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TOXICITY REDUCTION IN LEATHER TANNING WASTEWATER BY IMPROVED COAGULATION FLOCCULATION PROCESS

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ABSTRACT

The wastewater of leather industry which is one of the most widespread industries having large amount of water consumption and very high pollution loads, may be characterized by several key parameters including toxic pollutants exhibiting toxicity. Therefore the effluent of leather tanning industry must be handled carefully during both treatment plant design and operation.

The aim of this study was to improve the coagulation process for toxicity reduction of raw wastewater taken from a leather tanning district central treatment plant (Solofra, (Avellino, Southern Italy). A series of jar test experiments on three samples taken between February and July 2005, were performed using ferric chloride, ferrous chloride, aluminium sulphate and poly-aluminium ferric chloride (PAFC).

The optimum coagulation conditions for the first sample were determined as 8.5 pH and 900 mg l^{-1} dose of PAFC with the addition of $Ca(OH)_2$ which resulted in a 76% COD and 98% TSS removal and more than 50% of *D. magna* immobilization (at 50% dilution) reduction. Coagulation experiments performed on second and third samples showed that PAFC resulted in the highest COD removal among the coagulants tested The results that PAFC, recently developed coagulant, is the most promising one for leather tanning wastewater, thus, improved coagulation followed by biological treatment can result in safe effluent to aquatic environment.

KEYWORDS: leather tanning industry, coagulation process, poly-aluminium ferric chloride (PAFC), ferric chloride, aluminium sulphate, ferrous chloride, toxicity removal, *Daphnia magna*

1. INTRODUCTION

Italy produces more than 50% of European leather demand with 190 millions of m^2 per year, corresponding to 1.050.000 t per year of skin [1]. The transformation of raw or semi-pickled skins into commercial products requires high water consumption and the use of many chemical products. Therefore, leather tanning industry is classified with high organic loads and priority pollutants such as sulphite, chromium, synthetic tannins (Syntan), biocides [2, 3]. Coagulation-flocculation (CF) process, generally using inorganic coagulants such as aluminium sulphate (alum), ferric chloride ($FeCl_3$), ferrous sulphate ($FeSO_4$) has been applied to leather tanning wastewater to reduce organic load and suspended solids as well as to remove toxic substances, e.g. chromium before biological treatment. Ates *et al.* [4] investigated the effectiveness of alum and $FeCl_3$ based-CF for the treatment of homogenized inlet of a central treatment plant of leather tanneries district. All experiments resulted in >70% of COD removal. Total chromium was also effectively (<5 mg l^{-1}) removed by alum while it was almost completely removed using $FeCl_3$ as seen in Table 1. Kabdasli et al. [5] also reported 40-70% removal of COD and >99% of total chromium from leather tanning wastewater using $FeSO_4$, $FeCl_3$ and alum. Song et al. [6] obtained a removal range of 30-37% of total COD, 74-99% of chromium and 38-46% of SS using 800 mg l^{-1} of alum at 7.5 pH for pre-settled tannery wastewater containing 260 mg l^{-1} of SS, 16.8 mg l^{-1} of chromium, 3300 mg l^{-1} of COD at 9.2 pH. They reported that $FeCl_3$ proved better results than alum.

Table 1. The chemical settling of an homogenized raw wastewater from an organized leather tanning district [4]

Coagulant	Dose (mg l^{-1})	pH	COD (mg l^{-1})		Total Cr (mg l^{-1})	
			Initial	final	initial	Final
Alum+polyelectrolite	600+2	7.5	6145	1085	198	4.50
Alum+ polyelectrolite	400+2	8.5	4185	950	133	1.54
$FeCl_3$+ polyelectrolite	1000+2	8.1	4980	1140	135	<0.5
$FeCl_3$+ polyelectrolite	750+2	9.2	4650	1195	125	<0.5

Although a big part of the pollutants are removed by pre-coagulation and biological process is able to absorb the toxicants, nitrification process may still be influenced by the presence of bio-inhibitors at low levels [2]. Thus, advanced oxidation processes (AOPs) such as UV, ozone (O_3), pohotocatalytic oxidation and their combination [7,8], and Fenton reagent [8] have been used as pre-oxidation or post-oxidation of tannery wastewater [9]. However, due to high costs of these processes, CF still remains the more widely used one at present [6].

A number of toxicity monitoring and removal studies have been performed on leather tanning wastewater including acute toxicity on *Vibrio fisheri* , *Daphnia magna* [2, 10-11], sea urchins and marine algae [12].

The efficiency of CF is mainly influenced by raw wastewater characteristics, pH, temperature, coagulant type and dose and mixing velocity [13-15]. To improve the coagulation efficiency as well as to minimize residual coagulants in the effluent [16], new types of coagulations have been developed such as poly aluminium chloride (PAC), poly aluminium silicate (PASiC) and poly aluminium ferric chloride (PAFC) ($[Al_2(OH)_nCl_{6-n}]_m$.$[Fe_2(OH)_nCl_{6-n}]_m$) [17-18]. It was reported that PAFC gives better turbidity removal performance in the range of pH from 7.0 to 8.4. PAFC gives also good colour removal performance on suspension dyes and the actual wastewater. Therefore, PAFC is a high-effective and stable water treatment agent [18].

To our best knowledge, PAFC has not been applied for treatment of tannery wastewater except the CODISO tannery wastewater treatment plant (Avellino, Italy) where this study was performed. Because the previous results evidenced that coagulated samples displayed a severe toxicity on sea urchins and marine algae in CODISO treatment plant [12], this complementary study has been performed to enhance the coagulation efficiency as well as to compare the efficiency of PAFC with ferric chloride, ferrous chloride, aluminium sulphate on samples taken from the effluent of equalization basin (EQ) of the CODISO. Toxicity of raw and coagulated samples was monitored using *Daphnia magna* which is one of the bioassays referred by Italian Water Quality Discharge limits [19].

2. MATERIALS AND METHODS

2.1 Sampling site

In the Solofra district, the leather tannery wastewater is treated in a centralized wastewater treatment plant (CODISO) that receives wastewater from approximately 140 factories mostly producing leather for clothing, shoes and tapestry from goat and cattle skin. More than 3000 types of chemicals are used in the tanning process. These factories mostly work on semi-pickled and de-haired leather. The CODISO receives an inflow of 8,000 m^3 d^{-1}, and consist of an equalization basin followed by a coagulation and flocculation process and biological nitrification. Around 1000 mg l^{-1} of (PAFC) is currently used as coagulant and an anionic polyelectrolyte (1 mg l^{-1}) as flocculant in the treatment plant [12]. pH is adjusted over 8.5 using $Ca(OH)_2$ to remove effectively chromium.

2.2. Sampling and conservation

The samples were delivered to the laboratory in 1 h for chemical analysis and acute toxicity tests. The samples were kept refrigerated at +4 ^{0}C during analysis.

2.3. Jar tests

A series of Jar-test experiments were performed on raw wastewater applying 2 min rapid mixing (RM) at 100 rpm, 20 min slow mixing (SM) at 30 rpm and 30 min settling at three pH values (8.0, 8.5, 9.0 using NaOH or $Ca(OH)_2$ of 5 g l^{-1} solution).

CF experiments were performed using PAFC and comparatively with ferric chloride, ferrous chloride, aluminium sulphate and anionic poly-acrylamide-based flocculant (2 mg l^{-1}, Bierrechimica, Italy) which is currently used in the treatment plant. The dose of the coagulants was varied from 800 to 1200 mg l^{-1}. All experiments were performed at room temperature (20-25 ^{0}C).

2.4. *Daphnia magna*

The toxicity of raw and coagulated wastewater was measured using 24 h *D. magna* with and without and 50% dilution [20] to evaluate the influence of wastewater characteristics. For instance, there was found a positive relation between conductivity and juvenile daphnids mortality [21] while over 25 mg l^{-1} ammonia exhibited 50% of immobilization of daphnids [22].

Toxicity tests were performed quadruplicate using 5 daphnids in each test beaker with 100 ml effective volume. New born daphnids were grown in the laboratory at 16 h day light and 8 h dark periods supplying a 3000 lux illumination. They were fed with *Selenastrum capricornutum* (300.000 cells ml^{-1}) and baker's yeast (*Schizosaccharomyces cerevisiae*, 200.000 cells ml^{-1}). Room temperature was kept at 20^{o}C ± 1^{o}C and a minimum 6 mg l^{-1} of dissolved oxygen was supplied by air filtered through activated carbon. All solutions were prepared using bi-distilled water at pH 8.0. Results were expressed as a percentage of immobilised animals after 24 h.

2.5. Chemical analysis

All parameters representing the typical characteristics of leather tanning industry and treatment efficiency of chemical and biological treatment were measured according to Standard Methods [23] in the CODISO and University of Salerno laboratories. A Whatman GF/C filter paper with 1.2 µm pore size was used for total suspended solids (TSS) measurement and effluent COD analysis. BOD_5 was measured without adding any seed (OXI TOP, ISCO, Italy). Influent COD was measured after filtering the sample through 1.2 µm filter papers.

All chemicals used in this study were analytical reagent grade. $FeCl_36H_2O$ and $Al_2(SO_4)_3$ $18H_2O$ were obtained from Carlo Erba (Italy). Ferrous chloride and PAFC(PAF 180) were obtained from Chimpex Industries S.p.A. (Italy). The characteristics of PAFC are given in Table 2.

Table 2. Characteristics of PAFC

Characteristics	Value
Appearance	Green
Odor	Pungent
Density 20^{0}C	1.270-1.320 g ml^{-1}
pH 20^{0}C	2-2.5
Fe^{2+}	60-80 g l^{-1}
Al_2O_3	7.0-9.0%

3. RESULTS AND DISCUSSION

3.1. Toxicity and wastewater characterizations

According to statistical evaluations of inlet and outlet concentrations of COD and TSS parameters of the CODISO during 2002-2003 period, the average inlet COD and TSS concentrations were 7020 and 1520 mg l^{-1} respectively [24]. These values were in accord with the literature [4]. The average influent chromium (III) concentration was reported as 140 mg l^{-1} for the same period [12]. The average outlet values of both parameters (450 mg l^{-1} COD, 150 mg l^{-1} TSS) hardly complied with the sewer discharge limits (COD< 500 mg l^{-1}, TSS< 200 mg l^{-1} [19]). In that period, raw (R), coagulated (CF), biological effluent (B) wastewater samples and the conditioned sludge (CS) taken from the CODISO showed a toxicity ranking of effluents as CS > CF ≥ R >> B on sea urchins and marine micro algae for the wastewater characteristics given in Table 3 [12]. The toxicity in CF sample was attributed to the residual Al(III) and Fe(III) considering the previous findings [25,26].

Figure 1 shows the immobilization *D. magna* exposed to the coagulated effluents at different dilutions. The samples (S1.. S6) collected between 2002-2003 displayed 100% immobilization at 50% dilution. There was a significant decrease in toxicity of only S3 at 87.5% dilution. After 93.75% dilution the toxicity of all samples decreased and at 96.25% dilution all samples displayed less than 50% immobilization.

Table 3. Characterization of the wastewater samples from CODISO treatment plant [12]

Parameter / Sample	pH	COD (mg l^{-1})	TSS (mg l^{-1})	SO_4^{--} (mg l^{-1})	NH_4-N (mg l^{-1})	Cl^- (mg l^{-1})	Al (mg l^{-1})	Fe (mg l^{-1})
R	4-5	6475-7085	1400-1800	1640-1790	56-71	2550-3050	11.36	6.69
CF	8.3-8.5	2380-2700	200-300	--	60-67	2340-3000	30-50	20-35
B	8-8.2	300-510	80-220	1000-1550	30-34	2020-2340	1-1.8	0.7-1.1

R: raw wastewater; CF: post coagulation-flocculation; B: post biological treatment

3.2. Coagulation experiments

With the scope of the improvement of coagulation efficiency and reduce the toxicity, raw wastewater samples were taken from the CODISO in February (A) and June (B and C), 2005 (Table 4). The chemical parameters and toxicity results are shown in Table 4. As expected that the difference between Total (6855 mg l^{-1}) and filtered COD (1920 mg l^{-1}) values in accord with the high TSS value (2865 mg l^{-1}) on the first sample (A). Raw wastewater displayed 100% immobilization even at 25% dilution. High ammonia concentration (70.5) contributed to the influent toxicity up to 50% dilution (35 mg l^{-1}) [22], however, the 100% immobilization at 25% dilution can be explained due to the complex mixture toxicity of various recalcitrants present in wastewater. More than 75% of COD removal was obtained at all doses and combinations of the coagulants in accord with the previous findings [4,5].

As shown in Figure 3a, there was only 2% shift in COD removal when PAFC dose varied from 800 to 1200 mg l^{-1} at 9.0 pH while the immobilization of *D. magna* decreased from 80 to 40% (Figure 3b).

As seen in Figure 4a, the PAFC and $Ca(OH)_2$ combination proved higher COD removal than PAFC use alone, and COD removal efficiency of PAFC decreased by its elevated dose (1200 mg l^{-1}) *vs* pH (Sample A). Both 900 and 1200 mg l^{-1} PAFC doses resulted in high (>70%) *D. magna* immobilization at 8.0 pH while all coagulation experiments displayed less than 50% immobilization at 8.5 pH (Figure 4b).

In accord with the higher COD removal the supernatants of PAFC+$Ca(OH)_2$ combination coagulated samples showed lesser immobilization than PAFC used alone at 9.0 pH. Increasing pH from 8.5 to 9.0 shifted COD removal at 5% more for all doses of PAFC+$Ca(OH)_2$ combination (Figure 5a) while TSS removal fluctuated and varied over 96% (Fig 5b). Considering the point that the coagulation process is followed by biological process in the CODISO central treatment plant, 8.5 pH at which all coagulation doses proved less than 50% of *D. magna* immobilization at 50% dilution was assessed the optimum one. A dose of 900 mg l^{-1} PAFC would be satisfying in terms of COD and TSS removal as well as toxicity reduction and less sludge amount compared to $Ca(OH)_2$ combination. However, both the removal of metals such chromium and Al, Fe can be enhanced by the use of $Ca(OH)_2$ although chromium was completely removed by the use of $FeCl_3$ alone in a less strong tanning effluent [4].

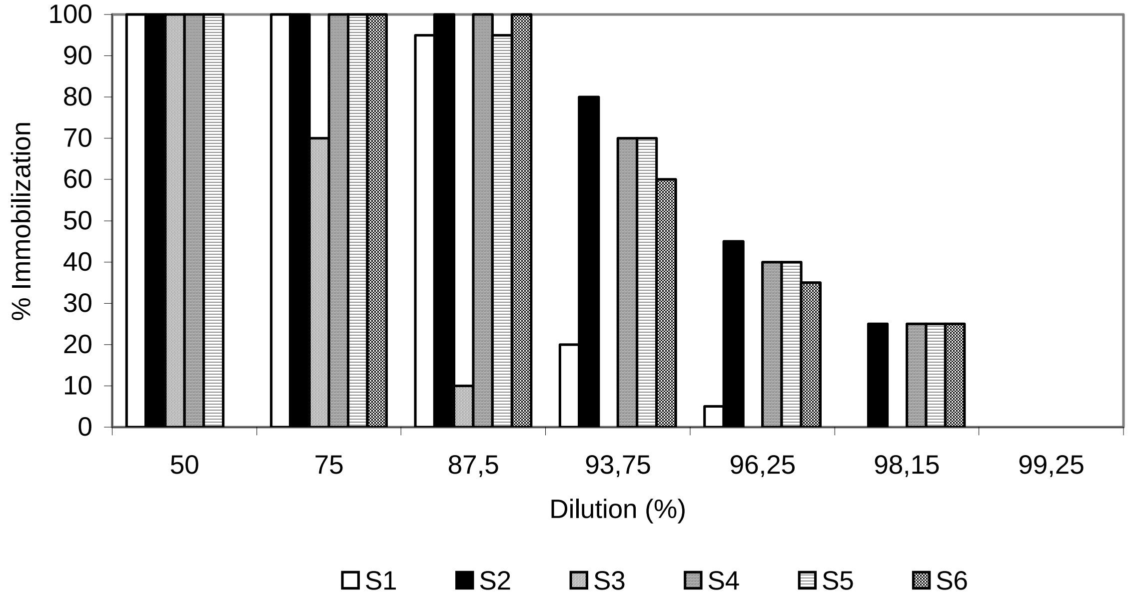
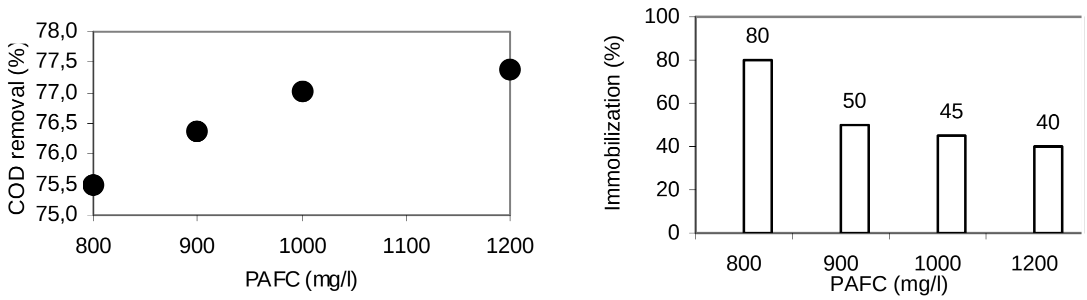


Figure 1. The immobilization of *D.magna* exposed to the effluent of the CF

Table 4. Wastewater characteristics for the samples taken in 2005 *

		A (9 February)			B (8 June)		C (23 June)	
Parameter	Unit	R+	EQ	CF	R	EQ	R	EQ
Total COD	(mg l^{-1})	6855	16465	1895	9567	12415	10410	14820
Filtered COD (1,2 µm)	(mg l^{-1})	1920						
BOD_5	(mg l^{-1})	2700	11860	65				
TSS	(mg l^{-1})	2865			3950	9200	4320	10660
Alkalinity	(mg $CaCO_3$ l^{-1})	1010		2125				
Chloride	(mg l^{-1})	2835			1985		2980	2481
Sulphates	(mg l^{-1})	745		55.8	1200	1000	750	400
Ammonia	(mgNH_4-N l^{-1})	70.5		0.50	95	95	80	81
Phosphate	(mg l^{-1})				3	2	3.4	2.0
Conductivity	(µmho cm^{-1})	8600	7.70	8.43				
pH	--	6.61				6.80	3.8	6.95

* abbreviations are the same with Table 3 (EQ: effluent of equalization basin).
+ coagulation experiments were performed on raw wastewater



(a) (b)

Figure 3. COD removal (%) (a) and *D. magna* immobilization (%) (b) of PAFC coagulated samples at 9.0 pH and 50% dilution for the Sample A

Comparative jar-test experiments using different coagulants (ferric chloride, ferrous chloride, aluminium sulphate and poly-aluminium ferric chloride (PAFC) on the second (B) and third (C) samples taken form EQ (having higher COD than Sample A due to sludge recycling in that time) during 2005 also indicated that the COD removal efficiency by PAFC was higher than the other coagulants. On the other hand, the increase in dose of the coagulants did not improve COD efficiency significantly, on the contrary at higher doses the COD removal decreased (Figures 6 and 7). Thus, 900 mg l^{-1} of PAFC is defined optimum dose for the CODISO treatment plant.

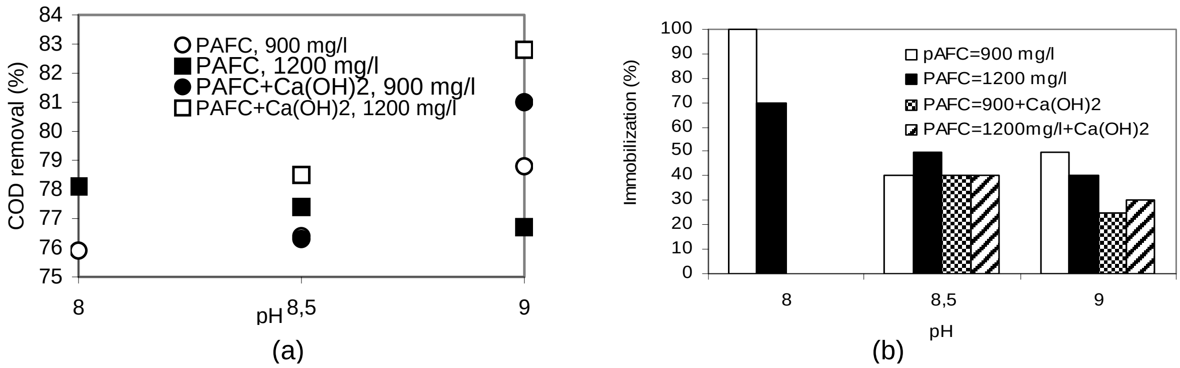


Figure 4. Comparison of COD removal (%) (a) and *D. magna* immobilization (%) at 50% dilution (b) among the coagulant doses and pH values on the Sample A

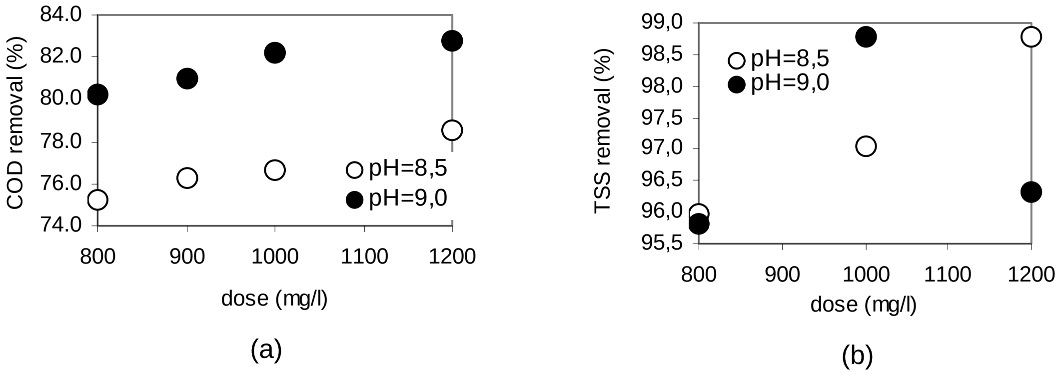


Figure 5. COD (a) and TSS (b) removal at pH 8,5 and 9,0 using PAFC+$Ca(OH)_2$ for the Sample A

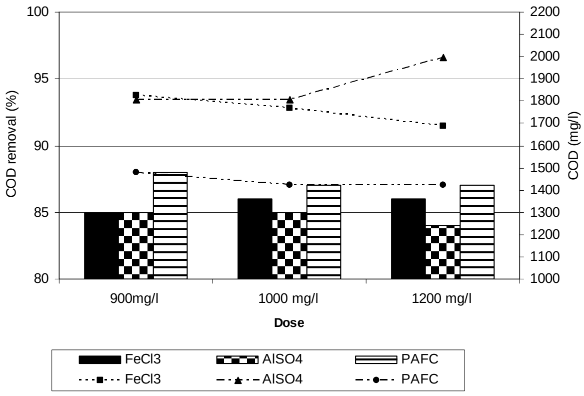


Figure 6. COD removal using different coagulants on the sample taken from equalization tank (Sample B) at pH 8,5 (pH was adjusted using NaOH)

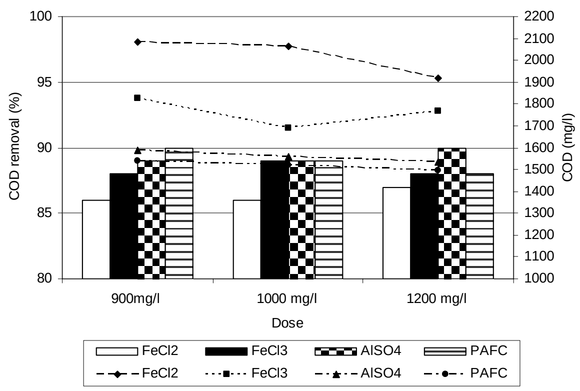


Figure 7. COD removal using different coagulants on the sample taken from equalization tank (Sample C) at pH 8,5 (pH was adjusted using NaOH)

CONCLUSIONS

This study aimed to optimize pH and coagulant dose for the wastewater originated from a leather tanning district (Southern Italy) to improve COD removal as well reduce the toxicity of the existing treatment process. Toxicity was monitored in raw and coagulated samples using *D. magna.*

The optimum conditions were assessed as 8.5 pH and 900 mg l^{-1} of PAFC with the pH adjustment by using $Ca(OH)_2$ which resulted in high removal of COD (>75%) and TSS(>95%) and reduced *D. magna* immobilization (<50%). Once the optimum conditions for PAFC was determined those were compared on two more samples by comparing different coagulants. The second series of Jar-tests also confirmed the conditions defined on the first sample.

The overall decrease in effluent toxicity following the CF effluent suggested an effective removal of toxic components from tannery wastewater, however, the policy of submitting wastewater to biological treatment before its release in receiving water bodies is necessary to reduce toxicity for protecting the aquatic environment.

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