Sigma J Eng & Nat Sci 36 (1), 2018, 261-270

Sigma Journal of Engineering and Natural Sciences
Sigma Mühendislik ve Fen Bilimleri Dergisi

Research Article

ASSESMENT OF CHEMICAL TRETABILITY OF FUR-SUEDE PROCESSING WASTEWATER TOGETHER WITH TOXICITY REMOVAL

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Received: 05.09.2017 Revised: 10.12.2017 Accepted: 15.02.2018

ABSTRACT

The aim of this study was to assess the conventional coagulation/flocculation treatability efficiency and the toxicity effect of chemically treated effluent on *Daphnia magna* for fur-suede processing wastewater. Three different conventional coagulants ($FeCl_3$, Al_2SO_4, $FeSO_4$) were used in this study and the best treatability conditions (coagulant type and dosage) were determined based on COD and Color removal efficiencies. After then, toxicity determination of raw and chemically best treated fur-suede processing wastewater were done using with *Daphnia magna* standard method. The results indicated that while the highest COD removal efficiency was determined for Al_2SO_4 as 86 % at 800 mgL^{-1} and pH=8.5, the lowest efficiency was found as 67 % for the same dosage of $FeCl_3$. On the other hand, Color removal efficiencies were found as 95-98 % for all coagulants and the best results was observed at Al_2SO_4 at 800 mgL^{-1} and pH=8.5. By the way, the best toxicity removal was calculated as 60% for effluents (50% diluted) treated with Al_2SO_4. These results show that as a first treatment step for fur-suede processing wastewater, chemical coagulation-flocculation with Al_2SO_4 provide the best performance both to remove COD and Color and also to decrease in toxic effect.
Keywords: Fur-suede wastewater, *Daphnia magna* toxicity, coagulant, COD and color removal.

1. INTRODUCTION

Wastewater from fur-suede processing is quite difficult industrial wastewaters in terms of treatability characteristics [1]. Furthermore, since large amounts of freshwater is needed to treat leather depending on the processes, the used raw material and many potentially dangerous chemicals such as chromium, synthetic tannins, oils, resins, biocides, detergents, are released [2,3] via process wastewaters. So, the main problem for tannery wastewaters is the chronic toxic effects caused by the mixture of many chemical compounds used in the leather tanning process. Because, they even remain after conventional treatment [4,5] or may inhibit nitrification process [6] and thus can be released to the environment.

The initial processes of fur-suede including washing, pickling and bating steps had the highest impact on the tannery wastewater. These steps contribute 40% on the flow and more than 50% on the Chemical Oxygen Demand (COD) load. They also release significant amounts of trivalent Chromium, Sulphide and Chloride which often induce inhibitory or toxic effects on biological treatment processes [1,7]. So, ideally and practically, Chromium (trivalent-Cr^{+3}) and Sulphide

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($S^{=}$) line wastewater strea ms are separated from the other wastewater streams such as washing and they are pre-treated for Chromium and Sulphide removal by coagulation/flocculation, respectively. Coagulation-flocculation generally utilizes inorganic metallic salts such as Al_2SO_4 (Alum), $FeCl_3$ (Ferric Chloride), $FeSO_4$ (Ferrosulphate) to remove organic/inorganic loads and total suspended solids (TSS) as well as to remove toxic substances, e.g. Chromium before biological treatment [8].

Ates et al. (1997) [9] researched the efficiencies of Al_2SO_4 and $FeCl_3$ for the treatment of wastewater collected from homogenized inlet of a central treatment plant of leather tanneries district. All experiments resulted in >70% of COD removal. Total chromium was almost completely removed using $FeCl_3$ (<5 mg L^{-1}) while it was also efficiently removed by Al_2SO_4. Kabdasli et al. (1999) [10] also reported 40-70% removal of COD and >99% of Total Chromium from leather tanning wastewater using $FeSO_4$, $FeCl_3$ and Al_2SO_4. Song et al. (2004) [11]obtained a removal range of 30-37% of total COD, 74-99% of Chromium and 38-46% of SS using 800 mgL^{-1} of Al_2SO_4 at 7.5 pH for pre-settled tannery wastewater containing 260 mg L^{-1} of SS, 16.8 mgL^{-1} of Chromium, 3300 mgL^{-1} of COD at 9.2 pH. They reported that $FeCl_3$ proved better results than Al_2SO_4. Moreover, Jochimsen et al. (1997) [6] reported that 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 . So, the studies carried out in the following years focused on the toxicity removal from tannery wastewaters. The use of single toxicity test is a satisfactory approach to evaluate the risk posed to freshwater organisms as reliable indices of the toxic impact of effluents in the aquatic environment [12]. The use of *Daphnia magna* in toxicology is accepted in several countries to monitor wastewater treatment systems, to establish quality criteria to determine permissible concentrations of pollutants, limits of impurity in water from natural effluents and to determine the efficiency of a good sanitation method [13].

Therefore; since there are limited researchs on evaluation of fur-suede wastewaters in the literature, this study intends to fill this gap and provide a case study information on toxicity assessment of fur-suede processing wastewater both raw and chemically treated with different coagulants. So, experimental part of this paper included an evaluation on COD, Total Organic Carbon (TOC), TSS and Color removals for various coagulant dosages considering eligble pre-treatment standard in Turkish Water Pollution and Control Legislation (TWPCL). After the best treatability conditions were determined, both raw and treated wastewater were examined in relation to *Daphnia magna* toxicity test.

2. MATERIAL AND METHODS

2.1. Survey Site

The fur-suede factory under examination, processes sheep and lamb skins to obtain fur-suede and it is located in the Çorlu Leather Organized Industrial District (ÇLOID)-Tekirdağ in the western part of Turkey [1]. It works five days a week with two shifts per a day, employing a total of 140 individuals. The capacity of the factory is 2400 ton of skins per year, corresponding to around 6.4 ton of skin per day. The factory can be classified in subcategory IV – Shearlings based on wastewater management [14] or it can be classified in subcategory VI – Sheepskin for suede according to industrial pollution classification in Turkey proposed by Tünay et al. (1995)[15].

2.2. Wastewater, Sampling and Conservation

Wastewater samples from fur-suede processing wastewater were collected every week in the period of one month from the factory effluent discharged in the channel connected to the central wastewater treatment plant of the ÇLOID. Samples were delivered to the laboratory within 1 h of collection for all subsequent analyses and they were kept refrigerated at +4 ^{0}C. Sampling conservation a nd analyses of all parameters were performed according to the Standard Methods [16, 17] and ISO 7887 [18]. The adjustment and measurement of pH was carried out using a pH meter (WTW pH315i).

2.3. Experimental Approach

The experimental approach began with a series of jar-test experiments which were performed on raw wastewater applying 2 min rapid mixing at 100 rpm, 20 min slow mixing at 30 rpm and 30 min settling at different pH values and coagulant dosages. A conventional Jar–test apparatus (VELP Scientifica, FC6S) equipped with four beakers with 1000 ml were used. Jar test trials were made at different coagulant types and dosages (200, 400, 600, 800 mgL^{-1}) at choosen pHs at which the solubilities of used coagulants are lowest (pH 8.5 for Al_2SO_4, pH 9.5 for $FeSO_4$ and pH 10 for $FeCl_3$ by adding 1N HCl or 1 N NaOH solutions) . The best treatability conditions (coagulant type and effective dosages) were assessed for COD, Color, TOC and TSS removal. After settling, supernatant samples were collected and filtered using coarse filter (Whatman filter paper no.40.) for further analysis. All experiments were performed at room temperature (20- 25 ^{0}C).

Aluminium Sulphate ($Al_2(SO_4)_3.18H_2O$), Ferric Chloride ($FeCl_3 .6H_2O$) and Ferrous Sulphate ($FeSO_4.7H_2O$) were used as coagulant. Solid Anionic Polyelectrolyte (A.P.E.) used as coagulant aid. All chemicals used in this study were purchased at analytical reagent grade. These compounds were purchased from Sigma Aldrich Group Company in Turkey. All analyses were performed according to the Standard Methods [16-18].

2.4. Toxicity Tests

Toxicity of raw and chemically best treated fur-suede processing wastewater was measured using 24 h *Daphnia magna* with or without and 50 % v/v dilution [19]. Room temperature was kept at 20^{o}C ± 1^{o}C and a minimum 6 mgL^{-1} of Dissolved Oxygen (DO) 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 immobilized animals after 24 h and 48 h.

3. RESULTS AND DISCUSSION

3.1. Effluent Characterization

Raw wastewater characterization of investigated fur-suede process factory, used in jar test experiments, is given in Table 1.

Table 1. Wastewater characterization of investigated plant used in jar test experiments

Parameters	**Unit**	**Raw Wastewater**
Total COD	$mg.L^{-1}$	1975± 12
Total TOC	$mg.L^{-1}$	340±3
Soluble TOC	$mg.L^{-1}$	188±13
Suspended Solid (SS)	$mg.L^{-1}$	560 ±6
Conductivity	$\mu mho.cm^{-1}$	7930±123
Color 436 nm 525 nm 620 nm	CN*(m^{-1}) CN*(m^{-1}) CN*(m^{-1})	74.5 55.7 44.4
Total Cr (T-Cr as Cr^{+3})	$mg.L^{-1}$	55±7.3
Total T-N**	$mg.L^{-1}$	29±1.7
Soluble T-N**	$mg.L^{-1}$	19±2.3
pH	-	5.65±0.7

*CN: Color number,** T-N: Total Nitrogen

Table 1 presents a typical tannery wastewater characteristics and shows a complex and strong wastewater structure especially with total COD about 1975 mgL^{-1}. The effluent characteristics of investigated plant are representative for the leather tanning wastewater and as similar to the values reported in the literature [20, 21, 12, 1].

3.2. Jar Test Trial Results

Three different conventional coagulants and four different dosages were used together with a coagulant aid for determination the best treatability conditions for fur-suede raw wastewater. The results and removal efficiencies are given at Table 2 and Figure 1.

Table 2. Treatability results of fur-suede raw wastewater

SETS	Dosage	pH	COD	TSS	TOC	T-N	Conductivity	Color			Total Color
	$mg.L^{-1}$		$mg.L^{-1}$	$mg.L^{-1}$	$mg.L^{-1}$	$mg.L^{-1}$	$\mu S.cm^{-1}$	Color Number, m^{-1}			Color Number m^{-1}
								436 nm	525 nm	620 nm	
SET-1	**$FeCl_3$ (10%)**										
Set-1.1	200	10	1261	135	207	28.4	8560	11.8	7.1	4.5	23.4
Set-1.2	400	10	687	80	217	29.5	9160	3.4	2.3	1.4	7.1
Set-1.3	600	10	556	85	211	24.2	9680	3.8	2.7	2.1	8.6
Set-1.4	800	10	647	95	212	30.3	9930	4.1	2.9	2.4	9.4
SET-2	**$FeSO_4$ (10%)**										
Set-2.1	200	9.5	1363	640	305	32.4	8100	73.4	46.5	34.9	154.8
Set-2.2	400	9.5	1177	490	261	34.3	8190	49.5	28.9	20.5	98.9
Set-2.3	600	9.5	485	320	216	38.2	8210	40.4	21.7	14.1	76.2
Set-2.4	800	9.5	417	85	214	37.3	8460	3.3	2.5	1.5	7.3
SET-3	**$Al_2(SO_4)_3$ (10%)**										
Set-3.1	200	8.5	1250	700	286	35.6	8350	111.3	88.2	76.1	175.6
Set-3.2	400	8.5	1206	520	219	34.6	8390	60.2	40.7	30.9	131.8
Set-3.3	600	8.5	657	165	162	36.3	8420	18.7	12.7	9.5	40.9
Set-3.4	800	8.5	270	60	144	36.9	8600	1.8	1	0.3	3.1

According to the Table 2 and Figure 1, Color removal was determined as approximately 87% at 200 mg L^{-1} $FeCl_3$ dosage while it was found 96% at 400 mgL^{-1} at pH=10. The worst color removal occurred at the lowest dosage of $FeCl_3$. Dosage increased to begin the color removal efficiency increase and reached close to each other. On the other hand, $FeSO_4$ and $Al_2(SO_4)_3$ experiments showed that the meaningful color removal efficiency can be obtained at 800 mgL^{-1} dosage as 96% and 98%, respectively. So, in this case, according to the color removal efficiency results, since $FeSO_4$ and $FeCl_3$ didn't present a good performance even at very high concentrations compared to $Al_2(SO_4)_3$ and were found more expensive option, $Al_2(SO_4)_3$ was assessed the best coagulant which provide the best color removal efficiency for this wastewater. There was no any color removal observed at 800 mgL^{-1} dosage $Al_2(SO_4)_3$. This situation can be explained by the fact that this dosage is not enough to break certain bonds since fur-suede processing wastewater presents a strong pollutants character. By the way, it can also be interpreted that Al_2 (SO_4) $_3$ could not be sufficiently dissolved during the jar test trial. Moreover, when COD removal efficiencies were assessed, while $FeCl_3$ concentration increased from 200 mgL^{-1} to 800 mgL^{-1}, COD removal increased from 36% to 72 %, the best COD removal efficiency was achieved as 72% at 600 mgL^{-1} $FeCl_3$ dosage at pH=10. $FeSO_4$ and $Al_2(SO_4)_3$ coagulants were also showed the similar intend. COD removal efficiency was calculated 31% at 200 mgL^{-1} $FeSO_4$ dosage at pH=9.5, while the highest removal efficiency was found 79 % at 800 mgL^{-1} for the same pH. On the other hand, when $Al_2(SO_4)_3$ dosages were increased from 200 mgL^{-1} to 800 mgL^{-1}, COD removal increased from 37% to 86 % at pH=8.5 and the highest removal efficiency was found 86% at 800 mgL^{-1} for the same pH . By the way, TOC removal efficiencies show similar trend like as COD. The highest TOC removal efficiencies were obtained at 600 mgL^{-1} $FeCl_3$, 800 mgL^{-1} $FeSO_4$ and 800 mgL^{-1} $Al_2(SO_4)_3$ as 38%, 37% and 58%, respectively. The best coagulant were found $Al_2(SO_4)_3$ for TOC removal. When TSS analysis were assessed, the best TSS removal efficiencies were determined as 86% for 400 mgL^{-1} $FeCl_3$ dosage at pH=10, 85% for 800 mgL^{-1} $FeSO_4$ dosage at pH=9.5 and 89% for 800 mgL^{-1} $Al_2(SO_4)_3$ at pH=8.5.

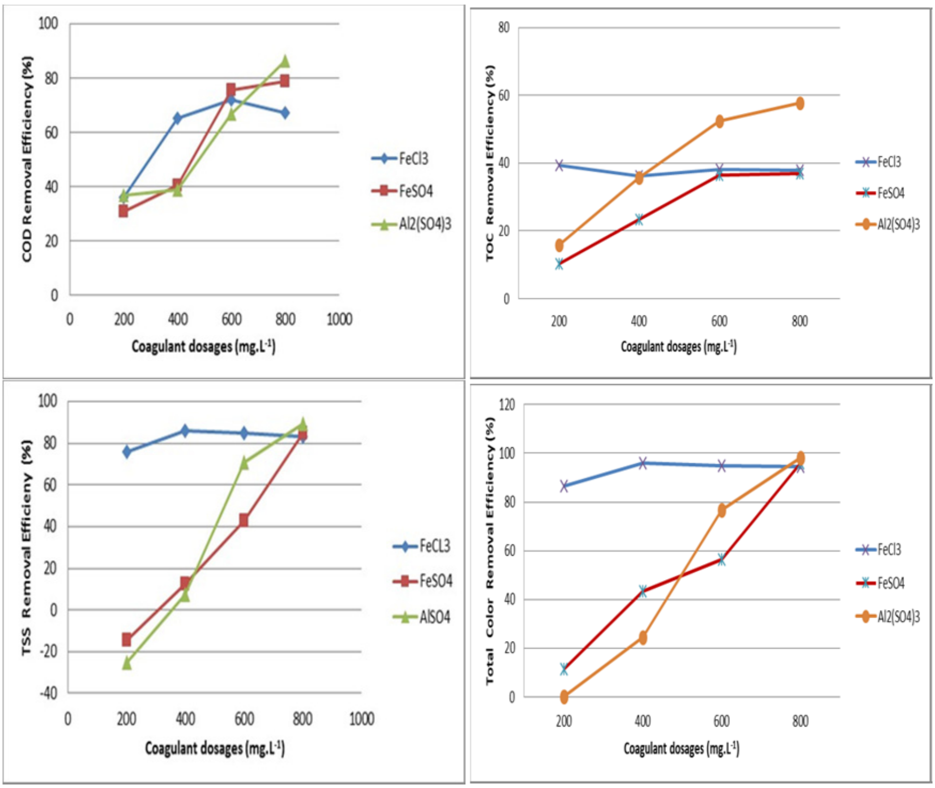

Figure 1. COD, TOC, SS and Total Color removal efficiencies obtained for different coagulants at treatability studies

As a conclusion, in terms of COD, TOC, Color and TSS removal efficiencies, optimum dosages of $FeCl_3$, $FeSO_4$ and $Al_2(SO_4)_3$ were found as 600 mgL^{-1}, 800 mgL^{-1}, 800 mgL^{-1}, with 72%, 79 % and 86% COD removal and 86%, 85% and 89 % TSS removal, respectively. So, in this case, according to the jar test trial results, since $FeSO_4$ and $FeCl_3$ didn't present a good performance even at very high concentrations compared to $Al_2(SO_4)_3$ especially for COD and TSS removal and were found more expensive option, $Al_2(SO_4)_3$ was assessed the best coagulant which provide the best COD and TSS removal efficiency for this wastewater. Song et.al. (2001)[22] found at an optimum pH of 7.5, the following removal efficiencies were attained by coagulation: 32%±35.6% (COD), 64.0%±69.3% (SS), 77±99% (chromium), 85%±86% (color) by respectively the addition of 800 mgL^{-1} of aluminium sulphate or ferric chloride [22]. So, this study results showed the best conformity with the literature in terms of COD and TSS parameters [9, 22]. Furthermore, Song et al. (2004) [11] had reported COD and TSS removal efficiencies more lower than this study results. It is taught that the reason of this may be due to the weak character of fur-suede wastewater used in this study unlike the literature.

3.3 Toxicity-Daphnia Magna

The toxicity of raw and coagulated wastewater at the best coagulant dosages determined in this study (Set 1-3: $FeCl_3$ -600 mgL^{-1} at pH=10, Set 2-4: $FeSO_4$ -800 mgL^{-1}at pH=9.5 and Set 3-4: $Al_2(SO_4)_3$ -800 mgL^{-1} at pH=8.5) were measured using 24 h and 48 h *Daphina Magna* standard method with and without 50 % dilution to evaluate the influence of wastewater characteristics in the scope of 3 sets. In all toxicity test sets, carried out without dilution, *Daphina Magna* were observed to have died. However, with 50% dilution, it has been found that certain toxicity removal was achieved depending on the coagulant type. For this reason, subsequent experiments were continued with 50% dilution. Toxicity test results are given at Table 3. According to these results, *Daphnia magna* shows moderately good vitality at 24 h period with 50% dilution. But when 48 h effects were considered, it was observed that all of the *Daphnia Magnas*' were died. The meaning of this can be explained that while there is most important toxicity at acute period, this case will result in high toxicity at long period. On the other hand, dilution had a positive effect on toxicity removal compared to the undiluted raw samples. The reason of it may be explained that the high toxicity of raw wastewater is due to the untreated. Furthermore, high COD, TOC, TSS and also Color of raw wastewater may be reasons for this case.

But, experimental results show that although raw wastewater is untreated, it was observed that a specific volume of dilution provide approximately 20 % toxicity removal. On the other hand, toxicity of chemically pre-treated wastewater diluted with 50% were calculated as averagely 70 % for $FeCl_3$ and provided best toxicity removal as 20% at Set 1-3. At this set, it was observed that the shape of the immobilized *Daphnia Magnas* were broken. But unlike this situation, they were maintained their transparent color during this period. Furthermore, toxicity of Set 2-4 was determined as averagely 60%, toxicity removal was found approximately 40% and it was observed that *Daphnia magna*s didn't protect their shape and with degradation, their color converted to a salmon color. It is thought that both the acidic properties of coagulant used in this set and $SO_4^{=}$, Fe^{+2} ion affects at high dosages may be the reason of the toxicity. On the other hand, the highest toxicity removal was achieved at Set 3-4 with Al_2SO_4. Averagely, 40% toxicity was determined for Al_2SO_4 coagulant at 50 % dilution and 60% toxicity removal was achieved. The reason of this can be explained as the highest coagulation efficiencies can be achieved with alum coagulant on the base of high COD, TOC, TSS and Color removal. By the way, it was reported in the literature that the toxic effect of aluminum ions have lower affect on the aqua life than iron ions. It was thought that this case may also has a positive effect on a little bit lower toxicity. In the literature, Kaptan, D. (2002) [23] researched the acute *Daphnia Magna* toxicity of textile wastewater and found that while the raw textile wastewater 100% toxic with 50% dilution, the toxicity of wastewater treatment plant effluent was determined 20% toxic with 50% dilution. Lofrano et. al. also studied leather tanning wastewater *Daphnia Magna* toxicity at several researches. They also found that the overall decrease in effluent toxicity following the coagulation/flocculation effluent suggested an effective removal of toxic components from tannery wastewater [7, 24, 25]. So, they suggested that it is useful approach to improve the coagulation process for toxicity reduction of raw wastewater taken from a leather tanning wastewater. This study results also showed that to improve COD and TSS removal as well as reduce the toxicity of the existing coagulation/flocculation treatment process, may be useful to remove of toxic components from fur-suede wastewater before subjecting to either biological treatment or discharge to receiving bodies. Especially, the policy of submitting tannery wastewater to biological treatment before it is discharged in receiving water bodies is necessary to reduce toxicity using alum coagulation for protecting the aquatic environment.

Table 3. The toxicity evaluation of raw and pre-treated fur-suede processing wastewater

SAMPLE NAME	İmmobil *Daphnia magna* number, 24 hour (50% Diluted Wastewaters) R1	R2	R3	R4	R5	Average Toxicity (%)	Standard Deviation (SD)	İmmobil *Daphnia magna* number, 48 hour (Without dilution) R1	R2	R3	R4	R5	Average Toxicity (%)	Standard Deviation (SD)
					SET-1						SET-1			
Control	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Raw wastewater	5	5	1	5	5	80	1,79	5	5	5	5	5	100	0,00
Set 1-3 (FeCl3-600 mg.L-1, at pH=10)	5	5	1	5	1	60	2,19	5	5	5	5	5	100	0,00
Set 2-4 (FeSO4-800 mg.L-1, at pH=9,5)	5	5	1	5	5	80	1,79	5	5	5	5	5	100	0,00
Set 3-4 (AL2 (SO4)3-800 mg.L-1, at pH=8,5)	5	1	1	5	1	40	2,19	5	5	5	5	5	100	0,00
					SET-2						SET-2			
Control	0	0	0	0	0	0	0,00	0	0	0	0	0	0	0,00
Raw wastewater	5	5	5	5	5	100	0,00	5	5	5	5	5	100	0,00
Set 1-3 (FeCl3-600 mg.L-1, at pH=10)	5	5	1	5	5	80	1,79	5	5	5	5	5	100	0,00
Set 2-4 (FeSO4-800 mg.L-1, at pH=9,5)	5	5	1	5	1	60	2,19	5	5	5	5	5	100	0,00
Set 3-4 (AL2 (SO4)3-800 mg.L-1, at pH=8,5)	5	1	1	5	1	40	2,19	5	5	5	5	5	100	0,00
					SET-3						SET-3			
Control	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Raw wastewater	5	5	1	5	5	80	1,79	5	5	5	5	5	100	0,00
Set 1-3 (FeCl3-600 mg.L-1, at pH=10)	5	5	1	5	5	80	1,79	5	5	5	5	5	100	0,00
Set 2-4 (FeSO4-800 mg.L-1, at pH=9,5)	5	5	1	5	1	60	2,19	5	5	5	5	5	100	0,00
Set 3-4 (AL2 (SO4)3-800 mg.L-1, at pH=8,5)	5	1	1	5	1	40	2,19	5	5	5	5	5	100	0,00

R: Replicate number, SD: Standard deviation (It should not be >5-10. Otherwise, the experiment should be replicatied according to ISO 1996)

4. CONCLUSION

This study aimed to asses of chemical tretability of fur-suede processing wastewater together with toxicity removal. The best treatability conditions were assessed as 8.5 pH and 800 mgL-1 of Al2(SO4)3 which resulted in high removal of COD (86 %), TSS(89 %), colour (98%) and reduced Daphnia Magna immobilization (60% toxicity removal). Toxicity was monitored in raw and coagulated samples using Daphnia magna test. The coagulation/flocculation process under the parameters examined is a satisfactory solution before biological process. However, this process must be well optimized as shown in this study to avoid elevated toxicity with respect to raw wastewater and toward the effluent submitted to biological treatment.

Acknowledgment

This study was funded by the Environmental Engineering Department of Namık Kemal University. Furthermore, we would like to thank Kerim Ekici and Burcu Salçin who are supported the experimental part of this study as a undergraduate students of our department.

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