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Physicochemical and Chemical Purification of Tannery Wastewaters

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Abstract

In this study the process of tannery wastewater treatment by electrocoagulation and coagulation with $FeCl_3$ followed by advanced oxidation processes (Fenton reaction, O_3/OH^-, O_3/H_2O_2, H_2O_2/UV) was investigated. Electrocoagulation resulted in a slightly better purification effect than coagulation. The purification effect obtained by AOPs decreased in the order: Fenton reaction $<O_3/OH^- <O_3/H_2O_2 <H_2O_2/UV$. A two-step process (coagulation + H_2O_2/UV method) resulted in 93-94% reduction of COD. Coagulation followed by Fenton reaction in 30 min. was recognized as the best method of purification of tannery wastewaters – COD was reduced by 85-88%. The concentration of ammonium ions was decreased by 62-64% when O_3/OH^- method was applied.

Keywords: tannery wastewaters, advanced oxidation Processes, hydroxyl radicals, coagulation, electrocoagulation.

Introduction

Compounds extracted from skin, reagents applied in tanning and products from their degradation are components of tannery wastewaters. [1-3]. Tannery wastewaters are characterized by high concentrations of pollutants and a great variety of composition which results from changeability of technological processes conducted in tanneries.

There are considerable dissimilarities in the concentration range of pollutants in tannery wastewaters given by different authors [1-5]. The main inorganic pollutants are chlorides, whose concentration ranges from several hundred to over 10,000 mg/l Cl^-. However, sulphate (VI) concentrations are usually a little lower. Other significant components are ammonium ions and sulphide ions, whose concentration ranges from tens to several hundreds mg/l. Moreover, the amount of organic pollutants is large – the COD value is usually several thousands mg/l O_2. The composition of organic pollutants in tannery wastewater is complex. Proteins, mainly collagen and their hydrolysis products – amino acids derived from the skin – are predominant, while other such as fats are in low concentrations [6]. The most important organics used in skin treatment – are tannins – natural, synthetic, fatty aldehydes and quinones [6]. Tanneries also use compounds like aliphatic amines, nonionic surfactants, oils, and pigments [6].

Most of these pollutants are in a soluble form, but a lot of them exist in suspension and only a few are colloids [5].

Physical, physicochemical and biological methods can be applied to purification of tannery wastewaters [1-3,7]. The most common physicochemical method used for purification, after physical treatment and pH correction, is coagulation by Fe and Al salts. This method is sometimes preceded by aeration in order to remove sulphides [3]. Instead of coagulation, electrocoagulation with iron anodes [3] or flotation and electroflotation can be applied, too [1].

Efficiency of tannery wastewaters pretreatment by coagulation significantly influences their final purification result. There are a number of studies focused on efficien-

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cy of the coagulation process with different salts. Talinli [8] stated that coagulation with high doses of lime assisted by non-ionic polyelectrolyte at pH 11 resulted in a 63% reduction of COD value (initial value 8200 mg) l O_2). Coagulation with $FeCl_3$ + lime at pH 8.8 reduced COD only by 43%. When this process was carried out under the same conditions with $Al_2(SO_4)_3$ reduction of COD was 47%. Results received from coagulation by Al and Fe salts but without lime addition were even lower [9].

Garrote et al. [9] conducted studies on the coagulation of tannery wastewaters (COD about 2500 mg/l O_2) with $FeCl_3$ and lime, without adding polyelectrolyte, at pH 8.5. A one-step coagulation with one big dose of $FeCl_3$ (100 mg/l) resulted in 82% COD reduction. When the dose of coagulant was bigger, reduction was lower. When the process was repeated under the same conditions the reduction of COD increased to 86%, but the third repetition improved the result insignificantly.

After coagulation (flotation) wastewaters are purified using biological methods (usually by active sludge). Such a three-step purification process not always brings desirable results. Sometimes the fourth step (adsorption on the organic carbon) must be applied, which results in removing 70-95% of remaining organic compounds [3].

Ozonation as a pretreatment process before biological purification has been studied intensively in recent years. Jochimsen et al. [10, 11] found out that the three-step process (biological purification – ozonation – final biological purification) brings the best results in the reduction of COD. During the first biological purification the majority of biodegradable components were removed, which resulted in reduction of ozone demand in the second step. Ozonation resulted in further reduction of organics contest, abatement their molecular mass and toxicity – improving their biodegrability.

Advanced oxidation processes (AOPs), based on the generation of hydroxyl radicals, are an increasingly popular method applied to the purification of many industrial effluents [12, 13]. Among many publications covering this subject no one devoted to tannery wastewaters has been found. This study aims to fill this gap.

The AOPs are perceived to be expensive. That is why they are often applied together with other methods. When the effluents contain hardly biodegradable organic substances, AOPs are used as a pretreatment step (before biological purification) or as a final step after phisicochemical treatment [12]. In this study the AOPs were the second step of the whole purification process and they were applied after coagulation.

Materials and Methods

After 3 hours of the sedimentation, wastewaters were subjected to the following processes:

- coagulation by $FeCl_3$ with pH correction (by NaOH solution) and flocculant addition
- electocoagulation with an iron electrode
- coagulation followed by AOPs (Fenton reaction, ozonation at pH 12.8 (O_3/OH^-), O_3/H_2O_2 and H_2O_2/UV methods.

Table 1. The composition of examinated wastewaters.

		Wastewaters			
		A	B	C	D
pH		6.75	8.8	7.5	7.7
Conductivity	µS/cm	5700	11020	14566	12950
Suspended solids	mg/l	72	140	390	389
Chlorides	mg/l Cl	3120	3600	4730	2860
Sulphates	mg/l SO_4	3200	4300	4900	3670
Ammonium nitrogen	mg/l N	142	608	404	274
Nitrite nitrogen	mg/l N	0.04	0.7	0.11	0.23
Nitrate nitrogen	mg/l N	1.0	1.1	1.4	0.9
Total nitrogen	mg/l N	172	785	505	354
Ortophosphates	mg/l PO_4	1.6	1.8	2.2	2.0
COD	mg/l O_2	2149	3920	2720	2417
BOD_5	mg/l O_2	696	-	904	720
Sulphides	mg/l S	27.2	143	9	18
Tanins	mg/l	-	-	20.2	11.8
Aninic surfactants	mg/l	21.2	20.0	134	43

The characteristics of wastewaters used in these studies are shown in Table 1.

Doses of $FeCl_3$ ranged from 100 to 800 mg/l. In this experiment polialuminium chloride and the following flocculants: Zetag 101, Zetag 48, Zetag 8, Magnofloc 156, Magnofloc 333, Magnofloc 336, at doses: 0.5 mg/l, 1.0 mg/l, 2.0 mg/l, were used. The effects of coagulation were evaluated after 1 h.

Wastewaters A, B and C were subjected to electocoagulation in plexiglass cuboid cell 200x120x70 mm. Two 10×10 cm electrodes were placed near the walls and the following current densities were applied: 0.5, 1, 2, and 3 A/dm^2. During this process the turbidity and COD were determined. When the solution became clear, the electrolysis process was disrupted and 1.0 mg/l Magnofloc 336 was added as a floculant. The solution was slowly stirred for 30 minutes and then sedimented for 2 h.

The studies on AOPs were conducted with wastewaters C and D, which were previously coagulated by $FeCl_3$ at optimal doses.

In the Fenton reaction at pH 3.5, Fe^{2+} was applied in concentrations: 500, 1000 and 1500 mg/l and doses of H_2O_2 were: 3000, 3500 and 4000 mg/l, respectively. The process O_3/H_2O_2 was carried out in a glass, cylindrical, one-litre reactor. Ozone was supplied at the constant flow rate – 400 mg/h. Doses of H_2O_2 were: 1200, 1500 and 1800 mg/l. The process H_2O_2/UV was carried out in a one-litre Heraeus photoreactor with a low-pressure mercury lamp (15 W, 254 nm). Doses of H_2O_2 were: 3000, 3500, 4000 and 4500 mg/l. These processes were monitored by COD, BOD_5, pH and H_2O_2 determination. In the Fenton process also Fe^{2+}concentration was measured after 30 and 240 minutes reaction time.

During the ozonation process, gases coming out from the reactor were absorbed in the KJ solution to determine ozone leaving the reactor. In O_3/OH^- process a scrubber with 0,1M HCl solution was used to determine the amount of NH_3 blown out.

Samples C and D (raw wastewaters, wastewaters after coagulation and wastewaters after coagulation followed by H_2O_2 /UV method) were subjected to GC-MS analysis. Hewlett-Packard 5890II/5971 gas chromatograph with HP-1, 24-m capillary column (0.2 mm i. d. and 0.33 µm dimethylopolisiloksan film thickness) was used. The column temperature was programmed at 5°C /min from 35°C to 310°C and then held for 15 min. Mass detector worked in a mode SCAN at 250°C for mass range 20 – 570 amu. Organic components were semi-quantified by comparing the integrated peak area of quantification ion with that of the pristan (0.5 mg/l). Wastewater samples (200 ml) were extracted using dichloromethane (15 + 10 ml) at pH 8 and pH 2. Before extraction, 0.1 µg of pristane (2,6,10,16 tetramethylopentadecan) in dichloro-methan solution was added to each sample. The extract was dried by anh. Na_2SO_4 and concentrated to ~5 ml. All samples from wastewater D had to be derivatized by diazomethane before GC analysis.

Results

Coagulation and Electrocoagulation

For wastewater A the best effect of coagulation was observed with $FeCl_3$ dose of 300 mg/l, without flocculant addition, at pH 8.6. At the initial pH 9.0 this effect was slightly worse. In order to improve the coagulation efficiency of wastewater B the two-step coagulation process was performed (the result of coagulation $FeCl_3$ in dose 800 mg/l with flocculants was not satisfactory). The best effect was observed when the process was carried out with $FeCl_3$ in doses 600 + 200 mg/l and Magnofloc 336 (2 mg/l) as an anionic flocculant. Zetag 101 (cationic) and Magnofloc 333 (non-ionic) brought slightly worse effects.

The best coagulation efficiency took place at doses of $FeCl_3$ (Mgnofloc 336: 600/2 mg) l for wastewaters C and 400/2 mg/l for wastewaters D. In every sample, all sulphides were precipitated.

Selected results of coagulation and flocculation are presented in Table 2. Final BOD_5 values, which are not placed in this table, are, respectively: 455 mg/l O_2 for wastewaters A (reduced by 34.6%), 590 mg/l O_2 for wastewaters C (reduced by 34.7%) and 455 mg/l O_2 for wastewater D (reduced by 38.2%). The addition of coagulant also caused an increase in chloride concentration and solution's conductance.

The following conclusions can be drawn from these results:

- The coagulation/flocculation effect depends first of all on a quality of suspended matter and colloids. Wastewater B contained less suspended matter than wastewaters C and D but particles were finer.
- The efficiency of the coagulation process was slightly affected by flocculants and also did not depend on the quantity of polyelectrolytes. It probably results from the fact that wastewaters contain particles: both positively and negatively charged.
- The lower drop in BOD_5 value compared to COD is caused by the fact that in the coagulation process the less biodegradable substances are removed more effectively. For less biodegradable components the ratio BOD_5/COD is lower than for substances which are easily biodegradable.

Table 3 presents the summarized results of studies on electrocoagulation process in optimal times for each current density. The final BOD_5 values, for conditions considered to be optimal, were: 435 mg/l O_2 for wastewater A (37.5% drop) and 577 mg/l O_2 for wastewater C (36.2% drop). Reactions are featured by equations 1, 2 and 3:

$$Fe - 2e^- \rightarrow Fe^{2+} \tag{1}$$

$$Fe^{2+} + 2OH^- \rightarrow Fe\,(OH)_2 \tag{2}$$

$$4Fe\,(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe\,(OH)_3 \tag{3}$$

Green precipitate Fe $(OH)_2$, which was formed during electrocoagulation, floated in the majority. Moreover, Fe $(OH)_2$ was oxidized to Fe $(OH)_3$ and settled down.

The following conclusions can be drawn from these results:

- COD drop in wastewaters after electrocoagulation followed by sedimentation in comparison to wastewaters only after electrocoagulation could be explained by equations 1, 2 and 3.
- Efficiency of electrocoagulation of wastewaters A and B was slightly better compared to coagulation by $FeCl_3$. It is evident from the COD and BOD_5 values. In contrast, for wastewater C a decline in COD after electrocoagulation was slightly lower than one noticed after coagulation.

Table 2. Results for wastewaters after coagulation with $FeCl_3$ solution.

Wastewater	Dose of $FeCl_3$ mg/l	Dose of Magnofloc 336 mg/l	COD mg/l O_2	COD decrease %	Suspended solids mg/l	pH
A	200	0	824	61.7	15	5.85
A	250	0	789	63.3	5	5.95
A	300	0	784	63.5	5	5.80
B	500	0	1890	54.3	40	6.05
B	600	0	1855	55.1	36	5.95
B	600	2.0	1740	55.6	31	6.0
B	600 + 150	2.0 + 1.0	1695	56.8	19	6.10
B	600 + 200	2.0 + 1.0	1661	57.6	9	6.0
B	600 + 250	2.0 + 1.0	1660	57.7	10	6.15
B	700 + 200	2.0 + 1.0	1680	57.1	11	6.10
B	600 + 200	2.0 + 1.0 *	1705	56.5	13	6.00
B	600 + 200	2.0 + 1.0**	1710	56.4	15	6.00
C	500	2.0	769	71.7	19	6.55
C	600	2.0	708	74.0	12	6.35
C	700	2.0	705	74.1	10	6.25
D	300	2.0	790	67.3	14	6.15
D	400	2.0	770	68.1	12	6.25
D	500	2.0	770	68.1	16	6.25

* – Zetag 101 used, ** – Magnofloc 333 used.

Table 3. Summary results for wastewaters after electrocoagulation (E) and after electrocoagulation followed by sedimentation (E-S).

Wastewater type	Current density A/dm^2	Time min.	COD mg/l O_2 (E)	pH	COD – mg/l O_2 (E-S)	COD decrease – % (E-S)	Voltage – V
A	0.5	30	685	9.0	660	69.3	2.6
A	1	10	680	8.4	658 *	69.4	4.0
A	2	8	690	8.5	690	67.9	7.1
B	1	60	1750	9.6	1550	60.5	3.7
B	2	30	1744	9.3	1518 *	61.3	6.6
B	3	30	1724	9.8	1522	61.1	8.9
C	1	30	760	9.1	742	72.7	3.8
C	2	15	755	9.1	734 *	73.0	6.7
C	3	10	765	9.0	750	72.4	9.0

* – conditions recognized as optimal

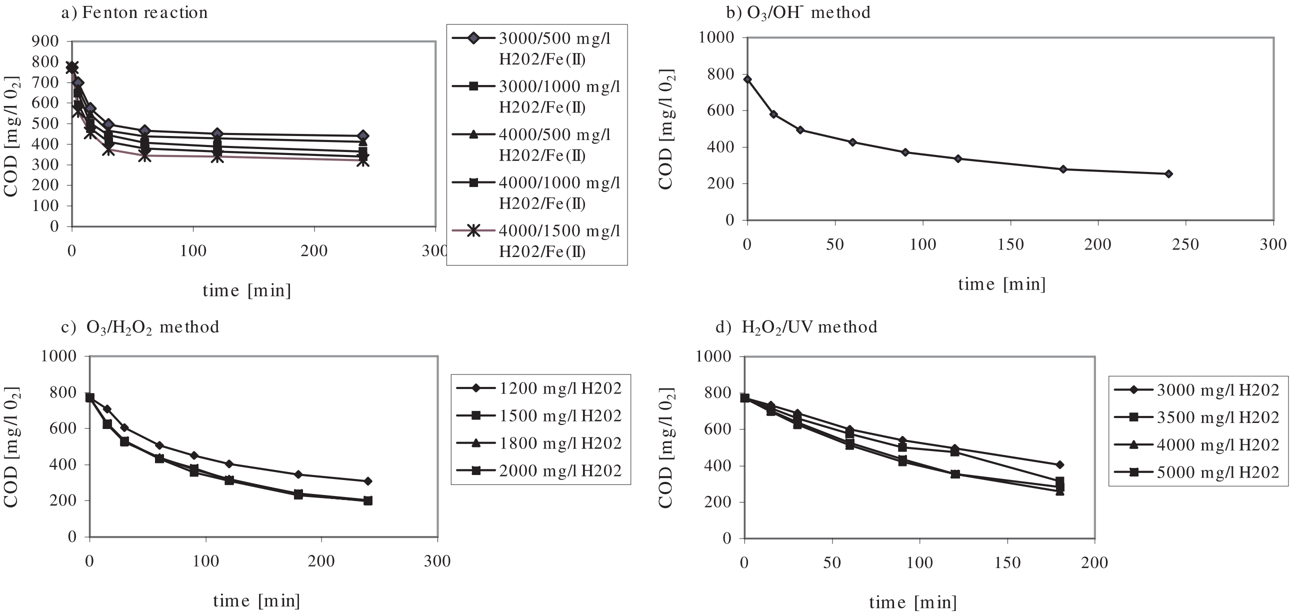

Fig. 1. Comparison of decrease of COD for wastewaters D during purification by different AOPs.

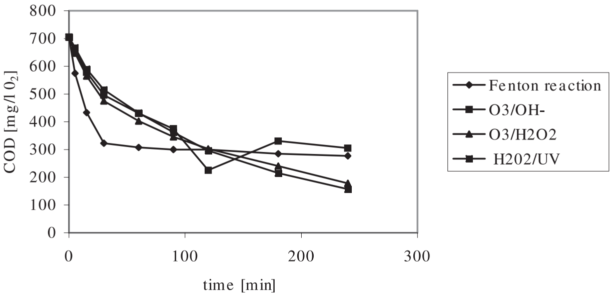

Fig. 2. Comparison of decrease of COD for wastewater C during purification by different AOPs, conducted in optimal conditions.

- The electrocoagulation process required a much greater amount of Fe than coagulation by $FeCl_3$. This amount was calculated by assuming that 96.5 Coulombs corresponded to 27.9 mg Fe^{2+} formation and that no other process took place on the anode. The amount of Fe^{2+} formed in electrocoagulation of wastewaters A, B and C at optimal conditions was, respectively: 173, 1042 and 521 mg/l Fe.
- An inconsiderable change in pH value in the case of electrocoagulation proves that anodically generated Fe^{2+} ions neutralized the catodically generated OH^- ions throughout Fe $(OH)_2$ precipitation in accordance with equation 2. In the case of wastewater B pH value increased more, which was caused by the greater amount of precipitated FeS. The oxidation and precipitation of remaining Fe^{2+} ions resulted in a 0.8 drop in pH value.

Advanced Oxidation Processes (AOPs.)

Fig. 1 presents relationship COD vs. time for all runs and methods for wastewater D. Fig. 2 depicts the same relationship for wastewater C but only for optimal doses of reagents. In Table 4 all results are summarized.

The following doses of reagents for wastewaters C and D were recognised as optimal: Fenton reaction (H_2O_2/Fe^{2+}) – 4000/1000 mg/l (for wastewater C) and 4000/1500 mg/l (for wastewater D), O_3/H_2O_2 method – 1500 mg/l and 1500 mg/l, H_2O_2/UV method – 4000 mg/l and 4000 mg/l. Extension of those doses didn't result in better efficiency.

The following conclusions can be drawn from these results:

- The efficiency of all methods was quite good. For 240 min. reaction time, the efficiency of the process was getting lower in the order: H_2O_2/UV> O_3/H_2O_2> O_3/OH^-> Fenton reaction.
- For a short time (30 min), this order was different. Fenton reaction proved to be the most effective process and the lowest efficiency was observed for H_2O_2/UV method. This lowest efficiency of H_2O_2/UV process could be excused by the presence in solutions fine suspension, which absorbs UV radiation. In the course of the process organic suspended solids underwent oxidation, which resulted in an increase of UV radiation penetrability and consequently the efficiency of H_2O_2/UV method was improved.
- Wastewaters purification by the Fenton reaction proceeds in two steps. The first stage was quicker than for other oxidation processes, while in the second stage the reaction speed was low. This was observed for all doses of Fe and H_2O_2 and could be explained by a very a quick reaction of hydroxyl radicals formation in the first stage (1) and inhibition of regeneration of Fe^{2+} in the second stage (2, 3), proved by the low concentration of Fe^{2+} (<20 mg) l) after 30 and 240 min of reaction time.

Table 4. Summary results of wastewater purification by AOPs conducted in optimal conditions.

Process	COD decrease after 30 min %		COD decrease after 240 min %		Total COD decrease after coagulation and oxidation %		BOD_5 decrease % oxidation/total	
	C	D	C	D	C	D	C	D
Fenton reaction	54.0	51.7	60.6	57.9	89.8	86.6	79.0/86.3	73.0/83.4
O_3/OH^-	30.1	29.5	63.7	63.7	90.6	88.4	75.5/84.0	75.7/85.0
O_3/H_2O_2	32.4	31.7	75.0	75.0	93.5	92.0	88.4/92.4	88.0/92.6
H_2O_2/UV	27.0	20.7	77.7	78.0	94.2	93.0	88.7/92.6	89.2/93.3

Table 5. Results of GC-MS: raw wastewaters (C), wastewaters after coagulation (C-k) and wastewaters after coagulation followed by H_2O_2/UV oxidation method after: 30, 120 and 240 min (respectivly: C-kH30, C-kH120 i C-kh240). Concentration in µg/l.

Compound	C	C-k	C-kH30	C-kH120	C-kH240
Isovaleric acid	700	640	510	410	277
Phenyl malonic acid	540	282	190	115	47
2-hydroxy-2-methyl propionitryle	170	92			
Benzyl malonic acid	160	75			
1-(2-methylpropoxy)-propanol-2	124	82			
Ethyl propyl ketone	80	60			
4-methylvaleric acid	70	71			
Dibuthyl phtalate	69	29	48	18	
Cyklohexane carboxylic acid	68	42			
Lactic acid	44	38	62	44	58
Palmitic acid	38	15			
1,2,3,4,4a,10,10a-oktahydro-1-phenanthrenecarboxylic acid	38	32			
Octadecanoic acid	36	33			
Isobutyric acid	28	25			
2,6,10-dodecatrienol	26	19			
Diisoocthyl phtalate	22	14			
Benzoic acid	20	10			
Hydroxybuthyl acetate	11	9			
2-ethyl caproic acid	10	7			
Caproid acid	10	4			
5-octylodihydro-2(3H)furanone	8	5			
Ethyl propyl keton			88	140	122
2,2-diethoxyethane			76	88	80
3-methyl butanol			68	28	12
Butyl methyl keton			24	60	10
Izopropyl propyl ether			18	39	10
3-hydroxybutanone-2			6	30	22
2,2-dietoxyethanol				20	36
Isoamyl alcohol				10	

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\bullet} \quad (4)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OH^{\bullet}_2 + H^+ \quad (5)$$

$$Fe^{3+} + HO_{2\cdot} \rightarrow Fe^{2+} + H^+ + O_2 \quad (6)$$

- BOD_5 values decreased much more than COD values in all processes, meaning that the oxidation processes lead to the formation of products of lower average biodegradability. However, the summary drop in COD and BOD_5 (83.4-93.3%) noticed at the end of the process, is comparable and was due to a greater drop in COD value during coagulation.
- The BOD_5/COD ratio (similar to the BOD_5/COD ratio for raw wastewaters) and high BOD_5 value in tannery wastewaters treated by AOPs prove that examined wastewaters after purification still contained biodegradable organics and biological purification methods can be employed.

No decrease of ammonium ion concentration was observed in the Fenton process. In the H_2O_2/UV method this drop was only 8%, while the ozonation at pH 12.8 gave a considerable drop in ammonium ions. In wastewaters C, the summary reduction of NH_4^+ concentration, noticed after 240 min ozonation, was 64% (37% of ammonium ions were oxidized and 27% were blown out from the solution). For wastewater D those values totalled 62% (37 and 25%).

The final nitrates (V) concentration after ozonation at pH 12.8 was 135 and 95 mg/l N for wastewaters C and D, respectively. It shows that 89.3% and 92.4% ammonia were transformed into nitrates (V):

$$3NH_3 + 4\,O_3 \rightarrow 3HNO_3 + 3H_2O \quad (7)$$

The decrease in pH value during this process was bigger than those expected from equation (4). It was caused by the generation of carboxylic acids, which was confirmed by GC-MS studies.

In all processes, where H_2O_2 was applied final concentration of this compound (the process was carried out in optimal conditions) ranged from 23 to 154 mg/l. When the initial concentration of H_2O_2 was lower, the drop in COD value was smaller, but the final concentration of H_2O_2 also was not so high.

GC-MS Studies

Compounds identified in wastewaters C and D (Tables 5 and 6) differ considerably. In both samples, dibutyl phthalate concentration was quite high. In wastewaters C, the summary concentration of impurities was about 2.3 mg/l, and the domination of carboxyl acids suggests that the biological oxidation of former organic contaminants was advanced. In wastewater D, the total concentration of organics identified was slightly lower (2.0 mg/l), but compounds containing nitrogen were in the majority – indol and five derivatives of pyridine. However, phenols were in the highest concentration. Indol, which is a product of protein fermentation, indicates a great advance in anaerobic degradation. The presence of 4-nonylphenol and 4-dodecylphenol probably resulted from the degradation of non-ionic surfactants.

The abatement of identified organics concentration achieved by coagulation was lower than the COD abatement. It could be expected, because in coagulation molecules with larger molecular weight (which cannot be detected by GC-MS) are more readily removed.

The tannery wastewater treatment by AOPs leads to the gradual oxidation of pollutants and to the generation of new compounds e. g. carboxylic acids, ethers, kethons and alcohols. That results in a great reduction of particular impurities' concentration and in their summary quantity. This reduction is close to abatement of COD value.

Discussion and Conclusions

Results of the investigations on tannery wastewaters treatment by coagulation – flocculation presented in this study are generally consistent with the results obtained by Garrote et. al. [9]. Optimal doses of coagulants vary widely due to large differences in concentrations of pollutants.

Results of the application of AOPs to tannery wastewater purification cannot be compared to other results, because no other bibliography concerning this subject has been found. But some searches on ammonium ions' removing efficiency using O_3/OH^- method were carried out by Hoigne and Bader [12]. They stated, that oxidation of ammonium ions by ozone at pH below 9 was slow. When pH value is higher, free ammonia is formed, which is almost completely (95%) oxidized to nitrates (V). Those results are slightly higher than those presented in this study. The rate of this process is proportional to the concentration of ozone and ammonia – the reaction is the second order one.

The effect obtained by electrocoagulation seems to be a little better in comparison with that obtained by coagulation. However, the results are equivocal. The unquestionable advantage of electrocoagulation is the lack of an increase in salinity – no reagents are added. On the other hand, coagulation by $FeCl_3$ is simpler.

The two-step purification – coagulation by $FeCl_3$ with polyelectrolyte and then one of the AOD method results in a very effective reduction of organic compounds (exceeds 90% COD and BOD_5).

Of four examined oxidation processes, the 30 min. Fenton reaction seems to be the most advantageous – satisfactory effect of organics removal, short reaction time, low price of equipment and energy.

After two-step treatment (coagulation + Fenton reaction) a quality of tannery wastewaters is still not acceptable. The purification should be continued using biological methods, including nitrification and denitrification. The COD (BOD$_5$ ratio in wastewaters after the two-step process and in raw solutions proved that treated ones still contain biodegradable organic compounds.

The effect of the two-step treatment presented in this study (coagulation and AOPs process) can be compared to the results obtained by coagulation and electrooxidation [13]. The same samples of wastewaters were treated by coagulation and then oxidated on Ti/SnO$_2$/PdO$_2$/RuO$_2$ anode (current density 2 A/dm^2). The experiment conducted for 43-47 minutes resulted in 82-84% COD reduction and the total elimination of ammonium ions.

Table 6. Results for GC-MS raw wastewaters (D), wastewaters after coagulation (D-k) and wastewaters after coagulation followed by H_2O_2/UV oxidation method in 240 min reaction time (D-kH).

Compound	D	D-k	D-kH
p-cresol	283	166	
Phenol	237	160	
Dibuthyl phtalate	158	104	31
Pyridine	149	100	
Lentionine	139	68	
2-bis(1.1-dimethyl etyl)phenol	135	48	
Cholesterol	116	40	
Indole	112	65	
4-nonylphenol	96	52	
4-dodecylphenol	94	46	
4-(1,1,3,3-tetramethylbutyl)phenol	91	35	
Cyklohekseno-3-methanol	88	58	8
4-(2,2,3,3-teramethylobutyl)phenol	75	40	
2-etenyl benzofurane	58	39	10
2-methylpyridine	54	38	
3.5-dimethylpyridine	52	32	
Aniline	38	31	
3-methylpyridine	30	24	
2,6-dimethylpyridine	52	12	
Butyric acid			35
Izovalerenic acid			34
3-methoxybuthanol-1			32
Tetrahydro-2H-pyranone-2			28
Malonic acid			17
Methylmalonic acid			15
Ethyl propyl ketone			15
1-methoxybutanone			14
Ethyl buthyl ketone			13
Lactic acid			10
Isoamyl alcohol			8
3-hydroxybutanone-2			6

Concentration in μg/l.

Conclusions

The process of tannery wastewater treatment by coagulation and coagulation with $FeCl_3$ followed by advanced oxidation processes (AOPs) is described. The purification effect obtained by AOPs decreased in the order: H_2O_2/UV> O_3/H_2O_2> O_3/OH^-> Fenton reaction. The two-step process – coagulation + H_2O_2) UV method allowed to reduce the COD value by 93-94%. The ammonia concentration was reduced by 62-64% by the O_3/OH^- method. The two-step purification-coagulation + 30 min. Fenton reaction was considered the optimal process for tannery wastewater purification – COD value was reduced by 85-88%.

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