by 91.1%.

Wastewater treatment using sorption in the activated carbon-zeolite system allowed to reduce 91.4% manganese content, 54% iron content on average and 81% nitrate(V) content. However, the method was not successful in reducing phosphate(V).

Based on the obtained results of measurements of sewage treatment with the Fenton method, the most advantageous proved to be the trial with the addition of 2-3 ml hydrogen peroxide without iron(III) compound due to the residual iron content in the tested sewage. The Fenton method also requires the use of mechanical filtration due to the elevated metabolic rate in wastewater.

For ozone treatment of sewage, this method reduced phosphates by 29.8% in the case of raw sewage and by 40% in the case of treated sewage. The method also reduced the content of nitrates by 60% in the case of raw sewage and by 91.6% in the content of iron in the raw sewage, and on average by 98.3% for the sewage treated with the coagulation method. Ozonation of wastewater allowed to reduce manganese content by 77.7%. However, due to the increase in the amount of suspended solids in the vicinity of the turbidity index, ozonation also requires filtration.

A new solution was brought forward in waste water treatment by installing an ozone generator with an exhaust air extraction system, assembly of a pressure filter with zeolite filling and a tank with a hydrogen peroxide solution just before the discharge of wastewater into the sewage system.

Conflict of Interest

The authors declare no conflict of interest.

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