GHTMDD – 499
Received: November 11, 2006
Accepted: April 16, 2007

Macedonian Journal of Chemistry and Chemical Engineering, Vol. **26**, No. 1, pp. 39–43 (2007)
ISSN 1857 – 5552
UDC: 628.34/.35

Professional paper

CONTINUOUS COMBINED BIOLOGICAL-CHEMICAL TREATMENT OF TANNERY WASTEWATER

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Tannery wastewater represents a serious environmental and technological problem mainly because it contains large amounts of refractory compounds, salts, ammonia, and surfactants. The objective of this work was to develop an economical long-term continuous method to enhance the treatment of tannery wastewaters. This paper reports a promising laboratory-scale performance of an innovative process, which is the combination of biological degradation, carried out on a glass column, with chemical treatment using lime and alum at optimum conditions. The latter step is aimed at simplifying the chemical structure of recalcitrant organic substances for enhancing their biodegradability. This study was carried out on a real final effluents coming from a centralized plant treating wastewater produced by nine different tanneries in Egypt.

Key words: biological; chemical; treatment; tannery; wastewater

КОНТИНУИРАН КОМБИНИРАН БИОЛОШКО-ХЕМИСКИ ТРЕТМАН НА ОТПАДНИТЕ ВОДИ ОД ИНДУСТРИЈАТА ЗА КОЖА

Отпадните води од процесот на штавење во индустријата за кожа претставуваат сериозен еколошки и технолошки проблем главно поради големата содржина на соли, амонијак и површинско-активни компоненти. Целта на овој труд е да развие континуиран економски оправдан процес за третман на отпадни води од овие индустрии. Овој труд презентира задоволувачки резултати на перформансите на иновативен процес во лабораториски услови. Новината на процесот е во тоа што тој е комбинација од биолошка деградација и хемиски третман; тој се одвива шаржно со додавање на вар и стипса. Биолошкиот третман се одвива во стаклена колона со активна кал. Методот на комбиниран хемиско-биолошки третман покажа задоволителни перформанси за пречистување на отпадните води од индустријата за кожа. Во трудот беа користени примероци од реални отпадни води од девет различни фабрики за преработка на кожа во Египет.

Клучни зборови: билошко-хемиски третман; штавилница; отпдни води

INTRODUCTION

Tanning is a process by which animal hides and skins are converted into stable and durable leather. The hides are treated with natural or synthetic chemicals to stabilize and cross-link their microscopic collagen fiber matrix. The potential environmental impacts of tanning are significant. Chrome tanning using basic chromium(III) sulfate is the most widely used technique. The toxic metal chromium is one of the most common and most damaging of the environmental pollutants associated with the tanning industry [1]. Extensive use of chromium in tanning results in discharge of chromium-containing effluents [2]. The effluents from these industries contain chromium(VI) and chromium(III) at concentrations ranging from tenths to hundreds of milligrams/liter. While chromium(VI) is known to be toxic to both plants and animals, and a strong oxidizing agent and a potential carcinogen [3], chromium(III) is generally only toxic to plants at very high concentrations, and is less toxic or nontoxic to animals [4]. Tannery wastes are classified as hazardous and priority wastes due to the presence of chromium [5]. Even if chromium(III) is discharged into the environment, there is no guarantee that it will remain in this chemical state. For example, landfilling of chromium(III) tannery waste with other acidic industrial wastes, or domestic sewage, which on decomposition can yield acidic conditions, can result in the oxidation of chromium(III) to chromium(VI) [6, 7]. Besides the trivalent chromium, tannery wastewater consists of acidic and alkaline liquors with sulphides, organic and other ingredients which are responsible for high BOD (Biological Oxygen Demand) and COD (Chemical Oxygen Demand) values, as well as high levels of fat and suspended solids [8, 9]. Wastewater may also contain residues of pesticides used to preserve hides during transport, as well as significant levels of pathogens [8, 9]. Discharging untreated tannery wastewater into the environment leads to detrimental chemical, thermal, and biological effects on aquatic, plant and human life. Treatment of tanning wastewater is difficult and represents a serious environmental and technological problem due to the presence of a series of chemicals with low biodegradabilities [10–18]. The present work was aimed at finding an economical continuous combined biological-chemical method for the treatment of tannery wastewaters.

EXPERIMENTAL

Nine samples were collected from the final effluents of nine different tanneries at El-Max, west Alexandria, Egypt. The physico-chemical characterizations of these samples are shown in Table 1. The minimum, maximum, and average values are shown in Table 2.

Table 1

The physico-chemical characterizations of the nine tannery samples

Parameter (unit)	T1	T2	T3	T4	T5	T6	T7	T8	T9
PH	10.4	3.3	9.8	1.3	8.8	10.4	6.9	6.9	4.7
BOD (mg/l)	3645	3510	4000	675	510	1500	1000	27000	420
COD (mg/l)	17907	5576	28127	6077	1551	7068	3141	53014	2591
TSS (mg/l)	29000	2400	30800	2800	600	1984	816	27960	464
Settleable solids 10' (ml)	900	1000	23	850	0	7	0	90	20
Settleable solids 30' (ml)	750	500	600	650	0.5	10	0	400	20
Oil and grease (mg/l)	35	105	106	26	228	72	47.2	131.6	55.6
Sulfides (mg/l)	1400	13	1360	110	158.4	740	58.4	7600	4
Total nitrogen (mg/l)	171.4	20.16	215	371.8	156.8	308	72.8	420	12.9
Phosphate (mg/l)	28.67	21.3	21.69	5.47	11.1	22.64	30.4	91.5	24
Phenols (mg/l)	0.008	0.557	0.322	0.304	0.32	1.7	1.1	1.2	0.1
Chromium (mg/l)	407.2	5.9	362	117.9	1.5	5	1.87	7.13	511

Table 2

The minimum, maximum and average values of the all tannery samples

Parameter (unit)	Minimum	Maximum	Average
PH	1.30	10.40	6.94
BOD (mg/l)	420.00	27000.00	4695.56
COD (mg/l)	1551.00	53014.00	13894.67
TSS (mg/l)	464.00	30800.00	10758.22
Settleable solids 10' (ml)	0.00	1000.00	321.11
Settleable solids 30' (ml)	0.00	750.00	325.61
Oil and grease (mg/l)	26.00	228.00	89.60
Sulfides (mg/l)	4.00	7600.00	1271.53
Total nitrogen (mg/l)	12.9	420.00	194.32
Phosphate (mg/l)	5.47	91.50	28.511998
Phenols (mg/l)	0.01	1.70	0.62
Chromium (mg/l)	1.50	511.00	157.72

METHODS OF ANALYSIS

Water samples collected from the effluent of the nine tanneries were subjected to analysis of some physico-chemical parameters before and after treatment. All the investigated parameters (pH, BOD, COD, TSS, settleable solids, oil and grease, sulfides, total nitrogen, phosphates, phenols and chromium) were determined according to standard procedures described in the standard methods for examination of water and wastewater by the American Public Health Association, APHA [19].

Treatment procedures

a) Chemical treatment

Samples were chemically treated by coagulation in batch experiments using lime and alum. Bach treatment was carried out using the jar test method described by Cohen, 1957 [20]. The optimum operating conditions for each coagulant such as pH and coagulant dose were investigated. In order to determine the optimum pH for each coagulant, different pH values ranging from 5 to 8 at a constant coagulant dose were examined. To study the effect of coagulant concentration, different coagulant doses ranging from 50 to 400 mg/l were examined at the predetermined optimum pH value. During the treatment each sample was placed under a state of rapid stirring (250 rpm) while the coagulant was added slowly to the solution under constant stirring for 3 minutes. The speed was reduced in a regular stepwise manner, covering a range of 100 every 60 seconds until the flocculation stage was reached. The speed was then maintained at 20–30 rpm for further 10 minutes for optimum flock formation. The characteristics of the chemically treated effluents were determined after 30 minutes settlement. Samples for analysis were taken by a suction device allowing the withdrawal of accurate amounts from jars for complete analysis.

b) Biological treatment

Aerobic biological treatment using activated sludge was used for treatment of the contaminated wastes on a glass column with dimensions of 60 cm long and 10 cm diameter. Activated sludge was let to set and was acclimatized for 20 days, after which the treatment was carried and the samples were collected from the system. The final retention time in the activated sludge process was 18 hr. Furthermore, the dissolved oxygen in the activated sludge unit was set, and the sludge concentration was around 3.5 g/l. Mixed chemical-biological treatment combination of chemical and biological treatment methods were·used to investigate their effect in the enhancement of the treatment process.

RESULTS AND DISCUSSIONS

The analysis of each of the composite samples of the wastewater revealed that the ability of the waste to settle was very high. The settleable solid after 10 min reached 478.33 ml and after 30 min reached 485.00 ml (Table 3). Hence, this type of waste can undergo highly efficient treatment if it is settled first. Accordingly, the primary settling step efficiently removed around 49 % of its COD concentration, and 52 % of its BOD concentration. Moreover, the chromium removal of the primary settling process was around 96 % of the chromium content in the influent. In addition, most of the pollutants (such as total nitrogen, oil and grease, TSS, sulfide, phosphates, phenols) are also decreased after the primary settling process. Nevertheless, efficient treatment method(s) were still needed after the primary treatment to meet the waste quality standards. Chemical treatment using either alum or lime at the predetermined optimum conditions helped in the removal of the following pollutant parameters: BOD, COD, TSS, oil and grease, sulfides, total nitrogen, phosphates, phenols and chromium. Although the chemical treatment succeeded in removing high amounts of the pollutant contents, the resulting waste still did not meet the regulations for the disposal of the waste in the sewer network. So, a second treatment process was needed to reach the waste quality of the standard limits of disposal. As a result of the high load of the pollution, represented by COD and BOD values of 7422 and 2680 mg/l for lime, and 6958 and 2500 mg/l for alum, respectively (Table 3), it was necessary to make acclimatization of the sludge for such load to have the ability to degrade. The acclimatization step lasted for around 20 days, after which the chemically treated influent underwent the biological treatment process. It took around 18 hr of retention time with the activated sludge to treat this effluent, and produce an effluent with a quality comparable with that of the regulatory standards (Table 4).

REFERENCES

[1] O. J.Hao, C. Shin, C. Lin, F. Jeng, Z. Chen, Use of Microtox Tests for Screening Industrial Wastewater Toxicity, *Water Science and Technology*, Vol. **34**, No. 10, pp. 43 – 50 (1996).

[2] J. Barnhart, Occurrences, uses, and properties of chromium. *Regul, Toxicol. Pharmacol.* **26**, 1, S3–S7 (1997).

[3] M. Costa, Potential hazards of hexavalent chromate in our drinkingwater, *Toxicol. Appl. Pharmacol.*, **188**, 1, 1–5 (2003).

[4] R. A. Anderson, Chromium as an essential nutrient for humans, *Regul. Toxicol. Pharmacol.* **26**, 1, S35–S41 (1997).

[5] I. Kroschwitz, M. Howe-Grant [Eds], *Kirk-Othmer Encyclopedia of Chemical Technology*. Fourth Edition, Volume **14**, 208– 226. John Wiley and Sons Inc., New York, Chichester, Bristbane, Toronto, Singapore (1995).

[6] P. M. Outridge, A. M. Schuehammer, Bioaccumulation and toxicology of chromium: implications for wildlife. *Reviews of Environmental Contamination and Toxicology*, **130**, 31–77 (1993).

[7] A. B. Mukherjee, Chromium in the environment of Finland. *The Science of the Total Environment*, **217**, 9–19 (1998).

[8] World Bank Group, *Pollution Prevention and Abatement Handbook*, Tanning and Leather Finishing, pp 404– 407, 1998.

[9] R. M. Harrison [Ed.], *Pollution causes, effects and control*. Third Edition, Chapter **6**: 123–143, The treatment of toxic wastes. The Royal Society of Chemistry, Cambridge, UK. ISBN 0-85404-534-1, 1996.

[10] A. Carucci, A. Chiavola, M. Majone, E. Rolle, Treatment of tannery wastewater in a sequencing batch reactor. *Water Sci Technol*, **40**, 1, 253–259 (1999).

[11] Cassano A, Molinari R, Romano M, Orioli E., Treatment of aqueous efluents of the leather industry by membrane process. A review. *J. Membr. Sci.*, **181**, 111–118 (2001).

[12] A. Cassano, R. A. Molinari, E. Drioli, Saving of water and chemicals in tanning industry by membrane process, *Water Sci Technol.*, **40** (4e5), 443–450 (1999).

[13] M. A. Chaudry, S. Ahmad, M. T. Malik, Supported liquid membrane technique applicability for removal of chromium from tannery wastes. *Waste Management*, **17**, 4, 211–218 (1997).

[14] J. Landgrave, A pilot plant for removing chromium from residual water of tanneries. *Environ. Health Perspect*, 103 (Suppl.), 63–65 (1995).

[15] Z. Song, C. J. Williams, R. J. Edyvean, Sedimentation of tannery wastewater. *Water Res.*, **34**, 7, 2171–2176 (2000).

[16] A. G. Vlyssides, C. J. Israilides, Detoxication of tannery waste liquors with an electrolysis system. *Environ. Pollut.*, **97**, 1–2, 147–152 (1997).

[17] W. M. Wiegant, T. J. J. Kalker, V. N. Sontakke, R. R. Zwaag, Full scale experience with tannery water management: an integrated approach. *Water Sci. Technol.*, **39**, 7, 169–176 (1999).

[18] Zheng Y, Bai D. Physi-chemical-biological treatment of tannery wastewater. *Industrial Water and Wastewater*, **32**, 5, 52–54 (2001).

[19] *Standard Methods for the Examination of Water and Wastewater* (20^{th} Edition). Edited by Lenore S. Clesceri, Arnold E. Greenberg and Andrew D. Eaton. Published by the American Public Health Association, the American Water Works Association and the Water Environment Federation, 1998.

[20] J. M. Cohen, Improved Jar Test Procedure. *J. Am Water Works Assoc.*, **49**, 1425 (1957).