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Solidification of tannery sludge with various binders

Feride Ulu

Gebze Technical University, Environmental Engineering Department, 41400, Gebze-Kocaeli, Turkey, fulu@gtu.edu.tr, ORCID: 0000-0002-9495-3958

ABSTRACT

The treatment of tannery sludge is an issue that has received considerable attention due to the potential of tannery sludge to cause severe environmental damage. In this study, the solidification process of the waste sludge of the Istanbul Tannery Organize Industry Wastewater Treatment Plant was investigated for safe disposal. The solidification technique was applied using various binders and their different mixtures, such as active carbon, gypsum ($CaSO_4/2H_2O$), fly ash, lime (CaO), zeolite, and different cement-sand mixtures on the laboratory scale. The essential parameters such as TOC, fluoride (F^- mg/l), chloride (Cl^- mg/l), sulfate ($SO_4^=$ mg/l), chromium (VI) (Cr^{6+} mg/l), and ammonium (NH_4^+ mg/l) were determined after solidification process at certain conditions. The analysis results of treated sludge samples were compared to the criteria for storage in the landfills in the Hazardous Waste Control Regulation (HWCR) as well as cost-calculation was done at optimum conditions. After the addition of 10% wt. $CaSO_4$ in the solidification study, the eluate concentration of TOC, Cl^- and $SO_4^=$ was below the limit values. When tannery sludge was solidified using CaO, the necessary criteria could not be obtained. On the other hand, with the addition of 33% CaO and 5% AC mixture TOC and AOX were observed below the limit values. The solidification was occured with mörtel + portland cement and 5% activated carbon additives and the desired limit values in HWCR were succussed for all parameters. Besides, with the addition of 30% zeolite, all parameters declined below the limit values.

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1. Introduction

Tannery industry wastewaters have severe hazards to the environment due to their high concentration of suspended solids, organic matter (COD and BOD values), inorganic compounds such as chlorides, sulfides, nitrogen-containing compounds (ammonia, nitrites, and nitrates), toxic metals complexes, especially chromium (used as tanning agent) and deep color content [1]. Generally, conventional processes such as adsorption [2], biological process [3,4], and advanced processes [5, 6, 7], etc. are carried out to remove these pollutants from tannery industry wastewaters. Tanneries in Europe usually discharge their wastewater effluents to large wastewater treatment plants. In contrast, in developing countries, those effluents are directly discharged without treatment into surface waters, rivers, lakes, and marine ecosystems [1]. Because of the widespread use of leather around the world, the sustainable management of produced wastewater and waste sludge from the tannery industry need to be highlighted more.

The tanning operation results in a high amount of waste sludge which is known a threat to the ecological biota [8]. Especially, the metal-containing sludges in tannery are one of the primary environmental problems due to the leaching of toxic metals into surface and groundwater. Since each wastewater treatment plant has different features, the character and amount of sludge produced change. Also, each country has different regulations regarding the utilization and/or safe disposal of tannery wastewater sludge. Because of these reasons, the optimal sludge utilization/application methods solution would differ from case to case.

In the literature, various techniques such as landfill, composting, anaerobic digestion [9], thermal treatment [10], aerobic stabilization and compaction and drying [11], pyrolysis [12], solidification and stabilization (S/S) process [13,14] for utilization and/or safe disposal of waste sludge have been studied.

S/S technologies use binders and additives to reduce pathogens, liquid volume, offensive odors, the mobility and toxicity of the pollutants in waste sludge, and transform a final product before its reuse or disposal in a landfill [15, 16].

Solidification refers to techniques that mechanically bind the waste and solidification reagents using organic and inorganic binders such as polyesters and epoxy resins; lime, gypsum, or zeolites, respectively [15, 17]. It does not necessarily involve a chemical interaction between the contaminants and the solidifying additives. On the other hand, stabilization refers to techniques that chemically reduce the hazard potential of waste by converting the contaminants into less soluble, mobile, or toxic forms. The stabilization mechanism of a solidified matrix can be chemisorption, adsorption, ion exchange, precipitation, surface complexation, passivation, chemical incorporation, and inclusion [15, 13].

In addition, as mentioned above, the other most common methods of sludge stabilization are biological processes of anaerobic mesophilic digestion and aerobic digestion under ambient conditions.

The aim of this study is to research the most appropriate solidification process for the waste sludge of the Istanbul Tannery Organize Industry Wastewater Treatment Plant, in order to make the waste sludge comply with the criteria for storage in the landfills in the Hazardous Waste Control Regulation. Different substances such as active carbon, gypsum ($CaSO_4/2H_2O$), fly ash, lime (CaO), zeolite, and different cement-sand mixtures were used for the solidification process on the laboratory scale. Besides, the cost analysis of the solidification process was done.

2. Materials and experimental procedure

2.1. Materials

The wastewater of all facilities in the Istanbul Leather Organized Industrial Zone is collected with a closed sewage system and treated at the Istanbul Tannery Organize Industry Wastewater Treatment Plant, before discharging.

Sludges were collected in the form of filter cakes from the Istanbul Tannery Organize Industry Wastewater Treatment Plant. The samples were taken from the outlet of the dewatering unit (belt press) and primary and secondary settling outlets. Two different commercial types of cement, mörtel (MC) and Portland (PC) cement, $CaSO_4/2H_2O$, CaO, fly ash (FA), and zeolite as additives were used to perform the solidification process of the tanning sludge. Table 1 shows composition of MC and PC.

Table 1 *Composition of MC and PC*

Additive	TOC [mg/L]	AOX [mg/L]	F^- [mg/L]	Cl^- [mg/L]	pH	Conductivity [µS/cm]
MC	<10	<0.02	<2	0	13	9670
PC	<10	<0.02	<2	0	13.3	14430

2.2. Characterization of the tannery sludge leachate

Turkish environmental regulations made the leaching test obligatory according to DIN 38414-S4 Standard [18]. The standard states that 100 g of dry waste sample is extracted by shaking with 1 liter of distilled water for 24 hours. After extraction, the solid and liquid phases are separated from each other by centrifugation or filtration method. The composition of sludge was analyzed according to the criteria of HWCR for safe disposal. Table 2 shows the analysis results of the tannery waste sludge eluate.

Table 2 *Comparison of eluate analysis results of tannery sludge sample with the criteria of HWCR*

*1.1.1. **Parameter / Sample***	**26.08.2021**	**07.09.2021**	**20.09.2021**	**10.10.2021**	**HWCR Hazardous Waste**
pH	8.00	7.7	7.45	7.92	4 – 13
TOC, mg/l	823	403.5	550	393	40 – 200
Arsenic (As mg/l)	0.008	0.005	0.003	<0.003	0.2 – 1
Lead (Pb mg/l)	1.17	0.95	0.146	<0.1	0.4 – 2
Cadmium (Cd mg/l)	< 0.02	< 0.02	<0.02	<0.02	0.1 – 0.5
Chromium (VI) (Cr^{6+} mg/l)	0.1	0.5	0.081	0.15	0.1 – 0.5
Copper (Cu mg/l)	0.18	0.11	0.05	0.030	2 – 10
Nickel (Ni mg/l)	0.2	0.16	0.064	0.0760	0.4 – 2
Mercury (Hg mg/l)	0.001	0.0015	<0.0001	0.001	0.02 – 1
Zinc (Zn mg/l)	0.51	0.35	0.406	0.225	2 – 10
Phenols (C_6H_5OH mg/l)	1.25	0.32	12.22	1.31	20 – 100
Fluoride (F^- mg/l)	73.8	13.5	38.57	5.6	10 – 50
Ammonium (NH_4^+ mg/l)	178	129.7	257	146	200 – 1000
Chloride (Cl^- mg/l)	1437	1527	1644	1133	1200 - 6000
Cyanide (CN^- mg/l)	0.13	0.12	<0.05	<0.05	0.2 - 1
Sulfate ($SO_4^=$ mg/l)	90	21.4	152	342	200 – 1000
Nitrite (NO_2^- mg /l)	0.13	0.18	0.082	0.013	6 – 30
(AOX mg/l)	2.09	1.25	1.09	1.25	0.6 – 3

2.3. Mixture preparation and characterization

Tannery sludge and the additives such as active carbon, gypsum ($CaSO_4/2H_2O$), fly ash, lime (CaO), cement, and zeolite were mixed in different proportions by following the addition of water to form homogenous mixtures. Mixing was carried out on a rotary mixer with a capacity of 3 to 5 kg per charge. After mixing, each mixture was placed in a tray 30 cm long, 24 cm wide, and 6 cm high. Afterward, they were weighed and left for 28 days under room temperature and humidity conditions. After 28 days of curing, the mixtures were weighed again. The leachate characteristics, TOC, chromium (Cr^{6+}), fluoride (F^-), chloride (Cl^- mg/l), sulphate ($SO^{4=}$ mg/l), and AOX, after each solidification experiment were determined for all the cured mixtures.

2.4. Analytical methods

The concentration of metals was determined by Flame Atomic Absorption Spectrophotometry, using the Perkin-Elmer AAnalyst 800 instrument. The organic matter content was measured by the TOC- Schimadzu, Japan analyzer. Ammonium nitrogen, AOX, nitrite, and sulfate were measured in accordance to Standard Methods (APHA, 1999) [19].

3. Results

3.1. Solidification studies with $CaSO_4$ and fly ash

The reaction of waste sludge with water results in an excessive amount of halogenated organic compounds, chloride, fluoride, and total organic carbon which can pass into the liquid phase. These pollutants leaching can be prevented by an appropriate solidification process using a mixture of sludge and additives materials such as activated carbon, zeolite, $CaSO_4.2H_2O$ (gypsum), fly ash, CaO, and cement.

The waste sludge was mixed with 4% and %10 of $CaSO_4$ and 10% of fly ash. The analysis results of the solidification processes at different rations were given in Table 3. When the results were examined, it was seen that TOC, chloride, and fluoride parameters declined below acceptable values with %10 $CaSO_4$. It was observed that the concentration of SO_4 in the eluate was above the limit value. The lowest $CaSO_4$ concentration succeed in reducing fluoride and chlorine values below the limit values.

Table 3 *Eluate composition of different solidification matrixes containing $CaSO_4$ and fly ash at different ratios*

1.1.2. Parameter / Sample **26.08.2021**	**Raw sample**	**4 wt.% $CaSO_4$**	**10 wt.% $CaSO_4$**	**10 wt.% Fly ash**	**Belt pres sludge**	**HWRC Hazardous Waste**
TOC, mg/l	823	207	33	520	823	40 – 200
Fluoride, mg/l	73.8	<0.2	<0.2	13	73.8	10 – 50
Chloride, mg/l	1437	517	571	574	1437	1200 - 6000
Sulfate, mg/l	90	2010	1982	2182	90	200 – 1000
AOX, mg/l	2.09	1.11	0.07	1.37	2.09	0.6 – 3

3.2. Solidification study with CaO

As a result of the solidification study performed with the addition of 5%, 7%, and 10% CaO, it was observed that the eluate concentration of fluoride and ammonium parameters decreased at all applied rates, and the chloride parameter declined below the limit values in the studies when 5% and 7% CaO were added, as seen in Table 4.

In addition, it was observed that the eluate concentrations of Cr^{6+} and total organic carbon parameters increased and exceeded the limit values.

Table 4 *Eluate composition of solidification matrixes at different CaO ratios*

1.1.3. Parameter / Sample **07.09.2021**	**Raw sample**	**5 % CaO**	**7 % CaO**	**10 % CaO**	**Belt Pres Sludge**	**HWRC Hazardous Waste**
TOC, mg/l	403.5	895	1732	1995	403.5	40 – 200
Fluoride, mg/l	13.5	<0.2	<0.2	<0.2	13.5	10 – 50
Chloride, mg/l	1527	732	1024	1395	1527	1200 – 6000
Sulfate, mg/l	21.4	58.2	101.6	97.6	21.4	200 – 1000
Cr^{+6}, mg/l	0.5	0.27	0.21	0.21	<0.01	0.1-0.5
Ammonium	129.7	28.4	42.4	43.2	129.7	200-1000

As shown in Table 5, the total organic carbon parameter, which increased as a result of the addition of CaO, could be reduced with the addition of 5% activated carbon.

Table 5 *Eluate composition of solidification matrixes containing CaO and active carbon at different ratios*

1.1.4. Parameter / Sample **20.09.2021**	**Raw sample**	**8 % CaO**	**16 % CaO**	**33 % CaO**	**8 % CaO + %5 active carbon**	**16 % CaO+ %5 active carbon**	**33 % CaO+ %5 active carbon**	**Belt Pres Sludge**
TOC, mg/l	550	1075	950	750	800	400	275	550
AOX, mg/l	1.09	0.28	0.356	<0.02	<0.02	0.042	<0.02	1.09

3.3. Solidification study with different cement mixtures

Solidification results with different cement mixtures were shown in Table 6 and Table 7. Mörtel cement contains 10% cement and 90% sand by weight, while Portland cement contains 100% cement. Mörtel cement and portland cement mixture were prepared as 75% Mörtel cement and 25% Portland cement. The cement and sand ratio of the mixture were 32.5% and 67.5%., respectively. The solidification process containing PC and MC could not achieve the limit value of TOC as 200 mg/l in the HWCR.

Table 6 *Eluate composition of solidification matrixes containing MC and PC at different ratios*

*1.1.5. **Parameter / Sample*** **20.09.2021**	**Raw sample**	**16 % MC**	**33 % MC**	**16 % PC**	**33 % PC**	**16 % MC+PC**	**33 % MC+PC**	**Belt Pres Sludge**
TOC, mg/l	550	200	600	550	325	600	300	550
AOX mg/l	1.09	0.16	0.10	0.10	0.18	0.232	<0.02	1.09
Chloride, mg/l	1644	850	845	474	905	875	683	1644
Fluoride, mg/l	38.57	4.55	<2	12.5	<2	4.8	22.2	38.57

The literature states ordinary PC and sludge with certain other additive including fly ash or other aggregates improves the physical characteristics and decreases the leaching losses from the resulting solidified waste [20]. As seen in Table 7, in the study carried out with the addition of 16% mörtel+portland cement + 5% activated carbon, the solidification results comply with the limit values specified in HWCR.

Table 7 *Eluate composition of solidification matrixes containing active carbon and Mörtel+Portland cement at different ratios*

*1.1.6. **Parameter / Sample*** **20.09.2021**	**Raw sample**	**16% MC+PC+ 5% AC**	**33% MC+PC + 5% AC**	**16% MC+PC**	**33% MC+PC**	**Belt Press Sludge**
TOC, mg/l	550	175	178	600	300	550
AOX mg/l	1.09	<0.02	0.218	0.232	<0.02	1.09
Chloride	1644	935	1000	875	683	1644
Fluoride	38.57	7.4	<2	4.8	22.2	38.57

The additives used in the study are cost-effective and widely available. Also, the equipment required for processing is simple to operate. The estimated cost for the solidification process using additives such as PC, MC, and AC is given below.

The additive of 16% includes 32.5% cement and 67.5% sand. The amount of additive content required for 200 tons/day of treatment sludge was 32 tons/day, and the amount of active carbon was 10 tons/day.

Cement amount= 32 ton/day x 0.325 = 10.4 ton/day
Sand amount = 32 ton/day x 0.675 = 21.6 ton/day
Active carbon amount = 10 ton/day

Cement cost= 10400 kg/day x 0.5 Euro/kg = 5200 Euro/day

Sand cost = 21.6 ton/day x 1.5 Euro/ton = 32 Euro/day
Active carbon cost= 10 000 kg/day x 5 Euro/kg = 50 000 Euro/day
Total cost= 5200 + 32 + 50 000 = 55 232 Euro/day

3.4. Solidification study with zeolite

As shown in Table 8, in the study carried out with the addition of 30% and 40% zeolite, the concentration of all parameters declined above the limit values specified in HWRC. The estimated cost for the solidification process to be made by preparing a 30% zeolite mixture is given below.

Zeolite amount: 200 ton/day x 0.30 = 60 ton/day
Zeolite cost: 60 ton/day x 444 Euro/ton = 26 666 Euro/day

Table 8 *Eluate composition of solidification matrixes containing zeolite at different ratios*

*1.1.7. **Param eter /Sample***	**Raw sample**	**10 wt.% zeolite**	**20 wt.% zeolite**	**30 wt.% zeolite**	**40 wt.% zeolite**	**50 wt.% zeolite**	**Belt Press Sludge**
10.10.2021							
TOC, mg/l	393	315	219	175	110	2	393
AOX mg/l	1.25	0.84	0.66	0.37	0.32	0.025	1.25
Chloride	1133	771	685	613	485	2	1133
Fluoride	5.6	4.4	4.5	3.8	3.7	0.35	5.6
Sulphate	342	371	220	199	18	4	342
$Chromium^{6+}$	0.15	<0.03	<0.03	<0.03	<0.03	<0.03	0.04

4. Conclusions

The solidification process converts the pollutants into an immobile phase and obtains easy handling. In the study, the solidification process using substances such as $CaSO_4$, fly ash, CaO, cement, and zeolite was applied to tannery sludge to find the most appropriate way to comply with the criteria for Storage in the Landfills in the Hazardous Waste Control Regulation. The efficiency of the process was determined in terms of halogenated organic compounds, chloride, fluoride, and total organic carbon concentration of leachate.

As a result of the study with the addition of $CaSO_4$, it was observed that all parameters, TOC, chloride, and fluoride declined below the limit value but the sulfate parameter reached above the limit values.

When the fly ash was used as an additive, a slight decrease was observed in the eluate concentrations of the chloride, TOC, and fluoride parameters, and an increase in concentration of the sulfate parameter exceeding the limit values was detected.

In the study conducted with CaO, it was observed that the concentration of the TOC parameter increased significantly, and concentrations of fluoride and chloride parameters declined below the limit values. But concentration of the chromium (Cr^{6+}) parameter increased. In the experiments with CaO, 20% TOC removal was achieved in the study with the addition of 5% activated carbon, but the removal at this rate was not successful in reaching the 200 mg/l level determined by HWCR for the TOC parameter.

In addition, in the solidification study performed with mörtel + portland cement and 5% activated carbon additives, all parameters complied with the criteria of HWCR.

The active carbon seems to be a successful absorbent that can be incorporated into cement. Also, the zeolite is a suitable and cost-effective material to form a solid product for safe disposal. It is more economical than another alternative, the mixture of PC, CM, and AC.ent ripple and THD value are reduced by the IBC model.

References

[1] Jallouli S., Wali A., Buonerba A., Zarra T., Belgiorno V., Naddeo V., & Ksibi M. "Efficient and sustainable treatment of tannery wastewater by a sequential electrocoagulation-UV photolytic process". Journal of Water Process Engineering, 38, (2020), 101642.

[2] Mia A. S., Ahmad F., Rahman M. "Adsorption of chromium (Cr) from tannery wastewater using low-cost spent tea leaves adsorbent". Applied Water Science, (2018), 8(5), 1-7.

[3] Zou X., Ma F., Yu J., Su Q., Gai L., Zhao W., & Xiao, S. "Pilot-scale Study on Removal of Pollutants in Tannery Wastewater and Sludge Reduction by Biological Synergist Effect". In IOP Conference Series: Earth and Environmental Science, 546 (3), (2020), 032041. IOP Publishing.

[4] Tran L. L., Tran T. T., Nguyen B. D., & Nguyen T. T. P. "Study of the treatment of tannery wastewater after biological pretreatment by using electrochemical oxidation on BDD/Ti anode". Desalination and Water Treatment, 137, (2019), 194-201.

[5] Isari, A. A., Mehregan M., Mehregan S., Hayati F., Kalantary R. R., & Kakavandi, B. "Sono-photocatalytic degradation of tetracycline and pharmaceutical wastewater using WO3/CNT heterojunction nanocomposite under US and visible light irradiations: a novel hybrid system". Journal of hazardous materials, 390, (2020), 122050.

[6] Rodriguez J., Ochando-Pulido J. M., & Martinez-Ferez A. "The effect of pH in tannery wastewater by Fenton vs. heterogeneous Fenton process". Chemical Engineering Transactions, 73, (2019), 205-210.

[7] Mohammed K., Sahu O. "Recovery of chromium from tannery industry waste water by membrane separation technology: health and engineering aspects". Science African, 4, (2019), e00096.

[8] Juel, M. A. I., Chowdhury, Z. U. M., & Ahmed, T. (2016, July). Heavy metal speciation and toxicity characteristics of tannery sludge. In AIP Conference Proceedings, 1754 (1),(2016), 060009. AIP Publishing LLC.

[9] Mpofu A. B., Welz P. J., & Oyekola, O. O. "Anaerobic digestion of secondary tannery sludge: optimisation of initial pH and temperature and evaluation of kinetics". Waste and Biomass Valorization, 11(3), (2020), 873-885.

[10] Kokkinos E., Proskynitopoulou V., & Zouboulis A. "Chromium and energy recovery from tannery wastewater treatment waste: Investigation of major mechanisms in the framework of circular economy". Journal of Environmental Chemical Engineering, 7(5), (2019), 103307.

[11] Alibardi L., & Cossu R. "Pre-treatment of tannery sludge for sustainable landfilling". Waste Management, 52, (2016), 202-211.

[12] Pietrelli L., Ippolito N., Reverberi, A., & Vocciante, M. "Heavy metals removal and recovery from hazardous leather sludge". Chemical Engineering, 76, (2019).

[13] Arthy M., & Phanikumar B. R. "Solidification/stabilization of tannery sludge with iron-based nanoparticles and nano-biocomposites. Environmental Earth Sciences, 76(4), (2017), 1-17.

[14] Lin H., Zeng L., Zhang P., Jiao B., Shiau Y., & Li D. "Solidification of chromium-containing sludge with attapulgite combined alkali slag". Environmental Science and Pollution Research, 29(9), (2022), 13580-13591.

[15] Montañés M. T., Sánchez-Tovar R., & Roux M. S. "The effectiveness of the stabilization/solidification process on the leachability and toxicity of the tannery sludge chromium". Journal of Environmental Management, 143, (2014), 71-79.

[16] Jayasankar R., & Mohan S. "Experimental studies on solidification and stabilization of tannery sludge". International Journal for Research in Applied Science and Engineering Technology, 6(4), (2018), 856-864.

[17] Pantazopoulou E., Zebiliadou O., Mitrakas M., & Zouboulis A. "Stabilization of tannery sludge by co-treatment with aluminum anodizing sludge and phytotoxicity of end-products". Waste Management, 61, (2017), 327-336.

[18] DIN 38 414 S4, German Standard Methods for Researching Water, Effluent Water and Sludge, Group S: Sludge and Sediments; Determining Leaching with Water (S4), (1984).

[19] Rodger B., and Bridgewater L. "Standard Methods for the Examination of Water and Wastewater. 23rd edition". Washington, D.C.: American Public Health Association, (2017).

[20] Juel Md A. I., Stabilization of Tannery Sludge Through Brick Production, Department of Civil Engineering Bangladesh University of Engineering and Technology, (2016).