Tannery Wastewater Treatment Using Activated Sludge Process System (Lab Scale Modeling)

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Abstract—A study was conducted to evaluate the feasibility of activated sludge process for the treatment of tannery wastewater in a lab scale model under local conditions. Wastewater was collected from chromium stage, Elmontazah tannery, Ein Elsira tanneries, Cairo, Egypt. The reactor was operated with the activated sludge process under batch mode using a tannery wastewater as feed. A lab scale model comprised of primary sedimentation tank (5 L), aeration tank (5 L) and final clarifier (5 L). The model was operated continuously for 120 hours of contact. The pH of wastewater was firstly adjusted till pH 6.5 to enhance biosorption capacity. The wastewater samples of the effluent were analyzed after time interval 2h, 6h, 12h, 24h, 48h, 72h, 96h and finally 120 h to find process efficiency. Results of the study demonstrated that the removal efficiency of about 98.3% and 98.4% for BOD₅ (Biological Oxygen Demand) and COD (Chemical Oxygen Demand) respectively, could be obtained under a HRT of 120 h. Results were also showed decrease in chromium ion, ammonia nitrogen, phosphorous and oil & grease concentrations up to 99.3%, 98.8%, 98.6% and 99.1%, respectively. Results were also showed decrease in the color absorbance. Activated sludge was characterized using SEM examination with EDAX analysis and FT-IR technique.

The kinetic coefficients k (maximum substrate utilization rate), Ks (half velocity constant), Y (cell yield coefficient) and Kd (decay coefficient) were found to be 1.2 day⁻¹, 209 mg/L, 0.18 and 0.039 day⁻¹, respectively. These coefficients may be utilized for the design of activated sludge process facilities for tannery wastewater.

Index Terms—Chromium, Municipal Activated Sludge, Organic loads, Tannery wastewater

I. INTRODUCTION

Although the leather tanning industry is known to be one of the leading economic sectors in many countries, there has been an increasing environmental concern regarding the release of various recalcitrant pollutants in tannery wastewater. Leather tanning is a wide common industry all over the world. It is considered one of the most important industries in Mediterranean countries. Because of their complex wastewater characteristics leather tanneries are generally located in so called organized industrial districts [1]. Tanneries are typically characterized as pollution intensive industrial complexes which generate widely varying and high-strength wastewater. Major problems are due to wastewater containing heavy metals, toxic chemicals, chloride, and high dissolved and suspended salts and other pollutants. A typical process flow sheet in an integrated leather tannery industry is shown in Fig. 1.

Chromium salts used during the tanning process generate two forms of chrome; hexavalent chromium and trivalent chromium. Hexavalent chromium is highly toxic to living organisms even at low concentration causing carcinogenic effect [2]. Trivalent chromium may be present in the waste or can be produced from the hexavalent chromium by chemical treatment. Soluble trivalent chromium causes toxicity in anaerobic digestion due to the accumulation of the metal in the intracellular fraction of biomass [3]. Several components in the effluent contain nitrogen as part of their chemical structure, which can lead to development of anaerobic conditions harmful to the aquatic life. The environmental protection regulations stipulate that industries are not allowed to emit sulfide and chromium in the wastewater [4]-[5].

In Egypt, the tannery wastewater is discharged directly to the main domestic sewage pipeline without proper treatment which adds difficulties to the sewer system and to the wastewater treatment plants [6]. The high concentrations of pollutants with low biodegradability in tannery wastewater represent a serious and actual technological and environmental challenge.

Treatment of tannery wastewater is carried out by physical or chemical or biological or combination of these methods [7]-[8]-[9]-[10].

Fig. 1 A typical process flow sheet in an integrated leather tannery industry
Treatment methods in which the removal of contaminants is brought about by biological activity are known as biological unit processes. Biological treatment is used primarily to remove the biodegradable organic substances (colloidal or dissolved) from wastewater. Basically, these substances are converted into gases that can escape to the atmosphere and into biological cell tissue that can be removed by settling. Biological treatment is also used to remove nutrients (nitrogen & phosphorus) from wastewater. With proper environmental control, wastewater can be treated biologically in most cases.

Biological treatment methods use microorganisms, mostly bacteria, in the biochemical decomposition of wastewater to stable end products. More microorganisms, or sludge’s, are formed and a portion of the waste is converted to carbon dioxide, water and other end products. Generally, biological treatment methods can be divided into aerobic and anaerobic methods, based on availability of dissolved oxygen [11].

Biological methods, like activated sludge process, are invariably employed for the secondary treatment of a large number of industrial wastewaters. Knowledge of the microbial kinetics and determination of the kinetic coefficients for a particular wastewater are, therefore, imperative for the rational design of treatment facilities [12]-[13].

Biological processes are usually prescribed for treating industrial effluents to reduce organic content as they have economic advantages over chemical oxidation [14]. However, high concentration of tannins and other poorly biodegradable compounds as well as metals can inhibit biological treatment [15]-[16].

The natural affinity of biological compounds for metallic elements could contribute to economically purifying heavily metal-loaded wastewater. Activated sludge MLSS (mixed liquor suspended solids) contain microbial cells and spores. These cells have been reported to be capable of trapping metals by cell wall components, altering metal uptake, absorbing into the cells by forming metal complex, producing metabolites extracellularly to chelate and precipitate these metals, or storing metals in the cytosol in association with various metal-binding proteins [17]. It also offers the advantage of having cell wall material which shows excellent metal-binding properties. The microbial cell wall of consists chiefly of neutral carbohydrate and hexosamine, with smaller amounts of lipid and protein [18].

The activated sludge process (ASP) is the most common and versatile biological process used worldwide for the secondary treatment of domestic, municipal and industrial wastewater. With the course of time, several modifications of the ASP have been made to improve the degree of treatment in accordance with stringent effluent standards. Optimization was also brought into account to reduce the establishment and operating costs of wastewater treatment plant [19].

In view of the above, the present study was undertaken with the objective to determine the ability of Activated sludge process to remove toxic constituents from tannery wastewater and to determine different kinetic coefficients for tannery wastewater so that these may be utilized for the design of treatment facilities in tannery sector

II. MATERIALS AND METHODS

A. Analytical methods and equipment used in the study:
   - T70® UV/VIS Spectrophotometer – PG instruments Ltd was used for colorimetric spectrophotometer measurements according to (20).
   - Cole Parmer Turbidity meter 0–200 NTU, Chicago, USA.
   - A Scanning Electron Microscope SEM with EDAX analysis (Inspect S. FEI Company, Holland) was used to characterize the surface of municipal activated sludge.
   - Functional groups in activated sludge process were determined by the Fourier transform infrared (FTIR) spectroscopy (Shimadzu S 201 PC spectrophotometer – Japan) in the transmittance % mode in the range 4000 – 400 cm⁻¹.
   - Flame atomic absorption spectrophotometer AAS (ICE 3000 series, AAS– Thermo Scientific) was used for the analysis of chromium ions using air acetylene - nitrous oxide flame technique.
   - EUTECH pH-700 instrument Singapore meter was used for measuring pH value, with a range of 0.00 to 14.00 and an accuracy of ±0.02.

B. Experimental Set-up:-

The activated sludge reactor, used for the present study, was developed in the laboratory. The lab scale model comprised of primary sedimentation tank having volume of about 5.0 L, aeration tank having volume of about 5.0 L and final clarifier having volume of about 5.0 L was used for the treatment study. The aeration tank was operated continuously for 120 hours of contacts. Primary and secondary clarifiers were operated for 45 minutes. The secondary clarifier was equipped with a trough to collect the effluent. The schematic diagram of the lab scale activated sludge reactor used in the study is shown in Fig. 2.

![Fig.2 Schematic diagram of the experimental set-up](image_url)

C. Samples collection site:-

Samples of wastewater from contaminated sites with tannery wastewater - chromium stage – Elmontazah
tannery, Ain El Sira, Cairo, Egypt, were collected, analyzed within 8h and stored in a refrigerator at 4°C.

D. Acclimation of Biomass and Reactor Start-up:-

Activated sludge was collected from a nearby drain from Zenin wastewater treatment plant. The pH of tannery wastewater was firstly adjusted using 0.1 M HCl and 0.1 M NaOH. The reactor was fed with tannery wastewater in primary aeration sedimentation tank for 45 min then transferred to the aeration tank for 120 hour, then transferred to the final clarifier for 45 min. The whole reactor content was kept under aerobic condition by supplying adequate air from aqua pumps, airflow capacity of 1.33 L.min⁻¹. Various parameters like pH, MLSS, Total suspended solids (TSS), sludge volume index (SVI), COD, BOD, chromium, ammonia nitrogen, phosphorous, oil & grease, Turbidity, dissolved oxygen concentration (DO) and temperature of the reactor were monitored regularly under different hydraulic retention time (HRT). The DO concentration in the reactor always maintained more than 2 mg.L⁻¹ during the continuous operation to ensure requirement of DO for carbon oxidation.

The removal percent was measured as:-

\[
\text{Removal \%} = (\frac{C_0 - C_f}{C_0}) \times 100
\]

Where, \(C_0\) and \(C_f\) are the initial and final concentrations (mg.L⁻¹), respectively.

E. Analytical Methods:-

All the parameters were analyzed according to the procedures described in the Standard Methods [20]. The analysis of each parameter was done in triplicate.

III. RESULTS AND DISCUSSION

Tannery wastewater is one of the most important sources of environment pollutants. The detailed composition of tannery wastewater sample before and after sedimentation tank is presented in Table 1. The pH value is around the acidity (around 4.0 pH unit). Scan spectrum curve of tannery wastewater sample showed the color absorbance along with different wavelengths from 400 nm to 600 nm was presented in Fig. 3.

Laboratory scale reactors are normally used to determine kinetic coefficients and usually employed for its easy operational control. The procedure is to operate the unit continuously for two hours to five days. COD, BOD, Turbidity, TDS, TSS, Ammonia, Phosphorous and Oil & Grease data for influent and effluent are determined against COD loading rate and F/M ratio as shown in Fig. 4 and 5. The reactor performance is also expressed in terms of design parameters like COD removal efficiency and food-to microorganism (F/M) ratio (COD basis). Therefore, the COD removal efficiency is plotted against COD loading rate and F/M ratio as shown in Fig. 6.

Table 1 Physicochemical analysis for tannery wastewater sample

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Before Sedimentation tank</th>
<th>After Sedimentation tank</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Abs.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>580nm m</td>
<td>0.296</td>
<td>0.294</td>
<td>Abs.</td>
</tr>
<tr>
<td>418nm m</td>
<td>0.396</td>
<td>0.372</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>4.01</td>
<td>4.06</td>
<td></td>
</tr>
<tr>
<td>Turbidity</td>
<td>540</td>
<td>465</td>
<td>NTU</td>
</tr>
<tr>
<td>TSS</td>
<td>2250</td>
<td>1800</td>
<td>mg/L</td>
</tr>
<tr>
<td>TDS</td>
<td>6600</td>
<td>6570</td>
<td>mg/L</td>
</tr>
<tr>
<td>COD</td>
<td>4100</td>
<td>3250</td>
<td>mg/L</td>
</tr>
<tr>
<td>BOD</td>
<td>2040</td>
<td>1690</td>
<td>mg/L</td>
</tr>
<tr>
<td>ammonia nitrogen</td>
<td>52</td>
<td>48</td>
<td>mg/L</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>63</td>
<td>58</td>
<td>mg/L</td>
</tr>
<tr>
<td>Oil and Grease</td>
<td>34.2</td>
<td>29.1</td>
<td>mg/L</td>
</tr>
<tr>
<td>Chromium</td>
<td>840</td>
<td>815</td>
<td>mg/L</td>
</tr>
</tbody>
</table>

Fig. 3 UV Scan Spectrum Curve for tannery wastewater sample
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Turbidity of tannery wastewater influent was higher with a value of 540 NTU indicating higher solids and organics. At HRT of 2h, the removal efficiency was 24.1 %, 4.2 % and 28.8 % for turbidity, TSS and TDS, respectively. At HRT of 72h, the removal efficiency was 84.3 %, 75.4 % and 86.8 % for turbidity, TSS and TDS, respectively. At HRT of 120 h, the removal efficiency was 99.1 %, 99.9 % and 98.8 % for turbidity, TSS and TDS, respectively. At HRT of 2h, the removal efficiency was 20.96 %, 24.9 %, 33.6 % and 38.1 % for ammonia nitrogen, Phosphorous, Oil & greases and chromium, respectively. At HRT of 72h, the removal efficiency was 86.3 %, 85.4 %, 86.8 % and 89.9 % for ammonia nitrogen, Phosphorous, Oil & greases and chromium, respectively. At HRT of 120 h, the removal efficiency was 98.8 %, 98.6 %, 99.1 % and 99.3 % for ammonia nitrogen, Phosphorous, Oil & greases and chromium, respectively as shown in Fig. 7, 8 and 9.

Fig. 10 Effluent ammonia nitrogen profile during continuous study

Total ammonia nitrogen, Phosphorous, Oil & greases and chromium tests were carried out on the settled wastewater collected to check the level of these nutrients for satisfactory biological treatment. The phosphorous was thus deficient and this deficiency could hamper a satisfactory biological treatment [16]. At HRT of 2h, the removal efficiency was 20.96 %, 24.9 %, 33.6 % and 38.1 % for ammonia nitrogen, Phosphorous, Oil & greases and chromium, respectively. At HRT of 72h, the removal efficiency was 86.3 %, 85.4 %, 86.8 % and 89.9 % for ammonia nitrogen, Phosphorous, Oil & greases and chromium, respectively. At HRT of 120 h, the removal efficiency was 98.8 %, 98.6 %, 99.1 % and 99.3 % for ammonia nitrogen, Phosphorous, Oil & greases and chromium, respectively as shown in Fig. 10, 11, 12 and 13.
Effluent color removal profile and scan spectrum curve showing decrease of the color absorbance along with different wavelengths from 400 nm to 600 nm during continuous study as shown in Fig. 14 and 15.

Fig. 11 Effluent phosphorous profile during continuous study

Fig. 12 Effluent Oil & Grease profile during continuous study

Fig. 13 Effluent chromium ions profile during continuous study

Effluent color removal profile and scan spectrum curve showing decrease of the color absorbance along with different wavelengths from 400 nm to 600 nm during continuous study as shown in Fig. 14 and 15.

Results also showed that the biomass achieved a good settleability within a studied period. Many authors recognized SVI as the best parameter for characterizing the sludge settling properties (28, 29). The measured values of SVI during batch study showed variation in the range from 35 to 72 ml.g\(^{-1}\). The SVI values obtained in the experiment are rather low, compared to the results reported by other authors. SVI gradually decreased along with the growth of biomass in the reactor as shown in Fig. 16. A proper SVI value, especially below 100 ml.g\(^{-1}\), is of great importance in the activated sludge process. The sludge bulking or filamentous bulking problem was not observed during both batch as well continuous studies since sufficient DO concentration (>2 mg.L\(^{-1}\)) was present in the reactor.

Evaluation of Kinetic Coefficients

Basic equations that describe the interaction between the growth of microorganisms and utilization of the growth limiting substrate in activated sludge processes are based on widely used Monod model. In a batch-growth culture system, the resulting expression for the rate of substrate utilization (RSU) as per Monod model can be written as follows [21]:

\[
\frac{X_0 T}{S_0 - S} = \left( \frac{K_S}{k} \right) \left( \frac{1}{S} \right) + \left( \frac{1}{k} \right)
\]  

(1)
In (1), $S_0$, $S$, $T$ and $X_0$ represent the initial soluble COD concentration (mgL$^{-1}$), final soluble COD concentration (mgL$^{-1}$), batch period (h) and MLSS concentration at the start of batch period (mgL$^{-1}$) respectively. $K_s$ and $k$ denote half-velocity constant or substrate concentration at one-half the maximum specific growth rate (mg CODL$^{-1}$) and the maximum rate of substrate utilization per unit mass of microorganisms (h$^{-1}$) respectively. The values of kinetic coefficients i.e. $K_s$ and $k$ can be estimated from the slope and intercept of (1) [19].

Similarly, considering endogenous decay, the resulting expression for the net rate of growth of biomass (RG) in a batch-growth culture system as per Monod model can be written as follows [21]:

$$r_g' = X_1 - X_0 = \frac{Y (S_0 - S)}{TX_0} - k_d$$  \hspace{1cm} (2)

In (2), $X_1$ is MLSS concentration at the end of batch period (mgL$^{-1}$) and the other parameters are mentioned earlier. $Y$ and $k_d$ denote the maximum yield coefficient (mg SS/mg COD) and endogenous decay coefficient (h$^{-1}$) respectively. The values of kinetic coefficients i.e. $Y$ and $k_d$ can be estimated from the slope and intercept of (2).

The batch study data under purely suspended growth condition i.e. initial and final biomass concentrations as well as initial and final soluble COD concentrations were arranged in accordance with (1) and (2) in order to evaluate the kinetic coefficients related to substrate removal and microbial growth [19].

Table (2) Kinetic coefficients for tannery wastewater

<table>
<thead>
<tr>
<th>Kinetic coefficient</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$</td>
<td>1.2</td>
<td>day$^{-1}$</td>
</tr>
<tr>
<td>$K_s$</td>
<td>209</td>
<td>mgL$^{-1}$</td>
</tr>
<tr>
<td>$Y$</td>
<td>0.18</td>
<td>--</td>
</tr>
<tr>
<td>$K_d$</td>
<td>0.039</td>
<td>day$^{-1}$</td>
</tr>
</tbody>
</table>

A comparison of kinetic coefficients for tannery wastewater with other industrial wastewaters would be interesting. Substrate utilization rate "k" for tanneries (1.2 day$^{-1}$) is less as compared to others and thus larger volume of biological reactor would be needed to treat tannery wastewater. This less value of "k" may be due to specific nature of tannery waste. Decay coefficient $K_d$ is quite low for tannery wastewater when compared with other industrial wastewaters, which indicates larger net sludge volumes resulting from biological treatment. Cell yield coefficient ($Y$) is comparable with other industrial wastewaters. Half velocity coefficient ($K_s$) is also comparable with the reported values.

SEM Examination

The microscopic structure of the dried sample was visualized to confirm the porosity of the sludge cake, as shown in Fig. 19. The SEM images revealed an irregular structure indicating different microbial types. The Electron Dispersed Analytical X-ray (EDAX) analysis observations performed on the sludge during microscopic examination as shown in Fig. 20 and Fig. 21 provide evidence of different removal efficiency in relation with time. It showed precipitation of chromium ions and salt ions on the surface, whereas, the activated sludge at 120h showed high precipitation percentage. The similar observation was obtained by [17]-[25]-[26].
Fig. 21 EDAX analysis of activated sludge process at 120h
Fourier Transform Infrared Spectrometry (FT-IR)

Another investigation related to the biosorption phenomenon is FT-IR. It is used for determination of functional groups in organic materials in frequency range from 500 to 4000 Cm\(^{-1}\). FT-IR is carried out to activated sludge as shown in Fig. 22. An interesting phenomenon is the presence of band intensity at (1000, 1410, 1600, 3450 Cm\(^{-1}\)). The results of FT-IR analysis suggested that the binding sites were most likely carboxyl groups where, carboxylic acid dimmers display very broad, intense O–H stretching absorption. Similar explanation was obtained by [27].

Fig. 22 FT-IR Spectrum of activated sludge process

IV. CONCLUSION

The purpose of this study therefore was to determine the efficiency of biological treatment using activated sludge process to remove toxic constituents from tannery wastewater. Microorganisms have been shown to take up heavy metals as well as organic loads from aqueous solutions. The sludge showed highly flocculated and good settleability. The reactor is expected to treat moderately strong wastewater within a reasonable time period of 120 h. Our findings revealed that the ability of activated sludge process at lab scale model to achieve a maximum removal efficiencies for color absorbance, heavy metals as well as organic loads from real tannery wastewater. So, it can be concluded that the activated sludge process could enhance the biosorption of color, organic contents and metal-polluted industrial wastewater. The kinetic coefficients k (maximum substrate utilization rate), Ks (half velocity constant), Y (cell yield coefficient) and Kd (decay coefficient) were found to be 1.20 day\(^{-1}\), 209 mg/L, 0.18 and 0.039 day\(^{-1}\), respectively. The determination of these coefficients may be helpful in (1) understanding the kinetics of substrate utilization (2) sludge production and (3) design of biological treatment facilities based on activated sludge process for settled tannery wastewater.

REFERENCES


Thus these coefficients have both academic value and practical significance.


