http://dx.doi.org/10.22161/ijeab/2.6.10 *ISSN: 2456-1878*

Treatment of Tannery Wastewater to Remove Hazardous Pollutants by Scoria (Volcanic ash) a Low cost Adsorbent

Mekonnen Birhanie, Seyoum Leta, Mohammed Mazharuddin Khan

Center for Environmental Sciences, Addis Ababa University, Addis Ababa, Ethiopia

***Abstract* —** *In present study Scoria, a volcanic ash identified as potentially efficient low-cost and locally available filter media as an adsorbent for the treatment of tannery wastewater and investigated as a filter media for tannery wastewater treatment with selected physicochemical parameters. This study had been conducted in Addis Ababa University from May to August 2016.The volcanic rocks were collected from volcanic cones of refit valley area of Oromia region, Ethiopia and their chemical characteristics were determined using XRF analysis. Batch mode comparative experimental study design has been carried out. The filter media was crushed and graded and effective size was determined by using standard sieve. The composite sample of wastewater was collected from Dire tannery, Addis Ababa Ethiopia. The physicochemical analysis of wastewater samples has been done before and after 24, 48, and 72 hours treatment using standard methods. Mean and standard deviations were calculated for each parameter. R statistical software was run for data analysis. Based on this investigation, characterization of the untreated tannery wastewater revealed that the mean concentration of BOD_5, COD, TSS or orthophosphate, ammonium, nitrite, nitrate, sulfide, sulfate and chromium were 1081±159.55, 12913±6874.7, 2426±515.2, 168±74, 314±59.9, 1.7±0.29, 124±12.8, 417±130.7, 1307±224 and 35.7±8.6 mg/l respectively. Nitrate removal efficiency of scoria was 99% at RT= 72 hours. However phosphate removal was better by scoria on the first 24 and 48 hours but then again at RT=72hours scoria removes 63% only. The efficiency of scoria shows from 75-77%. In the first 24 and 48 hours retention time scoria achieved 71% chromium reduction. Considering all the selected tannery wastewater parameters for this study, the average treatment efficiency of scoriawas58.8% and 63.4% at RT=24 hours, and 67.5% at RT= 48 hours respectively and equivalent result (68.3%efficiency)was obtained after 72 hours. The results shows scoria substrates has a potential to treat tannery wastewater.*

***Keywords*— Tannery Wastewater, Scoria, Filter Media, Removal efficiency, Wastewater parameters.**

INTRODUCTION

1.1 Introduction: Tanning is one of the oldest industries in the world Tannery effluent is among one of the most hazardous pollutants of industry. Major problems caused by tannery wastewater containing heavy metals, nutrients, toxic chemicals, chloride, lime with high dissolved and suspended salts, and other pollutants.

With the growth of population, the increasing requirement of leather and its products led to the establishment of large commercial tanneries. Tanneries are typically characterized as pollution intensive industrial complexes which generate widely varying, high-strength wastewaters. Nearly 30 m^3 of wastewater is generated during processing of one tone of raw skin/hide [1].

Tannery operation consists of converting of the raw hide or skin into leather which consume huge amount of water in several stages, generating an enormous amount of liquid effluents which are hazardous to the environment to which they are discharged, consequently, make it as a potentially pollution intensive industry. Tannery effluents again compromise the physical, chemical and biological properties of aquatic environment. Apart from the most toxic heavy metals like Chromium (Cr) chemical impurities of tannery effluents mostly includes the following dissolved substances such as inorganic salt cations (Fe, Zn, Cu, Ca, Na, etc.); anions such as SO_4^{2}, NO_3^{-} , PO_4^{3-} and parameters such as, BOD, COD, TSS, TDS etc.[2]. Therefore treating tannery wastewater using natural adsorbents is very important to protect the surrounding environment.

In Ethiopia Currently, there are more than 30 tannery industries in operation. Among them the majority found in Oromia region especially Mojo town and around six established in the capital city Addis Ababa. These tanneries have 153,650 sheep and goat skin soaking capacity and 9,725 cowhides soaking capacity per day. Together they also employ 4577 persons [3].

The total wastewater discharge estimation from tanneries is about 400 million m^3/year. About90% of world leather production uses chrome-tanning processes rather than vegetable tanning [4]. In Chrome tanning process

http://dx.doi.org/10.22161/ijeab/2.6.10 *ISSN: 2456-1878*

tanneries utilize chromium in the form of basic chromium-sulphate for hide stabilization against microbial degradation and provision of flexibility of the leather. In chrome tanning process about 60% - 80% of chromium reacts with the hides and about 20%- 40% of the chromium amount remaining in the solid and liquid wastes.

Tanneries generate wastewater in the range of 30 – 35 liter per kilogram of skin or hide processed with variable pH and high concentrations of suspended solids, BOD and COD. Major problems are due to wastewater containing heavy metals, toxic chemicals, chloride, lime with high dissolved and suspended salts and other pollutants [5]. Hexavalent chromium from tannery wastewater is one of the major concerns of environmental pollution. This is due to discharge of tannery wastewater in large quantities without or with partial treatment [6].

Developing countries face numerous challenges related to preserving the environment from industrial wastewater pollution. Like many other developing countries, Ethiopia also grieve from environmental pollution problems of wastewater particularly Tannery industrial wastewater. This issue seems to be a subject which has not yet received adequate attention during the development of Tannery industries. Certainly very little and/or no investment has been made in the past to wastewater treatment facilities compared to drinking water supply. Therefore, there is a need to develop an efficient and low-cost wastewater treatment technologies for the removal of heavy metals and other pollutants. Among these technologies, adsorption is a user-friendly technique for this purpose.

Adsorption has been identified as one of the most promising mechanism for removal of dissolved heavy metal fractions and nutrients from wastewater. Although commercial adsorbents are available for use in adsorption, they are very expensive, resulting in various new low-cost adsorbents being studied by researchers. Babel and Kurniawan [7], reviewed the technical feasibility of various low-cost adsorbents for heavy metals removal from wastewater and concluded that the use of low-cost adsorbents may contribute to the sustainability of the surrounding environment and offer promising benefits for commercial purpose in the future.

Therefore identifying potentially efficient low-cost and locally available filter media as an adsorbent is critical for proper practice of environmental management by tanning industries. On the other hand ordinary sand for filter media is costly because of construction expansion in the country, not available readily and not efficient in removal of pollutants by adsorption hence there is a need to substitute scoria instead of sand.

1.2 Adsorbents and Adsorption in Wastewater Treatment Technology: Adsorption is recognized as one of the most effective purification and separation technique used in industry especially in water and wastewater treatment. Although the commercially available adsorbents are efficient in removal of heavy metals, they are costly and some cannot be regenerated and recycled. A number of approaches have been recently studied for the development of cheaper and more effective adsorbents for metal removal. Many non-conventional low cost adsorbents, including natural materials, bio-sorbents, and waste materials have been studied and proposed by several researchers [8].

Adsorption is a user-friendly technique especially for the removal of heavy metals. This process seems to be most versatile and effective method for removal of heavy metal [9]. The adsorption process is being widely used by various researchers for the removal of heavy metals [10] from waste streams and activated carbon has been frequently used as an adsorbent. Despite its extensive use in the water and wastewater treatment industries, activated carbon remains an expensive material. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon.

Efficient methods of chromium removal from wastewater are important to attain environmental quality standards. Adsorption has been identified as one of the most promising method for removal of dissolved heavy metal from wastewater [11]. It has an advantage over other conventional methods due to its sludge free clean operation. Although commercial adsorbents are available for use in adsorption, they are very expensive, resulting in various new low cost adsorbents being studied by researchers. Babel and Kurniawan [7], reviewed the technical feasibility of various low-cost adsorbents for heavy metals removal from wastewater and concluded that the use of low-cost adsorbents may contribute to the sustainability of the surrounding environment and offer promising benefits for commercial purpose in the future.

1.3 Scoria as a low-cost Adsorbent: The volcanic ash scoria generally denser. Scoria is somewhat porous material with high surface area and strength with density larger than one. Scoria is an excellent media which holds water in its pores and allow air circulation to the root zone of the plant. Scoria is widely available in Rift valley area of Ethiopia.

Scoria is bomb-sized, generally vesicular pyroclastic rock with basaltic composition, which is reddish brown to black in color and is of low density. It has been used in several industrial applications, such as the manufacturing

http://dx.doi.org/10.22161/ijeab/2.6.10 *ISSN: 2456-1878*

of a lightweight concrete mixture, a heating-insulating material, low-cost fillers in paints, and sorbents [12,13]. Scoria is abundant in many places worldwide including Central America, Southeast Asia (Vietnam, etc.), East Africa (Ethiopia, Kenya, etc.), and Europe (Greece, Italy, Spain, Turkey, etc.) [14,13].

Fig.1:Red Scoria: Photo by Mekonnen Birhanie March/2016, Ethiopia

Sorption of contaminants onto scoria mainly takes place at the outside surface at the initial stage. Changes of ionic composition during sorption experiments suggest that cation exchange is likely the dominant mechanism of heavy metals sorption onto scoria, while considerable As(III) removal by scoria is explained by specific sorption of the neutral As(III) species and electrical adsorption of negatively charged As(V) species via As oxidation onto hematite. The experimental investigation conducted demonstrates that the scoria is able to concurrently reduce concentrations of heavy metals and arsenic in aqueous solutions. Jang *et al*. [15], recommend that scoria can be used as an economic and efficient sorbent to treat contaminated water with heavy metals.

Taking into account the growth of industrialization in Ethiopia and the expected demand for industrial wastewater management, low-cost, appropriate and eco-friendly approaches will play a critical role in the development of future wastewater treatment technology in the country. In this practical approach, this work deal with the principles of adsorption and filtration for the removal of contaminants from tannery wastewater by replacing this volcanic ashes (scoria) as a filter media instead of conventional sand.

I. MATERIALS AND METHODS

2.1 Study Area and Period: This study has been conducted in Addis Ababa University by transporting sample wastewater from Dire tanning industry from May to August 2016.

2.2 Study Design: Batch mode comparative experimental study design has been carried out to determine the efficiency of scoria a volcanic ash as a filter media on the treatment of industrial wastewater, the case of tannery wastewater filtration.

2.3Experimental materials, Design and setup Establishments: The volcanic rocks were collected from volcanic cones of refit valley area of Oromia region, Ethiopia around Naziret, (Scoria: 8°30' N 39°19' E) approximately 100km East of Addis Ababa. The rocks are local volcanic rocks with various chemical and mineralogical structure and transported to Addis Ababa University. The chemical characteristics of filter media was determined by XRF analysis.(Table.1.)

Table.1: Physical and Chemical Characteristics of Scoria

Chemical Composition	**Percent Weight of Scoria**
SiO_2	52.46
Al_2O_3	18.14
Fe_2O_3	5.40
CaO	9.40
K_2O	0.20
Na_2O	3.28
MgO	7.44
MnO	0.12
P_2O_5	0.36
TiO_2	0.41
H_2O	1.12
LOI*	2.08
pH	7.81
**Physical properties, Particle size = 0.075–0.425mm.	
Porosity (%)	36
Particle density (gcm^{-3})	2.96
Specific surface area (BET) ($m^2\ g^{-1}$)	2.49
Cation exchange capacity (CEC), mequiv. 100 g^{-1}	0.09

**LOI= Loss on ignition*

This filter medium was crushed and graded. Effective size was determined by using standard sieve. Based on the analysis the effective size (ES) (d_{10}) of media was 1.5–

http://dx.doi.org/10.22161/ijeab/2.6.10 *ISSN: 2456-1878*

4.5and the uniformity coefficient (UC) (d_{60}/d_{10}) is 3.5–4. After grading the filter material was washed by tap water and dray by sunlight for one week.

Filtration tank was made of metal sheet, with the following dimension, 60 cm height and 28 cm diameter and also was fitted with a half-inch an outlet tap(faucet)5cm above from bottom of tank. The filtration tank was installed at College of natural and computational science, Addis Ababa University. After installation the filter media was filled in the filtration tank 10cm depth with 10 – 25mm grain size drainage layer at the bottom, 30cm depth filter layer with a grain size of 1.5 – 4.5 mm at the middle and distribution layer (flat coarse gravel) was added 5cm depth at the top of the filter media to protect erosion of filter's top layer, then it is ready for sample tannery wastewater filtration.

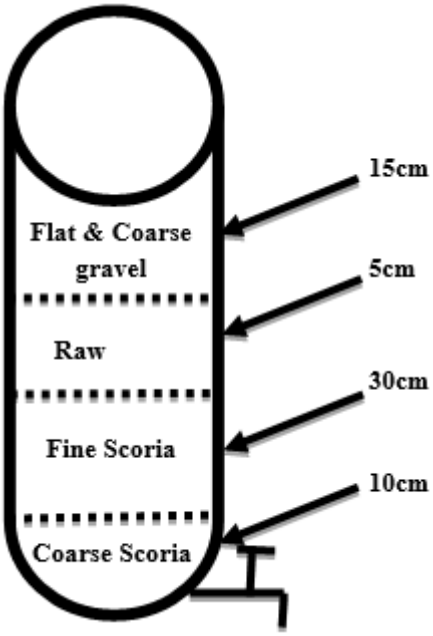

Fig. 2:Schematic layout of the Tanker Components of scoria filter

2.4 Wastewater Sample Collection and Filtration: The composite sample wastewater was collected from Dire tannery and transported to Addis Ababa University by using 40 liter plastic 'Jerican'. The onsite measurement of the physicochemical parameters were undertaken. The raw wastewater was added to the filtration tank at the time and a sample also transported to Addis Ababa EPA water and wastewater analysis laboratory and *Water Works Design and Supervision Enterprise* (WWDSE) for the raw wastewater characterization.

2.5 Filtrated Sample Collection and Laboratory Analysis: The physicochemical analysis of wastewater samples has been done before and after the treatment with the filter media, using standard methods. Optimum operating treatment time was determined for maximum removal of these impurities by running the experiment for 24, 48, and 72 hours, respectively. Filtrated Sample was taken by 2 liter plastic bottle after each fixed retention time that is after 24, 48, and 72 hours and transported to Addis Ababa EPA water and wastewater analysis laboratory and *Water Works Design and Supervision Enterprise* (WWDSE) after taking each sample.

The analytical parameters were pH, DO, BOD_5, COD, TSS, Ammonium N, Nitrite N, Nitrate N, Phosphate, Sulfide, sulfate and chromium. Onsite measurement of the wastewater like temperature, pH and DO were carried out at the site in the tannery environmental quality control laboratory using portable pH meter (Wagtech International N374, M128/03IM, USA) and DO meter (Hach P/N HQ30d, Loveland. CO, USA) for Dissolved oxygen and temperature.

COD, ammonium nitrogen, nitrite nitrogen, nitrate nitrogen, phosphate, Sulfide and Sulfate were measured by using spectrophotometer (Hach model DR/3900 portable spectrophotometer, Germany) according to Hach instructions. $BOD_5$and total Cr were analyzed using BOD sensor and inductive stirring system AQUA LYTIC model type ET618-4 and Flame Atomic Absorption Spectrophotometer (AAS), (model AAS NOUA-400, Germany) respectively. Total suspended solids (TSS) were determined according to the Standard Methods for the Examination of Water and Wastewater gravimetric method [16].

The removal efficiency of the filter media for the selected parameters were calculated as:

$$\% \text{ removal} = Ci - Cf/Ci \text{X } 100$$

Where C_i is the parameter concentration in the untreated wastewater and C_f is the parameter concentration in the treated wastewater.

2.6 Statistical Data Analysis: Mean and standard deviations were calculated to estimate the concentration of each parameter of the samples. The hypothesis has been tested by student t-test using R statistical software: R version 3.2.2 (2015-08-14),Platform: x86_64-w64-mingw32/x64 (64-bit) to determine whether an observed difference between the means of the groups is statistically significant or not, based on the treatment efficiency of the filter materials.

2.7 Data Quality Management: To assure quality of the data by minimizing the errors the following measures had been undertaken: Apparatuses were calibrated; expiry date of reagents had been checked before starting the real analysis and standard control also prepared. Each test had been triplicates.

http://dx.doi.org/10.22161/ijeab/2.6.10 *ISSN: 2456-1878*

II. RESULT AND DISCUSSION

3.1 Physicochemical **Characteristics of Dire Tannery Wastewater:** The raw wastewater was taken from Dire tannery around Asko area, Addis Ababa Ethiopia and transported to Addis Ababa EPA laboratory and water *works design and supervision Enterprise* (WWDSE) for physicochemical analysis. Based on this investigation the mean concentration of selected physicochemical parameters were presented at Table 2.

Table.2: Characteristics of Dire Tannery Wastewater June/2016

S.No.	Parameter	Concentration (mg/l) Except pH and T^o	Range
1	pH	9.1±3.1	6.5-12.5
2	T^o (^{o}C)	20.6±2.34	19-22
3	BOD_5	1081±159.55	924-1243
4	COD	12913±6874.7	8046-21025
5	TSS	2426±515.2	1849-2840
6	NH_4-N	314±59.9	259-378
7	NO_2-N	1.7±0.29	1.4-1.99
8	NO_3-N	124±12.8	110-135
9	PO_4-P	168±74	112-252
10	Sulfide	417±130.7	334-568
11	Sulfate	1307±224	1118-1555
12	Total chromium	35.7±8.6	28-45

This study revealed that the mean concentration of BOD_5, COD and TSS were 1081±159.55, 12913±6874.7 and 2426±515.2 mg/l respectively (Table 2.). This result is basically similar to different studies in Ethiopia with slight difference for different parameters for example a study done at Mojo tannery indicated that the mean concentration of COD was laid between 7950 to 15240 mg/l with the mean of 11123±563.9 mg/liter [17]. Another study also undertaken with same tannery wastewater showed that the mean concentration of BOD_5 was1054±448 mg/liter [18].But the concentration of total suspended solid was found from 1849 to 2840 (Table 2.) this is a bit greater than some studies for instance a study done in India indicated that 1244 mg/liter [19].

Nutrients like orthophosphate, ammonium, nitrite and nitrate concentration of Dire tannery were characterized in this study, the result revealed that 168±74, 314±59.9, 1.7±0.29, 124±12.8mg/l respectively. This result is comparable to a study done by Sivakumar *et al*., [20] which indicates the concentration of nitrate in untreated tannery effluent was 116mg/l. the result of ammonium is in the range of the results done at Bahir Dar tannery wastewater characterization (96-420 mg/l) [21]. According to Arasappan and Kalyanaraman [22], the nitrite concentration of untreated tannery wastewater was 1.3 mg/l almost parallel to this study finding which accounts 1.7±0.29mg/l (Table 2.). Whereas the concentration of orthophosphate in this study was 168±74 mg/l, this result shows that the concentration of phosphate in Dire tannery wastewater is higher than other study results done previously to characterize another tannery wastewaters. The variation may be due to the utilization of phosphorus containing chemicals for different purposes and tanning activities in Dire tannery.

The total suspended solid in Dire tannery found to be 2426 mg/l this result is more or less similar with results of tannery wastewater analyzed by [23]. The concentration level of both sulfide and sulfate were 417±130.7 and 1307±224 mg/l respectively. In this case the amount of sulfide found in this study wastewater was more or less equivalent to study done by [24] that is 380±50 mg/liter [25], also characterize the tannery wastewater based on their result the concentration of sulfate was 1517mg/l which is almost parallel to this investigation. In terms of chromium concentration, Dire tannery comprised 35.7±8.6 mg/lit similar to other different results presented from various tannery wastewaters in Ethiopia for example a study done by [17] indicates 32.2±5.7 mg/l. On the other hand two more study results found to be in the chromium concentration ranges of this investigation result 28-45 mg/l (Table 5.1) [18,26].

Even though Wastewater of each tannery process consists of varying pH and temperature values, this study results (9.1±3.1and 20.6±2.34^{o}C) respectively were analogous to different studies. Likewise a large variation exists in values of physicochemical parameters in general like BOD_5, COD, TSS, phosphate, sulfide, sulfate, etc. in every tannery wastewater characteristics, this may be because of different tanning process, methods, technology

http://dx.doi.org/10.22161/ijeab/2.6.10 *ISSN: 2456-1878*

and raw material utilization by various Tanning industries.

3.2 Tannery Wastewater Treatment by Filtration Technique Using Scoria as a Filter Media: Scoria is a volcanic rock found in the refit valley area of Ethiopia abundantly and different world. This study investigates the potential of this volcanic rock for the treatment of tannery wastewater using as filter media with three different retention time to filter out the sample wastewater. Based on this investigation scoria shows that promising result (Table 3).

Table.3: Tannery Wastewater Treatment Efficiency of Scoria as a Filter Media

Parameters	Mean Influent Concentration	Efficiency					
		RT= 24 hours		**RT= 48 hours**		**RT= 72 hours**	
		Mean Effluent Concentration	**% Removal**	**Mean Effluent Concentration**	**% Removal**	**Mean Effluent Concentration**	**% Removal**
BOD_5	1081±159.55	518±96	52	484±61.7	55	443±26	59
COD	12913±6874.7	6714±5735	48	6520±5398	50	5905±3621	54
TSS	2426±515.2	606±77.4	75	404±69.6	83	388±70.3	84
NH_4-N	314±59.9	213±5.9	32	230±11	27	296±23	6
NO_2-N	1.7±0.29	0.029±0.0035	98	0.039±0.0025	98	0.047±0.0035	97
NO_3-N	124±12.8	61.3±4.2	51	24.3±2.5	80	1.3±0.45	99
PO_4-P	168±74	73±54.9	57	66.7±53.4	60	63±3.5	63
Sulfide	417±130.7	111±12.5	73	106±22.9	75	96.7±6	77
Sulfate	1307±224	302±25.6	77	320±18.3	76	320±10	75
T. Chromium	35.7±8.6	10.4±1.29	71	10.2±1.26	71	11±1.22	69

According to this study, the maximum removal potential of scoria as a filter material for the reduction of BOD_5, COD and TSS from tannery wastewater was achieved at the retention time of 72 hours that accounts 59%, 54% and 84% respectively. In all of the three mentioned parameters the efficiency was directly proportional to retention time (Table 3).

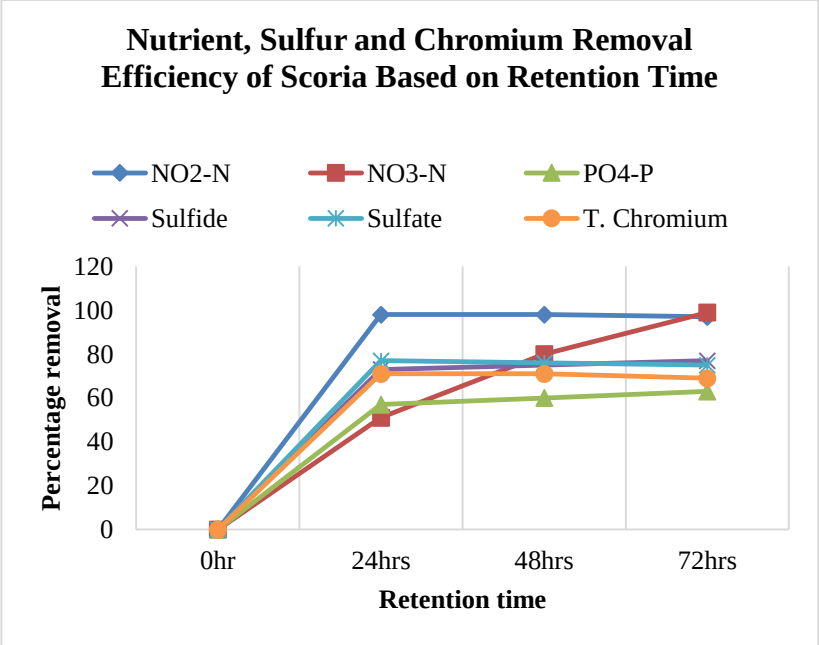

Fig. 3: Nutrient, Sulfur and Chromium Removal Efficiency of Scoria Based on Retention Time

The efficiency of scoria to reduce nutrients from tannery wastewater in general was high. The retention time and efficiency also directly related. In this study nitrite, nitrate and phosphate were reduce satisfactorily by 97%, 99% and 63% respectively after 72 hours (Table 3; Fig.3). This reduction may be obtained due to several mechanisms mainly adsorption, ion exchange, precipitation and finally filtration.

In this study significant reduction of nitrate was obtained which accounts 51%, 80% and 99% at RT= 24 hours, 48 hours and 72 hours respectively. One of the reason for this thought provoking results may be the retention time allowed is adequate for chemical equilibrium conditions to be reached between the filter material and nutrient in the wastewater in addition to the adsorption capacity of scoria. This study result shows that the same trend to a study done by [27] that indicates more than 95% nitrate removal efficiency from aqueous solution by adsorption mechanism. Another study result also analogous with this investigation that was done in 2004 by [28] to remove the nitrate from aqueous solution by using the original and activated red mud in batch adsorption technique. The similarity shown between the studies in terms of removal efficiency may be due to the similarity in the chemical composition of both scoria and red mud.

The result of phosphate reduction in this study was 57%, 60% and 63% at RT= 24 hours, 48hours and 72hours respectively. This result is almost in line with a study done in Ethiopia on the potential of scoria to reduce phosphate from aqueous solution that revealed 61% with 4mg/l initial concentration of the solution [29].

Wastewater from beam house of tanning industry contains high concentration of sulfide and sulfate ions. Since these effluents are toxic to aquatic environment, it is essential to reduce them and bring the discharge concentration levels of these species to below the toxic limit. In this study the better removal efficiency of both sulfide and sulfate by scoria filter were 77% at RT= 72 hours and 24 hours respectively (Table 3). In this study the adsorption technique is one of the efficient mode of physicochemical treatment for tannery wastewater likewise a study done in India on the treatment of tannery wastewater using adsorption technique and cactus powder as an adsorbent the result revealed that sulfate removal was found to be at the level of 90 % with initial concentration of 135 mg/l [30]. The reason for the result dissimilarity may be initial concentration and the adsorption potential of the adsorbents.

The concentration of chromium was reduce by 71%, 71% and 69% at RT=24 hour, 48 hours and 72 hours respectively. In the study of adsorption behavior of Cr(VI) onto macro and micro-vesicular volcanic rocks from water the maximum adsorption yield 77% for scoria was shown [31]. In another study it was observed that through increasing contact time, the removal efficiency of chromium in pre-determined optimum dose of scoria powder increased significantly from 73.28 to 86.63 % [32].

III. ACKNOWLEDGMENT

The first author was grateful to Addis Ababa University for the financial support in making the study a reality. The authors would like to forward their gratitude to Dire tannery management officials for their cooperation. Special thanks also forwarded to Dire Tannery environmental quality control laboratory head, Mr. Abdul Aziz Bilal for his kind assistance. Authors would like to acknowledge Addis Ababa EPA, WWDSE and JSE (Geochemical laboratory Directorate) directors, team leaders, laboratory assistances and technicians for their support during sample analysis. Authors' acknowledgement would not be complete without mentioning thanks to Dr. Teshome Soromessa, Chairman of Center for Environmental Science for writing supportive letters to different tanning industries.

REFERENCES

[1] Suthanthararajan R., Ravindranath E., Chits K., Umamaheswari B., Ramesh T., Rajamam S. (2004). Membrane application for recovery and reuse of water from treated tannery wastewater, *Desalination* 164, 151–156.

[2] Kawser Ahmed Md., Monika Das, Monirul Islam Md., Mosammat Salma Akter, Shahidul Islam and Muhammad Abdullah Al-Mansur (2011). Physicochemical Properties of Tannery and Textile Effluents and Surface Water of River Buriganga and Karnatoli, Bangladesh, *World Applied Sciences Journal* 12 (2): 152-159, ISSN 1818-4952.

[3] UNIDO (2012). United Nations Industrial Development Organization Vienna, Technical assistance project for the upgrading of the Ethiopian leather and leather products industry, Independent Evaluation Report Ethiopia, UNIDO project number: TE/ETH/08/008, available Online at *https://www.unido.org/fileadmin/user/Evaluation/Ethiopia_leather_valuation_FINAL_report_130208.pdf*.

[4] Rezic, I. and Zeiner, M. (2008). Determination of extractable chromium from leather, *Monatsheftefur Chemie -Chemical Monthly*, 140(3), pp.325-328.

[5] Durai G., Rajasimman M. and Rajamohan N. (2011). Kinetic studies on biodegradation of tannery wastewater in a sequential batch bioreactor, *Journal of Biotech Research*, 3:19-26.

[6] Lofrano, G., Aydn, E., Russo, F., Guida, M., Belgiorno, V., and Meric, S. (2008). Characterization fluxes and toxicity of leather tanning bath chemicals in a large tanning district area, *Water Air Soil Pollut.* 8, pp. 529-542.

[7] Babel S. and Kurniawan T. A. (2003). Low-cost adsorbents for heavy metal uptake from contaminated water: A review, *J. Hazard. Mat.* , 97, pp. 219-243.

[8] Kilonzo, F., Mutwiwa, U., Mutua, S., and Waweru, W. (2012). Evaluation of the use of constructed wetland in the treatment of tannery wastewater, *Kenya Science, Technology and Innovation Journal*, *ISSN 2079-5440*,PP. 16-22.

[9] Rao B.H., Dalinaidu A. and Singh D.N. (2007). Accelerated diffusion test on the intact rock mass, *Journal of Testing and Evaluation*, *ASTM*, vol. 35(2), pp. 111- 117.

[10] Ahmed R., Yamin T., Ansari M. S., and Hassany S. M. (2009). Sorption behavior of Lead (II) ions from aqueous solution onto Haro River sand, *The Nucleus*, vol. 24(6), pp. 475-486.

[11] Senthilkumar S., Bharati S., Nithynandhi D. and Subburam V., Bio sorption of toxic heavy metals from aqueous solution, Bioresour. Technol, 75,2000,163-165.

[12] Moufti, A.A. Sabtan, O.R. El-Mahdy, W.M. Shehata (2000). Assessment of the industrial utilization of scoria materials in Central Harrat Rahat, Saudi Arabia, *Eng. Geol*. 57: 155–162.

[13] Esayas Alemayehu, and Lennartz B. (2009). Virgin volcanic rocks: kinetics and equilibrium studies for the adsorption of cadmium from water, *J. Hazard. Mater*. 169: 395–401.

[14] Kwon, S.T. Yun, S.O. Kim, B. Mayer, I. Hutcheon (2005). Sorption of Zn(II) in aqueous solutions by scoria, *Chemosphere* 60: 1416–1426.

[15] Jang-Soon Kwona, b, Seong-Taek Yuna, Jong-HwaLeea, Soon-Oh Kimc, Ho Young Jo. (2010). Removal of divalent heavy metals (Cd, Cu, Pb, and Zn) and arsenic (III) from aqueous solution using scoria: Kinetics and equilibria of sorption, *Journal of Hazardous Materials*, 174: 307-313.

[16] American Public Health Association (APHA). (2005). Standard Methods for the Examination of Water and Wastewater.

[17] Seyoum Leta, Fassil Assefa and Gunnel D. (2003). Characterization of tannery wastewater and assessment of downstream pollution profiles along Modjo river in Ethiopia, *Ethiopian Journal of Biological Sciences*, 2 (2), 157 – 168.

[18] Tadesse Alemu Terfie and Seyoum Leta Asfaw, (2015). Evaluation of selected wetland plants for removal of chromium from tannery wastewater in constructed wetland, Ethiopia, *African Journal of Environmental science and technology* vol.9(5), pp. 420-427.

[19] Tamal Mandala, Dalia Dasguptab, Subhasis Mandala, Siddhartha Datta (2010). Treatment of leather industry wastewater by aerobic biological and Fenton oxidation process, *Journal of Hazardous Materials*, 180: 204–211, available at*www.elsevier.com/locate/jhazmat*.

[20] Sivakumar P., Kanagappan M. and Sam Manohar Das S. (2015). Physicochemical Characteristics of Untreated Effluent from Tannery Industries in Tamil Nadu: A Comparative Study, *Int. J Pharm Bio Sci.*, 6(1): (B) 446 – 451.

[21] Assefa Wosnie and Ayalew Wondi (2014). Bahir Dar tannery effluent characterization and its impact on the head of Blue Nile River, *Afr. J. Environ. Sci. Technol*., vol.8 (6), pp.312-318, available online at*www.academicjournals.org/AJEST*.

[22] Arasappan Sugasini and Kalyanaraman Rajagopal (2015). Characterization of Physicochemical Parameters and heavy metal Analysis of Tannery Effluent, *Int.J.Curr.Microbiol.App.Sci.* 4(9): 349-359, available at*http://www.ijcmas.com*.

[23] Saritha Banuraman and Meikandaan. T.P. (2013). Treatability Study of Tannery Effluent by Enhanced Primary Treatment, *International Journal of Modern Engineering Research (IJMER)*, Vol.3, Issue.1, pp-119-122, available online at*www.ijmer.com*.

[24] Islam B.I., Musa A.E., Ibrahim E.H., Salma A.A., and Babiker M. (2014). Evaluation and Characterization of Tannery Wastewater, *Journal of Forest Products & Industries*, 3(3): 141-150.

[25] Arasappan Sugasini and Kalyanaraman Rajagopal (2015). Characterization of Physicochemical Parameters and heavy metal Analysis of Tannery Effluent, *Int.J.Curr.Microbiol.App.Sci.* 4(9): 349-359, available at*http://www.ijcmas.com*.

[26] Asaye Ketema (2009). Evaluation of Selected Plant Species for the Treatment of Tannery Effluent in a Constructed Wetland System; *(Unpublished Thesis)*, Addis Ababa University, Available online at *en.wikipidia.org/winki/ITRC*.

[27] Nese and Ennil (2004). Nitrate removal from aqueous solution by adsorption onto various materials, *Journal of Hazardous Materials* B112: 155–162.

[28] Yunus Cengeloglu, Ali Tor, Mustafa Ersoz, Gulsin Arslan (2006). Removal of nitrate from aqueous solution by using red mud, *Separation and Purification Technology* 51: 374–378,available online at *www.sciencedirect.com*.

[29] Mekonnen Birhane, Alebel Abebe, Esayas Alemayehu & Embialle Mengistie (2014). Efficiency of locally available filter media on fluoride and phosphate removal for household water treatment system, *Chinese Journal of Population Resources and Environment*, 12:2, 110-115.

[30] Swathi M, Sathya Singh A, Aravind S, Ashi Sudhakar P.K, Gobinath R, Saranyadevi D. (2014). Experimental studies on tannery wastewater using cactus powder as an adsorbent, *Int. Journal of Applied Sciences and Engineering Research*, Vol. 3, Issue 2, available online at*www.ijaser.com*.

[31] Esayas Alemayehu, Soren Thiele-Bruhn, Bernd Lennartz (2011). Adsorption behavior of Cr(VI) onto macro and micro-vesicular volcanic rocks from water, *Separation and Purification Technology*, 78: 55–61, Available at *www.elsevier.com/locate/seppur*.

[32] Masoud Moradi, Lida Hemati, Meghdad Pirsaheb and Kiomars Sharafi (2015).Removal of Hexavalent Chromium from Aqueous Solution by Powdered Scoria-Equilibrium Isotherms and Kinetic Studies, *World Applied Sciences Journal* 33 (3): 393-400.