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Utilizing aluminum etching wastewater for tannery wastewater coagulation: performance and feasibility

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ABSTRACT

The main objective of this study was to investigate the feasibility of utilizing etching wastewater (EW) of aluminum (Al) coating industry as an alum substitute in industrial wastewater treatment. Our hypothesis was that Al-rich EW could be an effective substitute for commercial liquid alum used in a nearby (<10 km) tannery wastewater treatment plant (Corlu, Turkey). Bench-scale alum and EW jar tests along with an economic analysis were performed to test this hypothesis. Jar test results conducted using identical pH and Al doses showed that Al-rich EW performed similar to alum in terms of chemical oxygen demand (COD), suspended solids (SS), and turbidity removal. Regardless of its origin (alum or EW), 1 g of Al approximately removed 30 g COD and 20 g SS via a combined effect of coagulation and plain settling. Commercial alum and EW removed more than 95% of COD and turbidity; 60% of total COD from the tannery wastewater. Preliminary cost analysis showed that coagulant expenditure could be reduced by 40% if alum was substituted with EW.

Keywords: Aluminum industry; Etching spent liquor; Coagulant; Cost effectiveness; Jar test; Wastewater treatment

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1. Introduction

Tannery wastewater treatment is an important environmental issue, particularly in the developing countries delivering the majority of global leather production for the past two decades [1]. Beamhouse operation, tanyard processes, retanning, and finishing, are the stages of the tanning process that finishes leather; the process generates different kind and amount of wastewater depending on end products [2,3]. Chemical oxygen demand (COD), suspended solids (SS), Cr, sulfide, oil and grease, total Kjeldahl nitrogen (TKN), and pH ranges reported in the related literature to characterize wastewater from tannery industry varied greatly across and within the countries (Table 1): reported Cr, sulfide, oil and grease, TKN,

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Presented at the 2nd International Conference on Recycling and Reuse (R&R2014), 4–6 June 2014, Istanbul, Turkey and pH ranges were 11.2–258 mg L^{-1} (India; [4,5]), 35.8–860 mg L^{-1} (Turkey & India; [5,6]), 28–638 mg L^{-1} (Egypt & Thailand; [7,8]), 33–180 mg L^{-1} (India & Turkey; [9,10]), and 7–11 mg L^{-1} (Thailand & Ethiopia; [8,11]). Overall, tannery wastewater appears to have an alkaline pH ($7 < \text{pH} < 11$), a dissolved solids: total solids (TS) ratio of >80%, and a substantial amount of chloride, sulfate, TKN, and Cr [12–14]. Particulate solids that constitute a relatively small fraction of TS are highly settleable (e.g. >60%).

An array of biological and physicochemical processes, including coagulation can be used in tandem to treat tannery wastewater. Conventional coagulation is typically used in conjunction with plain settling to reduce COD, SS, turbidity, and metals (especially Cr) from wastewater. As the primary treatment operation preceding coagulation, settling delivers significant SS and Cr removal rates. For instance, Song et al. [15] reported that *ca.* 80% of the SS and Cr was removed from the wastewater using a 3-h settling period. Similarity of the SS and Cr removal rates can be attributed to the fact that Cr is predominantly associated with settleable SS. On the other hand, COD removal delivered in plain settling is relatively low (e.g. 40%), since the total COD is mainly in the dissolved form [15]. Hence, coagulation process can be considered particularly instrumental in decreasing the COD load of the downstream processes in the tannery wastewater treatment.

Previous studies have addressed the effects of coagulant type, coagulant dose, pH, flocculant type, and flocculant dose on pollutant removal rates associated with tannery wastewater. To our knowledge, coagulation performance of the following chemicals has been investigated: alum ($Al_2(SO_4)_3$), ferric chloride ($FeCl_3$), ferric sulfate ($Fe_2(SO_4)_3$), polyaluminum chloride, and bittern [16–20]. COD and SS removal performance results of the select studies are presented in Table 2. In some studies, flocculants and coagulant aids (e.g. polyelectrolytes, CaO, Na_2CO_3, $CaCO_3$, and Na_2SiO_3) have been used simultaneously with the coagulants to further improve pollutant removal performance [16,17]. When coagulant doses are normalized for their active metal (e.g. Al^{3+}, Fe^{3+}, and Mg^{2+}) concentrations, Al coagulants appear to be more effective as compared with Fe or Mg coagulants in terms of COD and SS removal. On the other hand, $FeCl_3$ sludge was reported to have better settling characteristics than alum sludge [15]. The physicochemical composition of tannery wastewater (e.g. total dissolved solids) is one of the major factors influencing coagulant performance. Amount of Al^{3+} that is necessary to remove 1 g of COD and 1 g of SS can be in the range of 10–80 and 10–900 mg, respectively [15,17,19]. Similarly, 50–150 mg of Fe^{3+} can be required to remove 1 g of COD from tannery wastewater [15–17]. Song et al. [15] investigated the effect of pH on $Al_2(SO_4)_3$ and $FeCl_3$ performance, and showed that maximum COD and SS removal occurred at pH 7–8, whereas maximum Cr removal required $\text{pH} > 9$. Although tannery wastewater is usually alkaline, some tanneries such as the ones operating in Corlu (Turkey) can produce slightly acidic wastewater. Wastewater pH can be adjusted by adding alkalinity (e.g. commercial bases) in order to perform coagulation under favorable pH conditions. Therefore, commercial coagulant and base consumption contribute to the operational costs of tannery wastewater treatment plants.

Aluminum (Al) coating industry typically uses the following processes in the given order to deliver its products: cleaning, etching, desmutting, anodizing, coloring, and sealing [21]. During etching process, a thin layer of Al is removed, and Al surface is given a matte appearance using a strong alkaline solution (e.g. 50–200 g L^{-1} NaOH) at a temperature of 50–60˚C. Al is typically rinsed following etching process, and spent rinse water may be mixed with etching wastewater (EW) depending upon the process configuration of the plant. Al and Na are the major elements, and $NaAlO_2$ is the predominant Al species in EW [21,22]. Anodizing is performed using an acidic solution at or around room temperature. Acidic and alkaline wastewaters generated by etching and anodizing are conventionally mixed for neutralization. The end product (i.e. anodizing mud) requires further treatment so that the industry can conform to environmental discharge standards. As a result of this conventional waste treatment and disposal practice, valuable non-renewable materials (e.g. Al, NaOH, and H_2SO_4) are lost or transferred out of the industrial production cycle. Therefore, alternative methods have been developed to recover and recycle industrially significant resources present in EW stream. An array of physicochemical processes that has been applied to remove Al from EW, and to regenerate and recycle caustic solution have received significant attention in the related literature, such as Al precipitation via hydrolysis and/or chemical (e.g. carbonates, lime, $Al(OH)_{3(s)}$, polyacrylamide, surfactants) addition, zeolite synthesis, ion exchange, and membrane separation [21,23]. Al industry can incur initial and operational costs due to the full-scale implementation of these processes.

There are studies where Al-rich sludge has been directly utilized as a coagulant for wastewater treatment [24,25]. However, to our best knowledge, there are no studies addressing a direct utilization of Al-rich industrial wastewater (e.g. EW) for coagulating other wastewaters. This lack of interest may be attributed to the economical and practical concerns related to wastewater availability or transportation of wastewater from its point of origin to its point of consumption. Our hypothesis was that Al-rich wastewater generated by the metal coating plants could be directly utilized for coagulating wastewater generated by the other industries. This could be a "win-win" approach since wastewater treatment costs of both industries that export and import Al-rich wastewater could be reduced.

The main objective of this study was to investigate the feasibility of utilizing EW for coagulating tannery wastewater. Specifically, potential use of EW from an Al coating plant by a nearby (*ca*. 10 km) tannery wastewater treatment plant, both of which were located in a highly industrialized zone of northwestern Turkey (Corlu) was addressed. In order to accomplish this objective, (1) bench-scale alum and EW jar tests were performed to compare tannery wastewater coagulation performance (COD, SS, and turbidity removal) of EW with that of a conventional coagulant, namely, alum, and (2) a preliminary economic analysis was carried out to quantify the financial incentive for the tannery wastewater treatment plant operators to switch from conventional Al coagulant to EW use.

2. Materials and methods

2.1. Wastewater sources and sampling

The tannery organized industrial zone (Corlu, Tekirdag, Turkey) consists of 118 tanneries and is capable of processing 25 million and 50 thousand metric tons (t) of ovine and bovine hide per annum, respectively. The zone delivers 37% of Turkey's national leather production. The wastewater treatment authority of the organized industrial tannery zone is mandated to perform excellent (*ca*. >98%) total Cr and sulfide removal under the Turkish Water Pollution Control Regulation (Turkish Ministry of Environment and Forestry 2005) (Table 3). The authority is also required to achieve high COD and SS removal rates (*ca*. 80–95%), whereas the mandated removal rates are comparably lower for TKN and oil–grease (Table 3).

Wastewater treatment plant of the industrial zone was commenced in 2007 and has a capacity of 36,000 $m^3 d^{-1}$. The plant has an equalization basin with the following three major components: (1) physical treatment: coarse/fine screens, pumping station, and grit/grease chamber; (2) chemical treatment: rapid/slow mixing basins and sedimentation basins; and (3) biological treatment: denitrification, aeration, and sedimentation basins. Chemical treatment unit of the plant uses alum ($Al_2(SO_4)_3{\cdot}18H_2O$) and consumes 55–80 mg Al^{3+} L^{-1} of wastewater (personal communication, Corlu Organized Industrial Tannery Zone Wastewater Treatment Authority). Al^{3+} availability factor and density of commercially available 52% liquid alum are 8.4% (w/w as Al_2O_3) and 1.3 kg L^{-1}, respectively [26]. Hence, liquid alum consumption of the plant ranges from 1.0 to 1.4 L (1.2–1.8 kg) m^{-3} of wastewater. Average alum consumption was calculated as 1.2 L or 1.5 kg m^{-3} of wastewater.

Sludge handling configuration has sludge mixing and thickening basins and belt filter presses. Two samples were collected from the equalization basin on different dates. The samples were analyzed for COD, SS, and turbidity, and saved for the subsequent chemical treatment study. One sample was obtained from the EW collection tank of an Al coating plant; this sample was characterized and subsequently used in jar testing.

2.2. Laboratory analyses

The EW sample was analyzed for total COD, total organic carbon (TOC), SS, turbidity, pH, Al, Co, Cr, Fe, Mg, Sb, Sn, Sr, Tl, V, Zn, Cl^-, NO_3^-, and SO_4^{-2}. The standard methods were used for all analyses [27]. COD was determined using a colorimetric closed reflux method (5220 D method, Hach digester and spectrophotometer; Loveland, CO, USA). Unfiltered aliquots from well-mixed samples were transferred into the screw-cap vials including the COD reagents. The vials were subjected to heat in a block digester, and total COD of the samples was determined analyzing the digested sample aliquots using a spectrophotometer.

Unfiltered aliquots of the wastewater samples were transferred into the TOC vials and the vial contents were processed by a TOC analyzer (TOC-V CPN; Shimadzu, Kyoto, Japan) to determine TOC content. Well-mixed aliquots of predetermined volume were obtained from the samples and subsequently passed through oven dried, desiccated, and pre-weighed filter papers using a vacuum suction apparatus. Moisture was completely removed from the filter papers by storing them at 105°C in a laboratory oven. The filter papers were placed into a desiccator and cooled down to the room temperature after they were removed from the oven. Mass of the solids was determined using an analytical balance, and SS concentration of the samples was calculated dividing the solids mass by the sample aliquot volume.

Turbidity and pH were determined using a turbidimeter (Portable DRT-15CE; HS Scientific) and a pH meter (WTW-315i; Weilheim, Germany), respectively. Aliquots of well-mixed samples were obtained and acidified using high-purity HNO_3. Debris and large particulates were excluded during subsampling when necessary. A dilution factor (DF) of 1,000 was used for quantifying Al since its concentration exceeded the maximum quantitation limit for DF smaller than 1,000. High-grade deionized water was used for dilution purposes. An inductively coupled plasma optical emission spectrometer (ICP-OES) was calibrated using calibration standards generated from a commercially available, certified multi-element standard for fully quantitative analysis (Optima 2100 DV; Perkin Elmer Inc., Waltham, MA, USA). A five-point calibration curve ($r^2 > 0.99$) was obtained for each element of interest. Recoverable Al, Co, Cr, Fe, Mg, Sb, Sn, Sr, Tl, V, and Zn concentrations of the samples were determined analyzing the acidified aliquots with the ICP-OES.

Subsamples from well-mixed samples were passed through 0.25-μm membrane filters (PTFE Minisart SRP 15) prior to the ionic content determination. The anions (Cl^-, NO_3^-, and SO_4^{2-}) were determined using an ion chromatograph (ICS-3000; Dionex, Sunnyvale, CA, USA). Calibration standards were prepared by diluting a certified multi-anion ion chromatography standard with high-grade deionized water. A five-point calibration curve ($r^2 > 0.99$) was established to measure the anion concentrations.

2.3. Jar testing

Coagulation–flocculation tests were performed using a laboratory-scale jar tester (Phipps & Bird, Model 7790-701B). Predetermined volumes of the 10% (w/v) $Al_2((SO_4)_3) \cdot 7H_2O$ coagulant solution were dosed into the jars containing a 1-L tannery wastewater. Alum doses were reported on an elemental basis (as Al^{3+}) by multiplying the alum concentration with the gravimetric conversion factor of 0.12. Ten percent (w/v) hydrated lime ($Ca(OH)_2$) solution was used for pH adjustment. The jars were subjected to a rapid mixing for 2 min and a slow mixing for 15 min. One mL of 0.1% (w/v) anionic polyelectrolyte solution was added into the jars at the beginning of the slow mixing period. Thirty min quiescent settling period followed the slow mixing. Supernatant was analyzed for COD, SS, and turbidity to determine the appropriate coagulant dosage and pH. Subsequently, more jar tests were performed substituting alum with EW. Al dosage and pH used in the EW jar tests were kept identical to those used in the alum jar tests in order to investigate the potential effect of EW composition on its coagulation performance.

2.4. Cost analysis

Information about unit liquid alum cost per t, average alum cost, transportation cost, alum treatment of the tannery wastewater per m^3, capacity of the operational treatment train, and designed and actual influent flow rates was obtained from the Corlu Organized Industrial Tannery Zone Wastewater Treatment Authority. Alum dosage data were also used instead of influent flow data since influent flow records were unavailable. Unit alum cost of the tannery wastewater treatment plant was 100 USD ton^{-1} (personal communication, Corlu Organized Industrial Tannery Zone Wastewater Treatment Authority).

3. Results and discussion

3.1. Wastewater characteristics

The EW exhibited alkaline characteristics similar to chrome-tannery wastewater analyzed by Ram et al. [9] and contained approximately 13 g L^{-1} Al (Table 4). Al complexes and $Al(OH)_{3(s)}$ are well known and effective coagulation agents in the wastewater treatment field [28]. Al-rich EW appeared to have the potential to supply the above mentioned coagulation agents for the chemical treatment of the wastewater. Calcium, Mg, and Fe are typically found as cations in the aqueous solutions and are known for their complexes participating effectively in the coagulation and subsequent precipitation and settling processes [28,29]. Iron and Mg contents of EW were substantially lower than its Al content (Table 4). Calcium content of EW was negligible due to the chemical nature of the process. Using the available data, coagulation power of EW could be mainly attributed to its Al content and alkalinity. Alkalinity content of EW was particularly important for the case being investigated in this study, since the pH of the slightly acidic tannery wastewater was needed to be elevated for effective alum coagulation. Operational pH of the coagulation unit varied between 7 and 7.5 (personal communication, Corlu Organized Industrial Tannery Zone Wastewater Treatment Authority).

Two representative tannery wastewater samples, hereafter samples #1 and #2, were obtained from the equalization tank of the organized industrial tannery zone wastewater treatment plant on two different days (Tables 3 and 5). Sample COD, SS, and turbidity were bracketed by the values reported elsewhere (Tables 1 and 5). COD and SS concentrations of EW amounted to less than 20 and 3% of the corresponding concentrations observed for the tannery wastewater (Tables 4 and 5). Therefore, COD and SS strengths of EW were substantially lower than those of the tannery wastewater. At the treatment plant, the physical treatment of the raw wastewater preceded the chemical (alum) treatment. Actual COD, SS, and turbidity

Table 1
Country specific COD, SS, and turbidity of tannery wastewater

Country	COD (mg L^{-1})	SS (mg L^{-1})	Turbidity (NTU)	Ref.
Brazil	1,803	526	–	[32]
Ethiopia	11,154 ± 1,627	–	–	[11]
India	5,650	5,025	–	[33]
UK	3,300 ± 150	260 ± 45	–	[15]
Pakistan	2,442 ± 377	1,233 ± 277	–	[19]
Iran	3,800 ± 5	573 ± 50	56 ± 1	[16]
Lebanon	4,222 ± 1,481	2,812 ± 1,523	3,642 ± 2,177	[18]
Turkey	2,513 ± 8,781	1,000 ± 4,740	–	[17]

Note: Values are given as mean ± standard deviation.

Table 2
Tannery wastewater COD and SS removal performance of coagulants

Coagulant type	Coagulant dose[a] (mg L^{-1})	COD removal (%)	SS removal (%)	Ref.
$Al_2(SO_4)_3$	88	36	38	[15]
	21	53	96	[19]
	60[b]	82	–	[17]
$FeCl_3$	166	36	46	[15]
	276[c]	75	–	[16]
	200[b]	77	–	[17]
Bittern ($Mg(OH)_2$)	270	45	95	[18]

[a] Coagulant dose is given on an elemental basis (i.e. Al^{3+}, Fe^{3+}, and Mg^{2+}).
[b] Coagulant was supplemented with 2 mg L^{-1} anionic polyelectrolyte.
[c] Coagulant was also supplemented with 600 mg L^{-1} Na_2CO.

concentrations of the chemical treatment influent were expected to be lower than those of samples #1 and #2. Probable implications of this issue were discussed below.

3.2. Coagulation performance of alum

Normalized alum dosage used on the samples (#1 and #2) was approximately 45 mg Al^{3+} g^{-1} of SS. Alum removed, SS, and turbidity very effectively (>95%) from both wastewater samples regardless of the coagulant dose (Table 6). On the other hand, COD removal rate lagged behind SS and turbidity removal rates. Similarly, Haydar and Aziz [19] reported 60% COD removal rate for chemically enhanced primary treatment of tannery wastewater (Fig. 1). Low COD removal can be attributed to the presence of a notable dissolved organic fraction that cannot be destabilized by alum addition. There were no dissolved COD data to support this argument in this study. However, dissolved organic carbon : TOC and soluble COD: total COD ratios of as high as 98 and 60% were reported for tannery wastewater, respectively [19,30].

The pH increase (7 vs. 7.5) did not appear to improve COD, SS, and turbidity removal noticeably (Table 6). This result highlights the need for a judicious use of chemicals, especially base(s), in full-scale tannery wastewater treatment. Minimizing chemical use without adversely affecting pollutant removal performance would be economically beneficial for a wastewater treatment plant since it would reduce the operational costs. Results of this study showed that a coagulant dose of 45 mg Al^{3+} g^{-1} SS removed COD, and especially SS and turbidity from tannery wastewater effectively at pH 7. Similar removal performances can also be attained by using alum doses less than 45 mg Al^{3+} g^{-1} SS (Fig. 1). Chemical dosing is typically set on a volumetric basis (i.e. a mass of coagulant dosed per unit volume of wastewater) at the wastewater treatment plants. Alum dosage varied between 55 and 80 mg Al^{3+} L^{-1} at the tannery wastewater treatment of interest. Based on our results, alum input could be adjusted as a function of the influent SS to supply a constant amount of Al^{3+}: SS (e.g. 45 mg Al^{3+} for every g of SS). This approach could be partic-

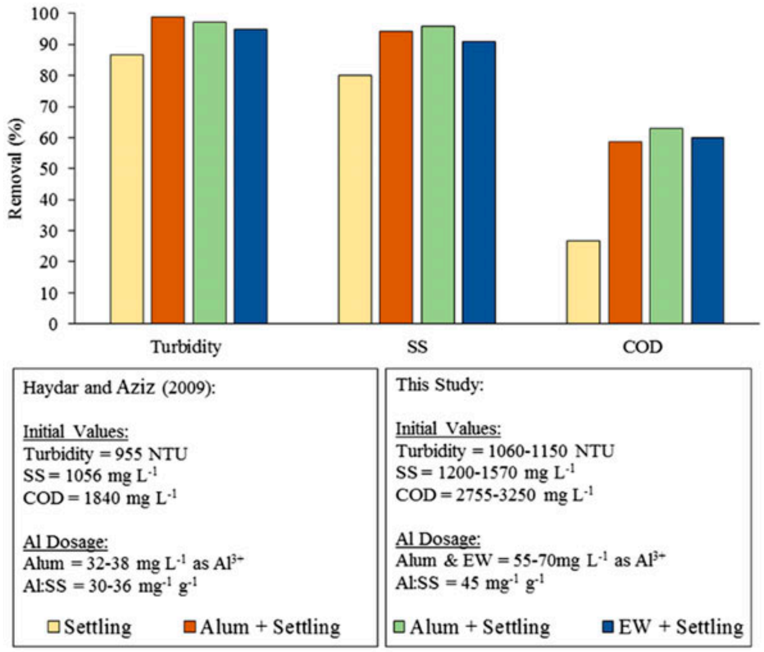

Fig. 1. Performance of “coagulant and settling” vs. “plain settling” in removing turbidity, SS, and COD from tannery wastewater.

ularly beneficial (e.g. reduced alum consumption) for the plants receiving tannery wastewater with highly variable composition such as SS concentration.

One gram of Al^{3+} added, removed approximately 30 g COD and 22 g SS from the liquid phase of tannery wastewater (samples #1 and #2). Our results agreed with the previous studies, which reported one gram Al^{3+} could remove 13–100 g COD and 1–100 g SS [15,17,19]. Control jars—receiving no alum—were not used in our study. Therefore, it is not possible to strip the effect of simple physical settling from the jar test results using the control data. To address this limitation, the related literature was reviewed to estimate the probable contribution of physical settling. Song et al. [15] showed the SS and COD concentrations of a tannery wastewater sample (with the initial SS and COD of 1,500 and 5,000 mg L^{-1}, respectively) decreased 75 and 38%, respectively, after a 1-h settling. In this study, a 30-min settling period was used. Assuming that the SS and COD removal rates were linearly correlated with settling time (settling time ≤ 1 h), quiescent settling could remove 38% of SS, and 19% of COD from the wastewater. This assumption is a realistic one based on the batch settling curve presented by Song et al. [15], and the COD and SS removal results of this study can be corrected for the physical settling. On average, the net removal rate became 21 g COD and 13 g SS per one g Al^{3+} added (samples #1 and #2). It must be noted that the previous rates were heavily dependent on the wastewater SS concentration. Haydar and Aziz [19] showed that the contribution of plain physical settling to the pollutant removal could be higher in a more dilute tannery wastewater (Fig. 1). The net removal rates for COD and SS were 16 and 4 g g^{-1} Al^{3+} added, respectively [19].

As noted earlier, this study was performed on the treatment plant influent (raw tannery wastewater). Instead of raw wastewater, physically treated wastewater was fed into the chemical treatment units at the full-scale plant. Our batch study results showed that the chemical treatment units dosed with 55 mg L^{-1} Al^{3+} could virtually remove all COD and SS provided that the upstream units reduced COD and SS concentrations by 62 and 52%, respectively. Mere physical treatment was not expected to attain a total COD removal rate as high as 60% because more than 50% of the total COD consisted of dissolved COD. On the other hand, physical solid separation operation was capable of removing half of SS [19]. Consequently, the wastewater treatment authority may achieve its SS performance target using the physicochemical treatment, whereas an additional treatment can be required to meet the effluent COD target consistently. Since the tannery wastewater treatment plant included biological treatment units downstream of the chemical units, COD (e.g. mostly dissolved) escaping from chemical treatment could be removed in the biological treatment.

Table 3
Typical influent characteristics of wastewater treatment plant of organized industrial tannery zone in Corlu (Turkey)

Variable	Influent concentration (mg L^{-1})	Discharge standard[a] (mg L^{-1})	Target removal (%)	Current influent load (kg d^{-1})
COD	2,500–4,000	200	92–95	7,500–12,000
SS	1,000–2,000	125	88–94	3,000–6,000
Total Cr	85–100	2	98–99	175–300
Sulfide as S	45–65	1	98–99	135–195
Oil–grease	50–60	20	60–67	150–180
TKN	60–70	45	25–36	180–210
	Influent value	Discharge standard[a]	–	–
pH	4–6	6–9	–	–

[a] Based on the "discharge standards to the receiving media" for 24-h composite samples except for the SS standard, which is for 2-h composite samples [34].

3.3. Coagulation performance of EW

One liter of samples #1 and #2 was dosed with 5.5 and 4.4 mL EW, respectively, at the beginning of the jar test. Sample pH was adjusted to the same pH values used in the alum jar tests (Table 6). The pollutant removal rates obtained in the EW jar tests mirrored those of the alum jar tests (Fig. 1). COD removal (*ca.* 60%) was lower than the SS and turbidity removal observed for both samples. Differences between the COD and turbidity removal performances of alum and EW appeared to be minuscule. Absolute difference between the percent COD and turbidity removal rates was ≤3%. The difference between the SS removal performances was higher (absolute difference was ≤6%). Results of this preliminary feasibility test showed that EW could be used as a liquid alum surrogate for coagulating tannery wastewater. Under this context, 1 g of Al in EW is almost equivalent to 1 g of Al in liquid alum.

Potential use of EW as a coagulant is most likely to have a significant impact on the coagulant consumption at the organized industrial tannery wastewater treatment plant. As noted earlier, typical liquid alum consumption of the plant was estimated at 1.2 L m^{-3} wastewater. Based on the EW jar test results, 5 mL EW was assumed to be consumed per L of wastewater (0.5% (v/v)). Volumetric coagulant consumption can quadruple if EW substitutes liquid alum at the full-scale. This may require a larger on-site coagulant storage facility and influences economic feasibility of the EW use as a coagulant.

Another issue pertinent to the use of EW as a coagulant is its pollutant content. Coagulants should not include significant amounts of regulated pollutants, since these pollutants can contribute to the wastewater strength. In this study, COD, and SS loads attributed to EW constituted ≤1 and 0.2% of the corresponding influent loads, respectively, (Tables 3 and 4). Contribution of EW to the overall Cr load of the plant was even less significant (i.e. ≤0.01%) (Tables 3 and 4). Potential EW contribution to the metal loads of the liquid and/or sludge streams was anticipated to be insignificant. The preliminary results suggested that EW could be used as a coagulant instead of alum without increasing the pollutant load of the treatment plant significantly. Exporting EW as a coagulant is one

Table 4
EW characteristics determined in this study

Variable	Unit	Value
COD	mg L^{-1}	520
TOC	mg L^{-1}	430
SS	mg L^{-1}	30
Turbidity	NTU	13
pH		12.5
Al	mg L^{-1}	12,640
Co	mg L^{-1}	0.05
Cr	mg L^{-1}	0.1
Fe	mg L^{-1}	1.0
Mg	mg L^{-1}	0.85
Sb	mg L^{-1}	0.1
Sn	mg L^{-1}	0.4
Sr	mg L^{-1}	0.04
Tl	mg L^{-1}	0.1
V	mg L^{-1}	0.48
Zn	mg L^{-1}	0.04
Cl^-	mg L^{-1}	447
NO_3^-	mg L^{-1}	252
SO_4^{2-}	mg L^{-1}	125

Table 5
Characteristics of tannery wastewater used in this study

Variable	Sample #1	Sample #2
COD (mg L^{-1})	3,250	2,755
SS (mg L^{-1})	1,570	1,200
Turbidity (NTU)	1,150	1,060

Table 6
Dosage and pH results of jar tests for alum coagulant

	Al^{3+} dosage ($mg\,L^{-1}$)	pH	COD removal (%)	SS removal (%)	Turbidity removal (%)
Sample #1	70	7.5	63	96	96
Sample #2	55	7.0	62	96	97

of the unconventional alternatives that can be pursued by Al coating industry. It must be noted that *in situ* Al and caustic solution recovery is another alternative deserving attention. These alternatives need to be assessed thoroughly in the future studies.

3.4. Cost analysis

Alum treatment of the tannery wastewater on average cost 0.15 USD m^{-3} of wastewater (cost range: 0.12–0.18 USD m^{-3} of wastewater). Annual alum cost of the plant can reach two million USD if the plant continuously and consistently operates at the design flow rate of 36,000 $m^3\,d^{-1}$. However, the plant currently has a substantially lower influent flow rate, and only one of its three parallel treatment trains is used. Capacity of the operational treatment train is 12,000 $m^3\,d^{-1}$. Unfortunately, influent flow records were unavailable. Therefore, we estimated the average monthly wastewater volume using the alum dose data. The plant currently consumes from 72 to 91 t of liquid alum per month (average monthly consumption was 82 t). Assuming an average alum consumption of 1.5 kg liquid alum m^{-3} of wastewater, average monthly volume of the wastewater treated at the plant was estimated at 55,000 m^3 per month. Corresponding monthly alum cost ranged from 6,800 to 9,500 USD and the average alum cost was 8,200 USD.

The liquid alum surrogate EW is regarded as waste and regulated in Turkey. Therefore, management of the Al plant is expected to have a willingness to give away EW for free or a minimal price to avoid the treatment costs. Transportation of EW from the Al plant to the wastewater treatment plant can constitute a cost item. Unit transportation cost was estimated at 0.01 USD kg^{-1} [31]. An EW volume of 443 m^3 was necessary for the chemical treatment of 88,600 m^3 wastewater per month. Assuming EW density as 1,100 kg m^{-3}, monthly EW consumption of the treatment plant amounts to *ca.* 500 t. Corresponding monthly transportation cost becomes *ca.* 5,000 USD. The transportation cost was assumed to be fully paid by the tannery wastewater treatment authority. If the tannery wastewater treatment switches from alum to EW coagulant, monthly chemical cost of the treatment is reduced from 8,200 to 5,000 USD, thus indicating a 40% reduction. This preliminary economic analysis was based on the assumption that EW cost was solely the function of transportation cost. Under the given constraints, utilization of EW could potentially reduce the chemical treatment cost from 0.15 (liquid alum) to 0.09 USD (EW) m^{-3} of tannery wastewater.

4. Conclusion

We performed a preliminary study to test the feasibility of utilizing EW from an Al coating plant as a commercial alum substitute at a nearby full-scale tannery wastewater treatment plant (Corlu, Turkey). COD, SS, and turbidity removal performance of the EW was compared against alum using laboratory-scale jar tests. Coagulant dose (55–70 mg $Al^{3+}\,L^{-1}$) and pH (7.0–7.5) used in the jar tests mimicked those of the full-scale wastewater treatment plant. Our results were promising; EW performed as well as alum in COD, SS, and turbidity removal from the tannery wastewater. Both coagulants removed more than 90% of the SS and turbidity, whereas their COD removal rate was approximately 60%. For every g of Al^{3+} added as alum or EW, 30 g COD and 20 g SS were removed.

There may be concerns about the utilization of an industrial wastewater as a coagulant since it may increase the pollutant load of the receiving treatment plant. Our preliminary assessment indicated that EW was unlikely to increase the pollutant load of the tannery wastewater treatment plant. Alum use incurs a coagulant expense for the tannery wastewater treatment plant. Substituting liquid alum with EW could potentially reduce the chemical treatment cost by 40%. A comprehensive work is necessary to study the operational, economical, and environmental aspects of EW utilization for wastewater coagulation. Lastly, an environmental and economic assessment of two EW management alternatives, "on-site resource recovery" vs. "export for off-site coagulation," would be of great benefit to the related industry.

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