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Abstract:

Tannery wastewater containing chromium and other pollutants poses a serious environmental issue, increasing biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), turbidity, and conductivity. Therefore, this research focuses on removing chromium ions from tanning wastewater and reducing the percentages of BOD, COD, TDS, turbidity, and conductivity using effluent from 4 leather tanning processes: deliming, liming, neutralization, and chrome tanning. The research was carried out without any chemical or biological treatment, using only mixtures of wastewaters at different proportions. Atomic absorption spectroscopy was used to determine the chromium concentration. Highest 99.99% chromium has been removed at the pH 8.4 for filtrated mixture of liming and chrome tanning effluent at the proportion of 2:1. Highest 88.15% BOD, 89.35% COD, 91.37% TDS, 94.48% turbidity, 92.08% conductivity removal has been observed for the filtrated mixture of neutralization and chrome tanning effluent at the proportion of 1:1. The pH of the individual effluent plays a in removal mechanism after mixing. To validate the results, a pseudo-first-order kinetic model, linear regression, sensitivity analysis, thermodynamic evaluation, and correlation analysis were performed, thereby supporting the findings and identifying the best removal ratios for each parameter. Thus, wastewater released from the tannery can be purified without biological or chemical treatment, promoting green industrialization and identifying the most cost-effective way to clean water.

Keywords: Chromium removal; Wastewater; Tannery-effluent; pH, Organic load

1. Introduction

The leather industry is projected to have a global trade value exceeding \$100 billion annually, underscoring its undeniable relevance to the global economy (Scopel et al., 2016). Bringing in foreign exchange strengthens the national economy and provides a significant number of jobs (Ebtasam et al., 2025; Tauhiduzzaman et al., 2024). The tanning industry is one of the most polluting sectors in terms of effluent volume and treatment complexity (Mia et al., 2017; Hossain et al., 2022). Tanning is the chemical process that turns animal skins into stable, durable goods called leather (Yusif et al., 2016). Tanning operations comprise many phases that yield diverse chemical compounds and dangerous components (Nagi et al., 2020; Hossain et al., 2023a). The tannery sector is well known for its excessive water consumption and wastewater discharge (Zhao et al., 2022). According to global statistics, leather markets process 300 million pieces of cowhide each year, generating roughly 300 million tons of tannery wastewater (Zhao & Chen, 2019; Nur-E-Alam et al., 2020). Tannery wastewater typically includes hair, proteins, acids, alkalis, chromium salts, sulfides, chlorides, tannins, solvents, dyes, auxiliaries, and numerous other compounds resulting from the multi-step tanning process (Zhao et al., 2022). Large volumes of dangerous contaminants, including heavy metals, are present in tannery wastewater (Ali et al., 2015; Hossain et al., 2023b). Pollutants classified as heavy metals are non-biodegradable substances that tend to accumulate in living things. Because heavy metals cannot be biodegraded into innocuous forms, they are hazardous (Gobinath et al., 2013).

For improved water resistance, flexibility, and a high shrinkage temperature, most tanneries worldwide (about 90%) use chromium salts in their tanning process, which is essential to the leather business (Tadesse & Guya, 2017; Hossain et al., 2024). During the bathing process, chromium reacts with the fibers in the rawhide or skin. The tanned hides are then wrung out and ready for finishing (Muhammad, 2022). Roughly 40% of the entire chromium quantity is left in the solid and liquid wastes after about 60% of the chromium salts react with the hides (Ahmed et al., 2016). Despite the relatively low toxicity of Cr (III), soil containing manganese oxides may oxidize Cr (III) to Cr (VI) when soluble Cr (III) is added. In the absence of oxidation to the Cr (VI) form, Cr (III) in the soil may remain immobilized (Abdulla et al., 2010). The strong oxidizing agent Cr (VI) can generate free radicals that may cause cancer in cells, which is the source of the toxicological concern. Seldom does Cr (VI) occur alone in nature; instead, it is frequently combined with other elements to create compounds like iron (II) chromite (FeCr_2O_4). From these molecules, Cr (VI) is then extracted for use. Therefore, any instance of Cr (VI) contamination in the environment is attributed to human activity (Genawi et al., 2020). Chromium removal from wastewater has been achieved using a variety of techniques, including ion exchange, chemical reduction and precipitation, reverse osmosis, photocatalytic processes, and adsorption, to address this pressing issue (El-Gawad et al., 2023).

Most tanneries that make crust leather, wet blue, or finished leather also contain chemicals, including trivalent chromium (Cr) and sulfides. High BOD (Biological Oxygen Demand) and COD (Chemical Oxygen Demand) values are caused by organic and other substances, which also constitute a significant pollution load and lead to expensive effluent treatment due to complex technologies and technical issues (Technologien et al., 2002). Most people agree that the best way to address the world's water shortage is through wastewater reclamation (Bedada et al., 2020).

Because tannery wastewater contains a number of low-biodegradable compounds, treating it is challenging and poses a significant technological and environmental risk. For this reason, throughout the nation where the leather tanning industry is present, the handling of tannery effluents is a major concern (Ahmed et al., 2016). Wastewater from tanneries is treated using physical, chemical, biological, or a mix of these techniques (Muhammad, 2022). However, improving the efficiency of biological processes and reducing the energy-neutral footprint and treatment costs are required to ensure sustainability in wastewater treatment (Moktadir et al., 2024). These methods have several drawbacks, including the inability to completely remove metal, the need for costly equipment and monitoring systems, high reagent or energy requirements, and the production of hazardous sludge or other waste products that must be disposed of (EL-Tayieb, 2017). All therapeutic approaches, however, have benefits (strengths) and drawbacks (weaknesses). For example, physical wastewater treatments, such as membrane filtration systems, are thought to be quite effective in eliminating the majority of wastewater pollutants, but they require a lot of pressure, which makes them very expensive. However, these systems are very sluggish processes that require extensive physical space. Biological or natural treatment techniques, on the other hand, are widely renowned for their remarkable adaptability to a wide variety of wastewater compositions. Additionally, chemical-based treatment methods, including electrochemical procedures, are well known for being dependable, space-efficient, easy to use, and adaptable to changes in wastewater composition. However, they also come with a high-pressure need and the potential to produce byproducts (Mkilima et al., 2021).

In the leather manufacturing process, skins or hides undergo several steps to become finished leather. Every step of leather processing releases wastewater into the environment. Liming, deliming, neutralization, and chrome tanning are steps in leather processing that contribute to water pollution. In this study, we focused on effluents that are released from these processes. Therefore, in this research, a new wastewater treatment process has been investigated where effluent of chrome tanning, liming, deliming, and neutralization operations from the tannery was used and mixed at different definite proportions to evaluate the reduction of parameters, i.e., Chromium (Cr) concentration, BOD, COD, TDS, turbidity, conductivity, and pH, compared to their separate value. Firstly, the parameters were assessed separately for deliming, liming, neutralization, and chrome tanning effluents, and were also assessed after mixing deliming-chrome tanning, liming-chrome tanning, and neutralization-chrome tanning wastewater at a fixed ratio to evaluate the effectiveness of the treatment process. After treatment, the results indicate a successful reduction in chromium concentration, BOD, COD, TDS, turbidity, conductivity, and pH in the wastewater, without the use of any external chemical reagents, and that the wastewater poses a lower environmental threat upon release from the tannery.

2. Materials and Method

2.1 Study area

The study area includes the Savar Tannery Industrial Estate, located in Hemayetpur, Savar, Dhaka, Bangladesh. The Savar Upazila is located at 23.8583° N (latitude) and 90.2667° E (longitude) and covers an area of 280.13 km² (Naher et al., 2021), which is shown in Figure 1. Three Tannery industries, namely Samina, Ruma, and Mukta industries, were selected for effluent collection. Liming and deliming wastewater were collected from the above three tanneries,

and neutralization wastewater was collected only from the Samina and Ruma tanneries. Those tanneries are renowned manufacturers of all kinds of leather. They also export crust and finished leather to the U.S.A. and European countries.

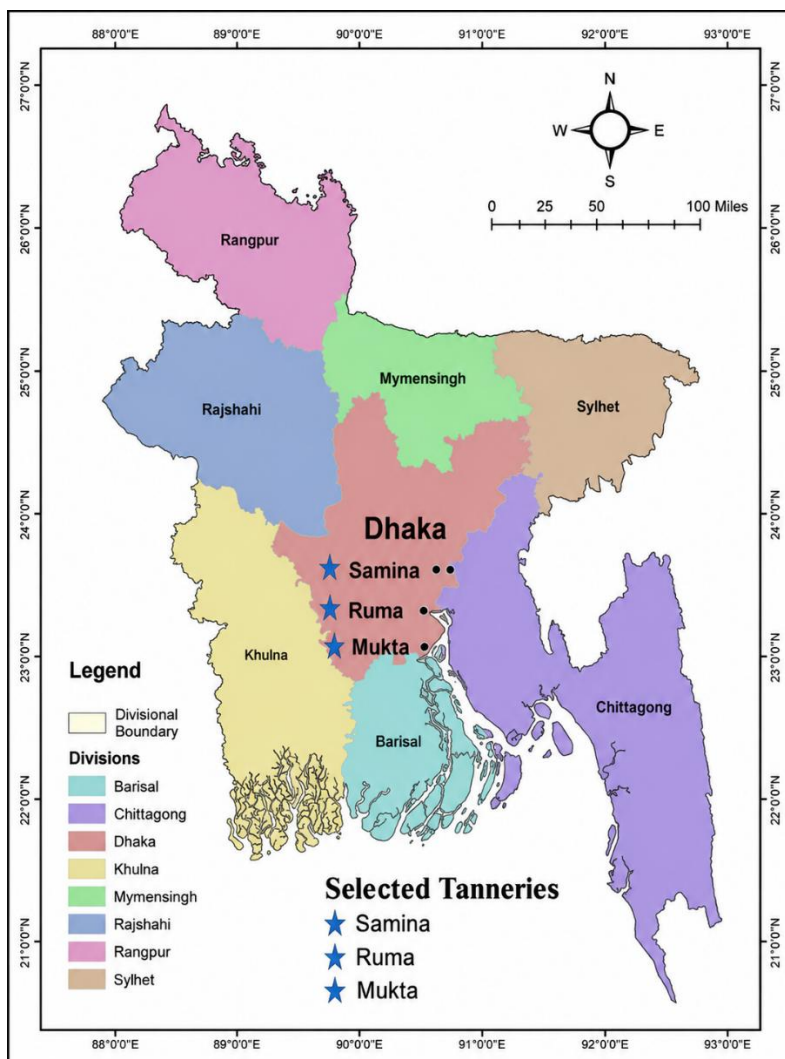


Figure 1. Map showing the location of the selected tanneries

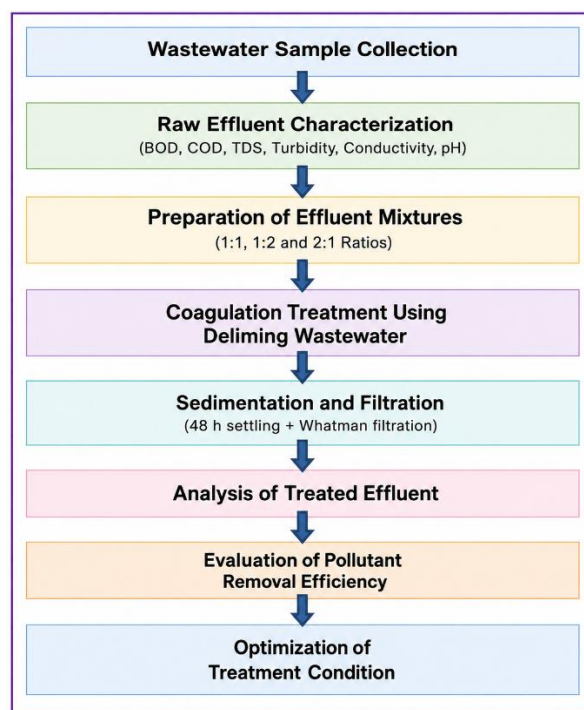
2.2 Sample collection

This study was conducted in 2022, and liming, deliming, and neutralization tannery effluents were collected from the outlets of three selected leather industries in the Savar leather processing zone in Dhaka, Bangladesh. Liming removes hair and epidermis. The hides are treated with a solution containing 3% sodium sulfide (25% sulfide) and 3% hydrated lime (calcium hydroxide) at a 200% float (i.e., 2 L of water per kg of skins or hides processed). Therefore, the lime effluent contained calcium hydroxide (Nazer et al., 2006). Using acids and/or acidic salts, the deliming phase is performed to minimize the surplus liming agents employed in the prior unhairing procedure. This procedure uses chemicals such as ammonium sulfate and metabisulfite (Cassano, 2015). The acid-wash step in leather tanning is

followed by neutralization. Oxalic and acetic acids have been used in the acid-wash procedure. As a result, the pH has dropped. The neutralizing step is completed to raise the pH. To neutralize the pH, neutralizing agents such as sodium formate and sodium bicarbonate are utilized (Ali et al., 2024). Chrome tanning effluent is also released into the environment after the chrome tanning process. For this investigation, all samples were collected directly from the discharge point of individual tanning operations. All the samples were collected following Hossain et al. (2023) and stored in polyethylene bottles at $4\pm1^{\circ}\text{C}$ in the laboratory.

2.3 Treatment process

Experiments were performed separately in a 500 mL beaker. For this investigation, deliming and chrome-tanning effluents, as well as neutralizing effluents, were mixed in different proportions presented in Scheme 1. Effluents were mixed at a proportion of deliming: chrome (1:1), deliming: chrome (2:1), and deliming: chrome (3:1). Liming and chrome tanning effluent were mixed at a proportion of liming: chrome (1:1), liming: chrome (2:1), liming: chrome (1:2) while neutralizing effluents and chrome tanning effluents were mixed at the proportion of neutralizing: chrome (1:1), neutralizing: chrome (2:1), neutralizing: chrome (3:1), neutralizing: chrome (4:1). After that a shaker rotating at 150 rpm was used to shook the beaker for an appropriate amount of time until equilibrium was established. The mixture was then allowed to settle for 48 hours at room temperature. After 48 hours, the mixture was filtered through Whatman filter paper, and the concentrations of Cr (VI), BOD, COD, TDS, turbidity, conductivity, and pH in the filtrate were measured to evaluate the effectiveness of the mixing treatment.



Scheme 1: Overall methodology of effluent collection, treatment, and analysis.

2.4 Tannery effluent characteristics and effluent analysis:

Firstly, the chrome tanning effluents, deliming, liming, and neutralization effluents were collected in a 500 mL beaker, and physical parameters were measured separately for each effluent. After that, the physical parameters were again measured for the mixture effluent of the above definite proportion. The physical parameters of raw tannery effluents, including Biological Oxygen Demand in 5 days at 20°C (BOD₅), Chemical Oxygen Demand (COD), conductivity, Total dissolved solids (TDS), turbidity, pH, and chromium, were measured. Wastewater pH was measured with a pH meter (PG1800, Multitec); conductivity was measured with an electrical conductivity meter (C 708, Analion); and turbidity was measured with a turbidity meter (DM-C2, Digimed). A digester block (AT 525) and a photo colorimeter (AT 1P) were used to measure chemical oxygen demand (COD), while HACH equipment (2173B, Hach) was used to assess biochemical oxygen demand (BOD). AAS-7000 SHIMAZU, an atomic absorption spectrophotometer, was used to measure the content of chromium.

2.5 Calculation of removal percentage of tannery effluent parameter:

Each parameter was assessed after mixing at different ratios, using the following formula for removal percentage.

$$\text{Percentage removal (\%)} = (C_{\text{initial}} - C_{\text{final}}) / C_{\text{initial}} \times 100$$

Where C_{initial} is initial concentration (or amount) and C_{final} is final concentration after 48 hr.

2.6 Pseudo-First-Order Kinetic Model

The pseudo-first-order kinetic model was applied to evaluate the apparent chromium removal behavior for deliming-chrome tanning and neutralization-chrome tanning processes. The model is expressed as:

$$\ln\left(\frac{C_0}{C_t}\right) = k_1 t$$

where $C_0(\text{mg}\cdot\text{L}^{-1})$ is the initial chromium concentration, $C_{48}(\text{mg}\cdot\text{L}^{-1})$ is the chromium concentration after treatment time 48h, $k_1(\text{h}^{-1})$ is the apparent pseudo-first-order rate constant, and $t(\text{h})$ is the treatment time.

In this study, a fixed settling and reaction time of 48 h was employed for all experiments. Although time-resolved concentration profiles were not available because observations were made only after 48 hrs, apparent pseudo-first-order rate constants were calculated to enable comparative evaluation of chromium removal efficiency across different mixing ratios, treatment processes, and tanneries.

2.7 Determination of Kinetic Parameters

For each experimental condition, the apparent pseudo-first-order rate constant (k_1) was calculated using the following equation:

$$k_1 = \frac{1}{t} \ln\left(\frac{C_0}{C_t}\right)$$

Chromium concentrations before and after treatment were determined analytically, and the natural logarithm of the concentration ratio was used to compute k_1 . The calculated rate constants were compared across different alkaline effluent mixing ratios to assess the influence of alkalinity dosage on chromium removal behavior. To evaluate the consistency of the kinetic model, linear regression analysis was performed by plotting $\ln\left(\frac{C_0}{C_t}\right)$ as a function of mixing ratio. The coefficient of determination (R^2) was used as an indicator of model adequacy.

2.8 Thermodynamic Analysis

Chromium removal from liming-chrome tanning wastewater is predominantly governed by equilibrium-controlled physicochemical processes, including the precipitation of chromium hydroxide $[\text{Cr}(\text{OH})_3]$ and the formation of complexes with alkaline constituents. Under these conditions, thermodynamic analysis provides a suitable framework for evaluating the spontaneity and feasibility of the removal process. The standard Gibbs free energy change (ΔG°) was therefore calculated to assess whether chromium removal occurs spontaneously under the experimental conditions employed.

The standard Gibbs free energy change (ΔG°) for chromium removal was calculated using the following thermodynamic relationship:

$$\Delta G^\circ = -RT \ln K$$

Where R is the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T is the absolute temperature (K), and K is the equilibrium constant for the chromium removal process. The equilibrium constant (K) was estimated based on chromium concentration measurements before and after treatment using the following expression:

$$K = \frac{C_0 - C_e}{C_e}$$

Where $C_0(\text{mg}\cdot\text{L}^{-1})$ is the initial chromium concentration, and $C_e(\text{mg}\cdot\text{L}^{-1})$ is the chromium concentration at equilibrium following treatment. All thermodynamic calculations were performed assuming constant temperature conditions, and ΔG° values were reported in $\text{kJ}\cdot\text{mol}^{-1}$.

2.8 Statistical Analysis

The linear regression model parameters were determined in Microsoft Excel to describe the relationship between the treatment ratio and the removal efficiencies of BOD, COD, TDS, turbidity, and conductivity for the Ruma, Samina, and Mukta tanneries in the deliming-chrome and neutralization-chrome processes. The slope represents the rate of change in removal efficiency with respect to the treatment ratio, while the intercept indicates the system's theoretical baseline removal efficiency. The coefficient of determination (R^2) was used to assess the goodness of fit of the linear models. Sensitivity was quantified as the average absolute value of regression slopes from linear models across three tanneries. It compares the strength of each water quality parameter's response to changes in the treatment ratio using regression-derived slopes. Averaging across tanneries reduces site-specific bias and provides a generalized assessment of parameter sensitivity.

2.9 Combined Performance Index (CPI) Analysis

For the liming-chrome tanning process, the performance index was calculated based on the removal efficiencies of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), turbidity, and electrical conductivity. The combined performance index (PI) was calculated as the arithmetic mean of the percentage removal efficiencies of the selected parameters according to the following expression:

$$PI (\%) = \frac{1}{n} \sum_{i=1}^n R_i$$

Where R_i is the percentage removal efficiency of parameter i , and n , is the total number of parameters considered. In this study, equal weighting was assigned to all parameters to provide an unbiased and integrated assessment of treatment performance. The PI value ranges from 0 to 100%, with higher values indicating superior overall treatment efficiency. The index was used as a comparative tool to identify the optimal mixing ratio and to assess the consistency of process performance across different tannery wastewater sources.

2.10 Pearson correlation model

To evaluate the strength and relationship between treatment ratio and pollutant removal efficiency during the deliming-chrome and neutralization-chrome tanning process, Pearson correlation analysis was performed. The correlation analysis used experimentally obtained percentage removal efficiencies of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), turbidity, and electrical conductivity at different neutralization-to-chrome effluent mixing ratios. The Pearson correlation coefficient (r) was calculated using the following equation:

$$r = \frac{\sum(x - \bar{x})(y - \bar{y})}{\sqrt{\sum(x - \bar{x})^2 \sum(y - \bar{y})^2}}$$

Where x represents the treatment ratio, y represents the pollutant removal efficiency (%), and $\bar{x}$ and $\bar{y}$ are the respective mean values. The absolute value of the correlation coefficient ($|r|$) was also reported to facilitate comparison of correlation strength irrespective of direction. All correlation analyses were performed using Microsoft Excel and were computed using the built-in CORREL function. Correlation values were interpreted based on commonly accepted statistical criteria, where $|r| > 0.9$ indicates a very strong correlation, $0.7 < |r| \leq 0.9$ indicates a strong correlation, and $|r| \leq 0.7$ indicates a moderate to weak correlation.

3. Results and Discussion

3.1 Characterization of raw tannery effluent of deliming and chrome tanning operation and effect of mixture:

Characterization of raw tannery effluent of de-liming and chrome tanning operation from several tanneries has been shown in Table 1, and the effect of the mixture has been shown in Table 2. Reports from Table 1 illustrated that the range of BOD (5310-4010 mg/L), COD (18100 – 9810 mg/L), TDS (64100-53100 mg/L), turbidity (1150 – 910 NTU), conductivity (131100-106100 μ s/cm), chromium (1000.3-1724.3 mg/L), and pH (9.0- 2.8). The analysis reports

indicate that the untreated tannery effluents were highly polluted and harmful to fish and other aquatic life. Table-2 shows the effect of wastewater mixture on the percentage removal of BOD, COD, TDS, turbidity, conductivity, and chromium ion. After filtration of the mixture, deliming effluent with chrome tanning effluent at proportions of (delime 1:1chrome, delime 2:1 chrome, delime 3:1 chrome), the BOD concentration decreased by 67.62% - 81.9%. The maximum level of BOD removal was reached at a proportion of (delime 1:1 chrome). As the delime dose increased, the percentage reduction in BOD decreased. The COD concentration decreased by 82.32% to 74.10%. The maximum percentage of COD removal was 82.32% (at a delime: chrome ratio of 1:1). As the delime dose increased, the percentage reduction in COD removal decreased significantly. The TDS, turbidity, and conductivity decreased by 83.42% to 73.12%, 91.05% to 84.34%, and 83.57% to 72.69%, respectively. The maximum removal was achieved at a delime-to-chrome ratio of 1:1. As the delime dose increased, the percentage removal of TDS, turbidity, and conductivity decreased significantly. Figure 2(a), (b), (c), (d), (e) depict the change in the removal percentage of BOD, COD, TDS, turbidity, and conductivity, respectively, with the change in the proportion of deliming effluent and chrome tanning effluent. Overall, at the 150:50 ratio, we obtained the lowest evaluated physicochemical characteristics compared to others. Thus, we suggest that sustainable reduction of Chromium (III) and organic load may be achieved by increasing effluent mixing ratios. However, variations in physicochemical quality are most likely due to individual manufacturing conditions, the use of chemicals for different operations, initial effluent quality, etc.

Table 2 also shows the effect of wastewater coagulation on chromium removal and indicates that chromium removal depends on delime dose, pH, and initial chromium concentration. As the delime dose and solution pH increased, more chromium was removed from the effluent. Higher chromium removal percentages are observed as pH increases across all deliming effluent doses. 99% of chromium was removed at pH 6.9-7.4. After the addition of the deliming effluent at proportions of (delime 1:1 chrome, delime 2:1 chrome, delime 3:1 chrome), the chromium concentration decreased by 98.58% - 99.98%. However, this result is higher than that reported by other authors for chromium removal (Abdulla et al., 2010; Bedada et al., 2020; Aguilar-Ascón et al., 2024). Chrome concentration decreases with the increase of pH, and the optimum removal of chromium from effluent is near pH 7.

Table 1: Characterization of raw tannery effluent of deliming and chrome tanning operation

Name of Tannery	Effluent	BOD mg/L	COD mg/L	TDS mg/L	Turbidity NTU	Conductivity (µs/cm)	P ^H	Chromium mg/L
Ruma Tannery	Delime	5310	18100	54100	950	117100	8.5	1000.3
	Chrome tanning	4100	11100	63100	1090	125150	2.9	
Samina Tannery	Delime	4910	17110	53100	910	106100	8.9	1724.5
	Chrome tanning	4210	10500	60100	1050	119100	3.1	
Mukta Tannery	Delime	5100	19100	57100	940	115500	9.0	1524.4
	Chrome tanning	4010	9810	64100	1150	131100	2.8	
ISI/ISW-BDS Standard limit (Chowdhury et al. 2015).		30/250	250/400	2100			6-9	2

Table 2: Effects of mixture for different proportions of deliming and chrome tanning effluent

Name of tannery	Parameter	Proportion 1:1 (50:50) mL	P ^H	Percentage of removal (%)	Proportion 2:1 (100:50) mL	P ^H	Percentage of removal (%)	Proportion 3:1 (150: 50) mL	P ^H	Percentage of removal (%)
Ruma Tannery	BOD	1700	5.9	81.9%	2100	6.3	77.58%	3010	6.9	68.01%
	COD	6210	5.9	78.73%	6110	6.3	79.08%	7150	6.9	75.51%
	TDS	2110	5.9	81.99%	22500	6.3	80.80%	31500	6.9	73.12%
	Turbidity	197	5.9	90.34%	221	6.3	89.17%	297	6.9	85.44%
	Conductivity	41150	5.9	83.01%	43150	6.3	82.18%	60500	6.9	75.02%
	Cr removal %	14.2	5.9	98.58%	7.3	6.3	99.27%	1.4	6.9	99.86%
Samina Tannery	BOD	1910	5.7	79.06%	2250	6.1	75.33%	2750	6.5	69.85%
	COD	5310	5.7	80.77%	5510	6.1	80.04%	7150	6.5	74.10%
	TDS	19100	5.7	83.13%	23100	6.1	79.60%	30150	6.5	73.37%
	Turbidity	181	5.7	90.77%	228	6.1	88.37%	307	6.5	84.34%
	Conductivity	37510	5.7	82.01%	47150	6.1	79.06%	61500	6.5	72.69%
	Cr removal %	10.5	5.7	99.33%	7.1	6.1	99.67%	0.9	6.5	99.98%
Mukta Tannery	BOD	1850	5.9	79.69%	2310	6.0	74.64%	2950	6.4	67.62%
	COD	5110	5.9	82.32%	5450	6.0	81.51%	6820	6.4	76.41%
	TDS	20100	5.9	83.42%	24100	6.0	80.12%	29500	6.4	75.66%
	Turbidity	187	5.9	91.05%	206	6.0	90.14%	262	6.4	87.46%
	Conductivity	40510	5.9	83.57%	47510	6.0	80.73%	58550	6.4	76.26%
	Cr removal %	13.9	5.9	99.09%	7.5	6.0	99.61%	1.1	6.4	99.93%

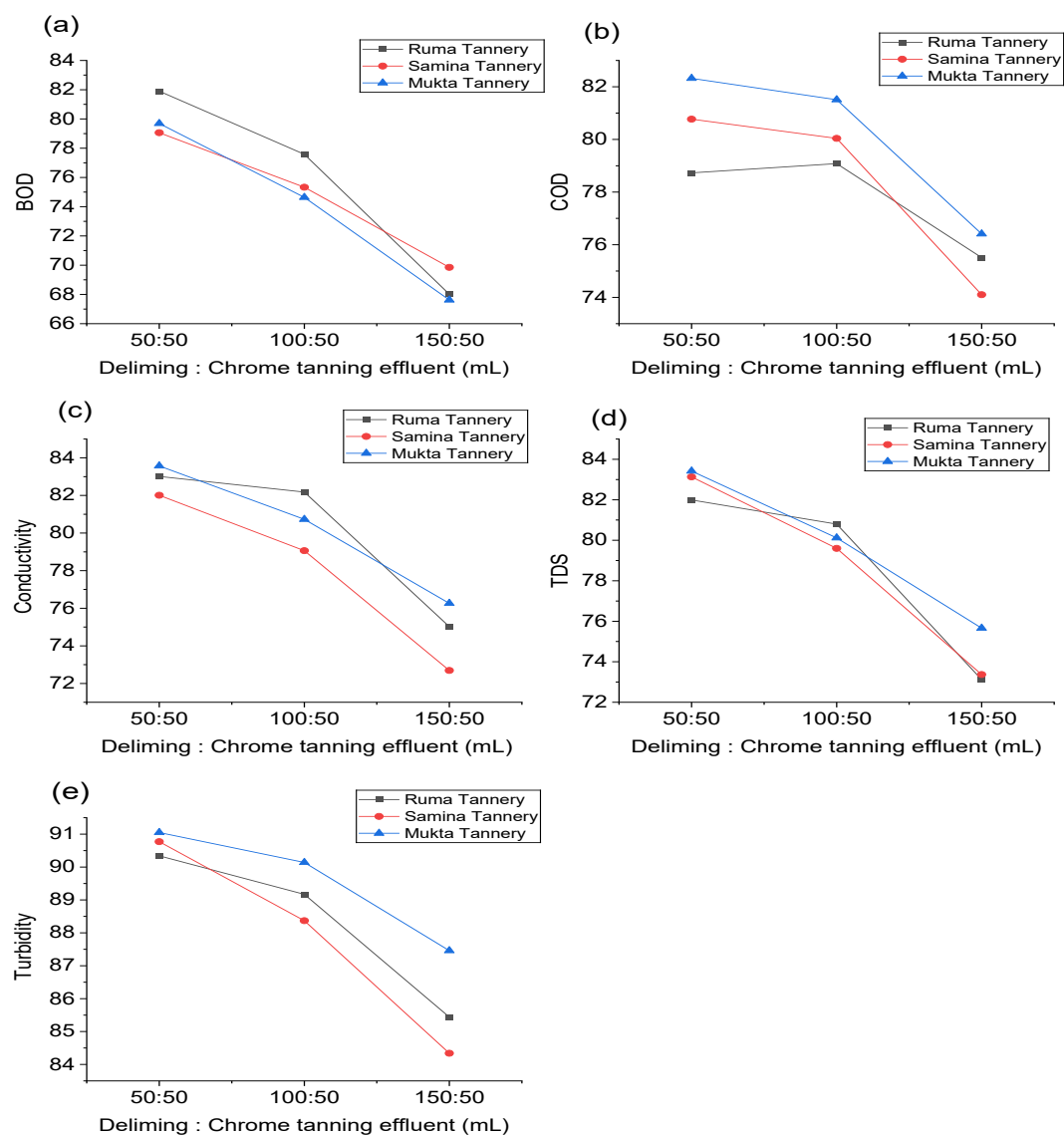
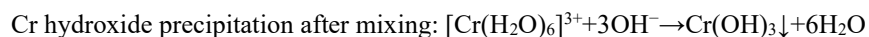
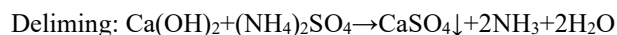


Figure 2. Changes in characteristics for the mixture of deliming and chrome tanning effluent

3.1.1 Chemical reaction of the mixture of deliming and chrome tanning effluent:

The deliming phase removes excess liming chemicals from the prior unhairing procedure using acids and/or acidic salts. This procedure uses compounds such as ammonium sulfate and metabisulfite (Cassano, 2015). The main objective of the deliming operation is to reduce pH and remove lime from the leather. In this operation, Ammonium Sulfate $[(\text{NH}_4)_2\text{SO}_4]$ is used as a deliming agent, and in the tanning operation, chromium is the main inorganic pollutant released from the effluent. Whereas the main objective of chrome tanning is to fix the tanning agent at collagen-reactive sites, thus stopping the putrefaction reaction, and liming is an unhairing operation. Tanning wastewater also

contained MgO, syntan, and other tanning agents. After mixing the deliming process wastewater and chrome tanning effluents at different pH levels, ionic interactions increase, and adjusting the pH to the precipitation range promotes the precipitation of chromium as $\text{Cr}(\text{OH})_3$. It was also observed that the removal mechanism is propagated by hydroxide precipitation and co-precipitation with organic matter. Due to the flocculation of $\text{Cr}(\text{OH})_3$, organic adsorption into flocs occurred, thereby enhancing the reduction of BOD, COD, and turbidity through sedimentation. The following are the reactions of the deliming-chrome tanning process



In this process, no other external alkali or reducing reagent is used to reduce chromium. Cr precipitates naturally due to its mixing chemistry. So it is a cost-effective and easily adoptable process for the tanning industry.

3.1.2 Apparent pseudo-first-order kinetic analysis of Cr removal

The apparent pseudo-first-order kinetic model (Figure 3) was applied to evaluate chromium removal from the deliming-chrome tanning wastewater system using chromium concentrations measured before and after 48 h of settling. The calculated apparent rate constants (k_1) ranged from 0.0886 to 0.1369 h^{-1} for Ruma tannery, 0.1063 to 0.1575 h^{-1} for Samina tannery, and 0.0979 to 0.1507 h^{-1} for Mukta tannery, depending on the deliming-to-chrome tanning effluent ratio. In all cases, k_1 increased with increasing deliming effluent proportion, indicating enhanced chromium removal kinetics under higher alkalinity and sulfate availability. The increase in apparent rate constants with increasing deliming effluent ratio confirms that chromium removal is governed by chemically controlled processes, primarily complex formation and hydroxide precipitation. Higher deliming dosages increase solution pH and sulfate concentration, thereby accelerating the conversion of soluble chromium species into insoluble complexes. The linearized kinetic plots exhibited good correlation coefficients ($R^2 = 0.86\text{--}0.94$), validating the applicability of the pseudo-first-order kinetic model. The slight variation in R^2 values among different mixing ratios may be attributed to the simultaneous occurrence of multiple removal mechanisms, including complexation and precipitation, which is typical in heterogeneous wastewater systems. Although intermediate time-dependent measurements were not collected, the apparent kinetic approach based on equilibrium concentrations is widely accepted for chemically controlled wastewater treatment systems.

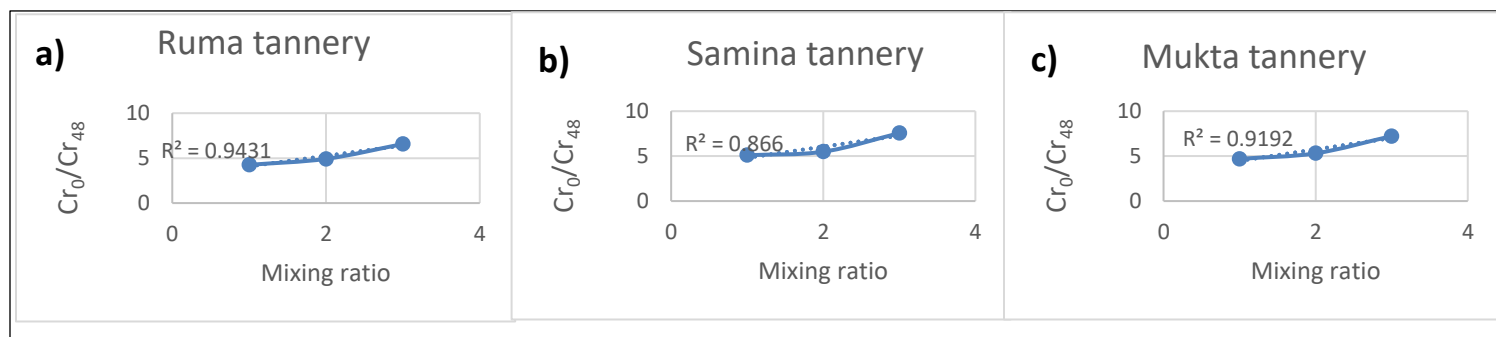


Figure 3. Pseudo-first-order kinetic model graph for deliming-chrome tanning process

3.1.2 Linear regression model and sensitivity analysis

The linear regression analysis in Table 3 showed negative slopes for all parameters across the three tanneries, indicating a consistent decrease in removal efficiency as the treatment ratio increased. BOD removal exhibited the steepest negative slopes among all parameters, particularly for Ruma (−6.94) and Mukta (−6.03), indicating high sensitivity of biodegradable organic matter to changes in treatment ratio. Samina tannery showed a comparatively lower slope (−4.60), suggesting relatively more stable BOD removal behavior. High R^2 values (>0.95) for BOD across all tanneries indicate an excellent linear fit and strong dependence on treatment ratio. COD removal showed comparatively lower slope magnitudes, ranging from −1.61 (Ruma) to −3.33 (Samina), indicating weaker sensitivity to the treatment ratio than BOD. Correspondingly, COD exhibited lower R^2 values, particularly for Ruma (0.667), suggesting that COD removal is influenced by additional factors beyond treatment ratio.

TDS and conductivity showed moderate negative slopes (−3.88 to −4.88) and relatively high R^2 values (>0.83), indicating a strong, consistent linear relationship with treatment ratio. These results suggest that dissolved solids and ionic species are moderately affected by changes in dilution or treatment conditions. Turbidity removal demonstrated moderate sensitivity to treatment ratio, with slopes ranging from −2.45 (Ruma) to −3.21 (Samina). High R^2 values (>0.91) indicate good linear model performance, reflecting consistent particulate removal behavior across tanneries. Overall, the regression analysis confirms that treatment ratio is a key controlling parameter for deliming–chrome wastewater treatment performance, with its influence being most pronounced for BOD removal and least significant for COD.

Sensitivity analysis in Figure 4 showed that BOD removal was most sensitive to the treatment ratio ($|m| = 5.86$), followed by TDS and conductivity. Turbidity showed moderate sensitivity, whereas COD displayed the lowest sensitivity to changes in the ratio. This indicates that organic load removal is more strongly influenced by treatment ratio than by inorganic and physicochemical parameters. The higher sensitivity of BOD to treatment ratio may be attributed to the dilution-dependent nature of biodegradable organic matter, whereas COD includes both biodegradable and seemingly refractory components, resulting in a weaker dependence on ratio.

Table 3: Linear regression model parameters for deliming–chrome wastewater treatment at different tanneries

Name of Tannery	Parameter	Slope	Intercept	R^2 value
Ruma	BOD	-6.94	89.72	0.954
	COD	-1.61	80.99	0.667
	TDS	-4.43	87.50	0.848
	Turbidity	-2.45	93.21	0.916
	Conductivity	-4.04	88.18	0.834
Samina	BOD	-4.60	83.95	0.988
	COD	-3.33	84.97	0.831
	TDS	-4.88	88.46	0.975
	Turbidity	-3.21	94.25	0.979
	Conductivity	-4.66	87.24	0.957
Mukta	BOD	-6.03	86.05	0.991
	COD	-2.95	85.99	0.850
	TDS	-3.88	87.49	0.992
	Turbidity	-3.88	87.49	0.992
	Conductivity	-3.65	87.49	0.983

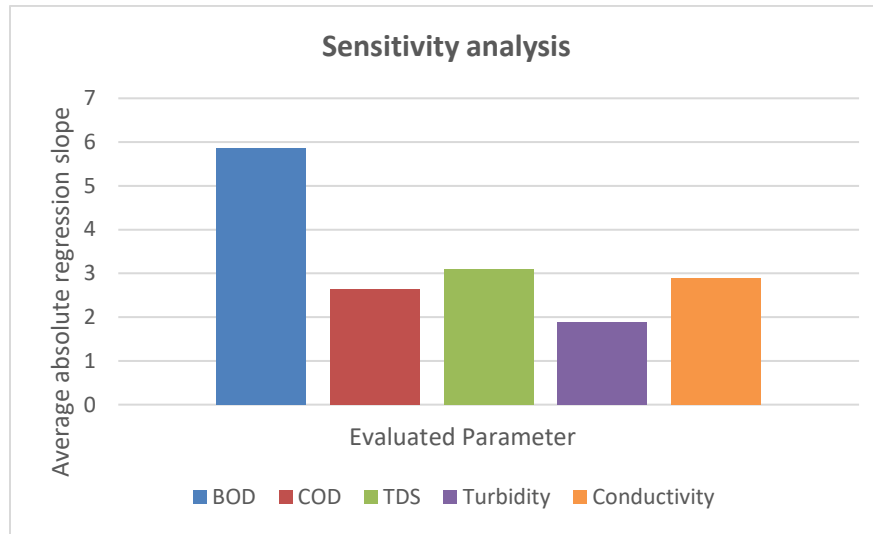


Figure 4. Sensitivity of water quality parameters to treatment ratio based on regression slopes

3.1.3 Correlation analysis

Table 4 presents the Pearson correlation coefficients (r) describing the relationship between treatment ratio and pollutant removal efficiency for the deliming–chrome process across three tanneries. All parameters exhibited strong to very strong negative correlations with treatment ratio, with absolute correlation coefficients ($|r|$) ranging from 0.81 to 0.99. BOD, TDS, turbidity, and conductivity showed particularly strong correlations ($|r| \geq 0.91$) for all tanneries, while COD also demonstrated a strong negative correlation. The consistency of high $|r|$ values across the Ruma, Samina, and Mukta tanneries indicates a robust and systematic dependence of treatment performance on variation in ratios. The strong-to-very-strong negative correlations observed across all water quality parameters confirm that increasing the treatment ratio consistently reduces pollutant removal efficiency during the deliming–chrome process. The very high $|r|$ values for BOD, TDS, turbidity, and conductivity indicate that these parameters are highly sensitive to ratio variation, which agrees with the large regression slope magnitudes obtained from linear modeling.

Table 4: Pearson correlation coefficients between treatment ratio and pollutant removal efficiency for the deliming–chrome process

Name of tannery	Parameter	r value	r
Ruma	BOD	-0.97	0.97
	COD	-0.81	0.81
	TDS	-0.92	0.92
	Turbidity	-0.95	0.95
	Conductivity	-0.91	0.91
Samina	BOD	-0.99	0.99
	COD	-0.91	0.91
	TDS	-0.98	0.98
	Turbidity	-0.98	0.98
	Conductivity	-0.97	0.97
Mukta	BOD	-0.99	0.99

COD	-0.92	0.92
TDS	-0.99	0.99
Turbidity	-0.99	0.99
Conductivity	-0.99	0.99

Note: absolute value of r (0.70-0.89=strong, 0.90-1.00=very strong)

3.2 Characterization of raw tannery effluent of liming and chrome tanning operation and effect of mixture:

Table 5 illustrates the characterization of raw tannery effluent from liming and chrome tanning operations, and the effect of the mixture of liming effluent and chrome-tanned effluent is shown in Table 6.

The range of BOD (6500 to 4110 mg/L), COD (19500 to 10500 mg/L), TDS (61100 to 53100 mg/L), turbidity (1210 to 1010 NTU), conductivity (122100 to 107100 $\mu\text{S}/\text{cm}$), chromium (1805.3 to 1120.2 mg/L), and pH (13.2 to 2.4). The reports showed that raw tannery effluent is heavily polluted and harmful to fish and other aquatic life. These values were much higher than the standard limits for ISI and ISW-BDS (Chowdhury et al. 2015).

Table 6 shows the effect of wastewater mixture on the removal of BOD, COD, TDS, turbidity, conductivity, and chromium ions. After filtration of the mixture of liming effluent with the chrome tanning wastewater at a proportion (lime 1:1 chrome tanning, lime 2:1 chrome tanning, lime 1:2 chrome tanning), the BOD concentration decreased by 78.23%-70.08%. The optimum percentage of BOD removal is achieved at a proportion (chrome 1:1 lime). BOD removal is most effective within a pH range of 6 to 7. The COD concentration decreased from 81.53% to 74.18%. COD removal is most effective near neutral pH. The maximum percentage of COD removal was reached at a proportion (lime 1:2 chrome tanning). The TDS, turbidity, and conductivity were reduced by 81.96%-71.45%, 91.48%-87.04%, and 81.91%-72.14%, respectively. The maximum removal percentage of TDS, turbidity, and conductivity was achieved at a proportion of (lime 1:2 chrome tanning). TDS, turbidity, and conductivity removal showed better results near neutral pH. Figure 5 (a), (b), (c), (d), (e) depict the change in the removal percentage of BOD, COD, conductivity, TDS, and turbidity, respectively, with the change of the proportion of liming effluent and chrome tanning effluent.

Table 6 also illustrates chromium removal from effluent. The optimum percentage of chromium removal was reached at pH 8.0-8.4. However, an increase in pH from 6 to 8.4 represented a better effect on chromium removal. After the addition of liming effluent with chrome tanning wastewater at a proportion of (lime 1:1 chrome tanning, lime 2:1 chrome tanning, lime 1:2 chrome tanning), the chromium concentration decreased by 98.31%-99.99%. This result is higher than the chromium removal reported by Bedada et al. (2020), Edwar Aguilar-Ascón et al. (2024), and Abdulla et al. (2010). The maximum percentage of chromium removal was reached at a proportion of (lime 2:1 chrome). As the lime or chrome tanning effluent dose increased, the percentage of chromium removal decreased slightly.

Table 5: Characterization of raw tannery effluent of liming and chrome tanning operation

Name of tannery	Effluent	BOD ₅ mg/L	COD mg/L	TDS mg/L	Turbidity	Conductivity ($\mu\text{S}/\text{cm}$)	Chromium mg/L	pH
Samina	Liming	6110	18150	58100	1010	116100		12.8
	Chrome tanning	4500	12100	61100	1150	122100	1120.2	3.2
Ruma	Liming	6500	19500	58150	1100	115300		13.2
	Chrome tanning	3150	10500	59510	1050	118120	1805.3	3.0
Mukta	Liming	5750	19100	53110	1210	107100		13.0
	Chrome tanning	4110	12900	59320	1150	121000	1550	2.4
ISI/ISW-BDS Standard value (Chowdhury et al. 2015).		30/250	250/400	2100			2	6-9

Table 6: Effects of mixture for different proportions of liming and chrome tanning effluent

Name of tannery	Parameter	Proportion 1:1 (50 : 50) mL	P ^H	Percentage of removal (%)	Proportion 2:1 (100 : 50) mL	P ^H	Percentage of removal (%)	Proportion 1:2 (50 : 100) mL	P ^H	Percentage of removal (%)
Ruma	BOD	2400	6.5	75.13%	2810	8.1	70.88%	2110	6.1	78.13%
	COD	6110	6.5	79.63%	6710	8.1	77.63%	6315	6.1	78.95%
	TDS	24510	6.5	79.10%	27150	8.1	76.86%	24150	6.1	79.41%
	Turbidity	211	6.5	90.19%	263	8.1	87.77%	251	6.1	88.33%
	Conductivity	47500	6.5	79.65%	53210	8.1	77.21%	43560	6.1	81.34%
	Cr removal %	7.5	6.5	99.59%	0.5	8.1	99.97%	23	6.1	98.73%
Samina	BOD	2310	6.7	78.23%	3100	8.0	70.78%	2710	6.0	74.46%
	COD	6500	6.7	78.51%	7810	8.0	74.18%	7010	6.0	76.83%
	TDS	23100	6.7	80.62%	27360	8.0	77.05%	21500	6.0	81.96%
	Turbidity	203	6.7	90.60%	280	8.0	87.04%	255	6.0	88.19%
	Conductivity	45110	6.7	81.06%	53110	8.0	77.70%	43100	6.0	81.91%
	Cr removal %	5	6.7	99.55%	0.2	8.0	99.97%	19	6.0	98.31%
Mukta	BOD	2510	6.4	74.54%	2950	8.4	70.08%	2150	5.9	78.19%
	COD	6720	6.4	79%	7450	8.4	76.72%	5910	5.9	81.53%
	TDS	27150	6.4	75.85%	32100	8.4	71.45%	21010	5.9	81.31%
	Turbidity	201	6.4	91.48%	281	8.4	88.09%	227	5.9	90.38%
	Conductivity	53150	6.4	76.70%	63550	8.4	72.14%	43100	5.9	81.11%
	Cr removal %	6.7	6.4	99.57%	0.2	8.4	99.99%	24.3	5.9	98.43%

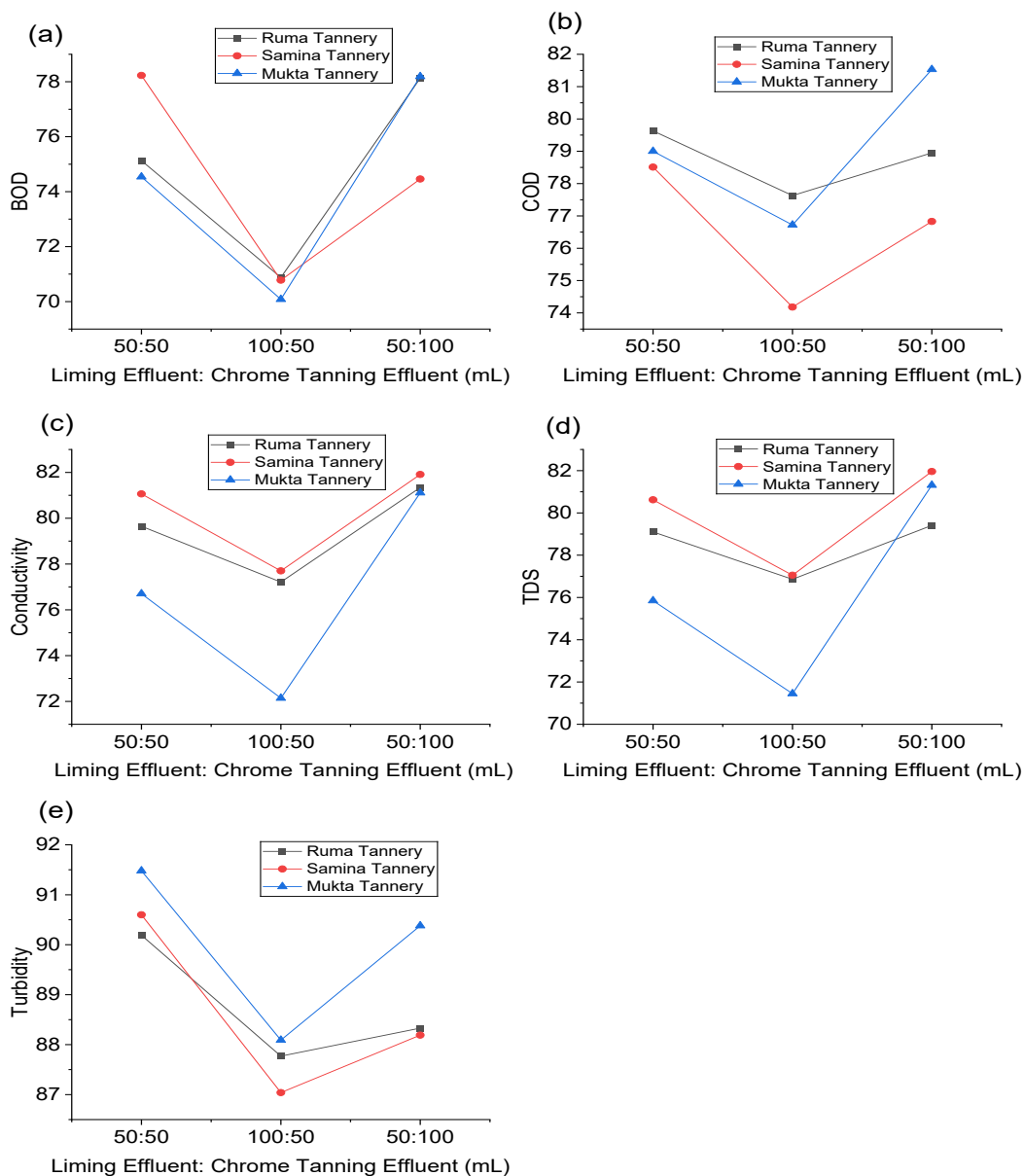


Figure 5. Changes in characteristics for the mixture of liming and chrome tanning effluent

3.2.1 Chemical reaction of the mixture of liming and chrome tanning effluent:

By introducing alkali into the hide, liming aims to separate the fiber bundles and remove any undesirable hair. In this case, lime is usually supplied prior to the occurrence of alkaline swelling caused by the addition of sodium hydroxide and sodium sulfide. The hides are treated with 3% sodium sulfide, 25% sulfide, and 3% hydrated lime (calcium hydroxide) in a 200% float solution. Therefore, the lime effluent contained calcium hydroxide (Nazer et al., 2006). Upon mixing liming effluent containing excess calcium hydroxide with chrome tanning wastewater, the increase in

pH promotes the precipitation of chromium(III) as chromium hydroxide. The primary removal mechanism is hydroxide precipitation rather than simple acid-base neutralization. Dissociated hydroxide ions from Ca(OH)_2 react with Cr^{3+} species to form insoluble Cr(OH)_3 , which subsequently settles. The resulting chromium hydroxide flocs also facilitate co-precipitation and adsorption of organic matter, contributing to reductions in turbidity, BOD, and COD. In addition, the removal of dissolved ions occurs through the formation of sparingly soluble salts such as CaSO_4 , which decrease TDS and conductivity. On the other hand, if the pH is high, the Cr hydroxide goes back into solution, which is why a moderate pH range is needed to keep the Cr as a precipitate. The following are the reactions of the liming-chrome tanning process

Liming: $\text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2\text{OH}^-$

Cr in chrome effluent: $\text{Cr}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Cr(OH)}^{2+} + \text{H}^+$

Precipitation: $2\text{Cr}^{3+} + 3\text{Ca(OH)}_2 \rightarrow 2\text{Cr(OH)}_3 \downarrow + 3\text{Ca}^{2+}$

Redissolution at high pH: $\text{Cr(OH)}^{3+} + \text{OH}^- \rightarrow [\text{Cr(OH)}_4]^-$

3.2.2 Thermodynamic validation for Cr removal

Chromium removal during liming-chrome tanning (shown in Table 7) is governed by chemical equilibrium and precipitation, not time-dependent kinetics; therefore, thermodynamic feasibility (ΔG°) is more appropriate than kinetic modeling. The calculated standard Gibbs free energy change (ΔG°) values for the liming–chrome tanning process were negative for all tanneries and mixing ratios, confirming the spontaneous nature of chromium removal. ΔG° values ranged from -10.10 to $-22.19 \text{ kJ}\cdot\text{mol}^{-1}$, which is characteristic of physicochemical processes such as precipitation and complex formation rather than adsorption. Increasing the alkaline effluent ratio led to more negative ΔG° values, indicating a stronger thermodynamic driving force for chromium hydroxide formation. Among the tested ratios, the 2:1 mixing ratio exhibited the most negative ΔG° across all tanneries, suggesting optimal thermodynamic conditions for chromium removal. These results demonstrate that chromium removal during liming–chrome tanning is governed primarily by thermodynamic equilibrium rather than kinetic limitations.

Table 7: Calculated standard Gibbs free energy change (ΔG°) at different ratios for the liming-chrome tanning process for Cr removal

Name of the tannery	Ratio	ΔG° in kJ/mol
Ruma	1:1	-13.586
	2:1	-20.2954
	1:2	-10.8096
Samina	1:1	-13.4082
	2:1	-21.3832
	1:2	-10.1006
Mukta	1:1	-13.4877
	2:1	-22.1878
	1:2	-10.2956

3.2.3 Performance Index analysis

From Figure 6, we can say all parameters exhibited a decrease in removal efficiency at a ratio of 2:1, followed by an increase at 1:2, indicating the presence of an optimum treatment ratio in the liming-chrome process. Unlike the deliming-chrome process, which showed a strong linear relationship between ratio and removal efficiency, the liming-chrome process exhibited non-linear behavior with a clear optimum ratio. Therefore, linear regression and slope-based sensitivity analysis were not applied for the liming-chrome process; instead, the performance index (PI) was determined at different ratios for the three tanneries, as shown in Figure 6. The performance index, calculated as the average removal efficiency of BOD, COD, TDS, turbidity, and conductivity, ranged from 75.7% to 82.5%. For all three tanneries, the lowest PI was observed at a 2:1 ratio, while higher values were observed at 1:1 and 1:2 ratios. The maximum PI values were recorded at the 1:2 ratio for Ruma (81.23%) and Mukta (82.50%) tanneries, whereas Samina showed comparable performance at 1:1 and 1:2 ratios.

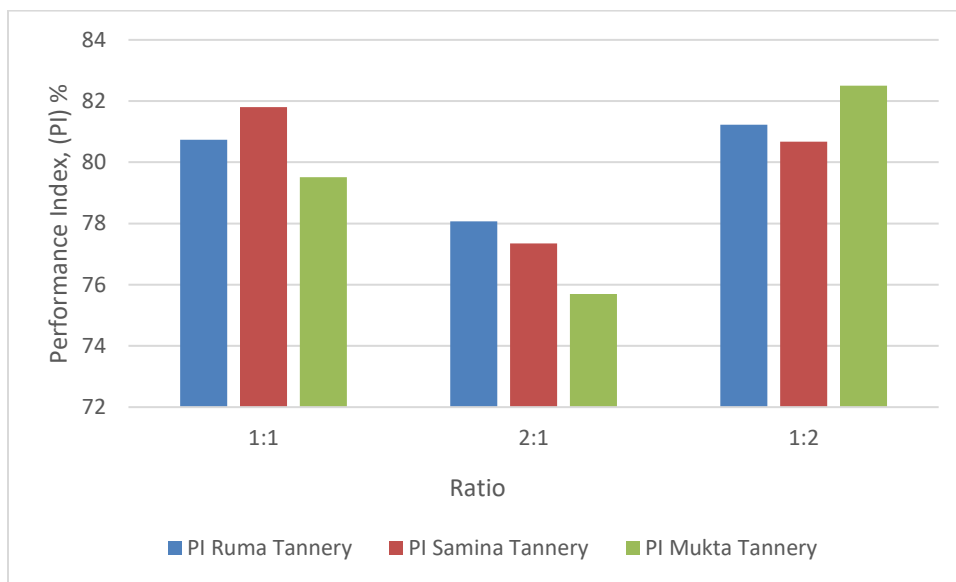


Figure 6. Combined performance index of liming–chrome treatment at different ratios

3.3 Characterization of raw tannery effluent of neutralization and chrome tanning operation and effect of mixture:

Table 8 depicts the characterization of raw tannery effluent of liming and chrome tanning operation, and the effect of the mixture of liming effluent and chrome tanned effluent is shown in Table 9.

The analysis in Table 8 indicates that the untreated effluent contains highly toxic compounds, and the BOD, COD, TDS, and chromium levels were much higher than the prescribed standards. The range of BOD (5150 to 2910 mg/L), COD (12970 to 7211 mg/L), TDS (63150 to 44500 mg/L), turbidity (1210 NTU to 701 NTU), Conductivity (127500 to 89500 $\mu\text{S}/\text{cm}$), chromium content (1104.1 to 1510.1 mg/L), and pH (2.8 to 7.4) in the raw tannery effluent.

Table 8: Characterization of raw tannery effluent of neutralization and chrome tanning operation

Name of tannery	Name of operation	BOD ₅ (mg/L)	COD (mg/L)	TDS (mg/L)	Turbidity NTU	Conductivity (µs/cm)	Chromium (mg/L)	pH
Ruma	Chrome tanning	4150	11500	61500	1210	124500	1104.1	2.8
	Neutralization	3210	7320	44500	724	89500		7.4
Samina	Chrome tanning	5150	12970	63150	1070	127500	1510.1	3.4
	Neutralization	2910	7211	49500	701	101510		7.4
Standard value ISI-2000/ ISW-BDS (Chowdhury et al. 2015)		30/250	250/400	2100			2	6-9

optimum level of reduction was achieved at a proportion of (chrome tanning 1:1 neutralization). As the neutralization effluent dose increased, BOD reduction decreased. The COD concentration decreased from 89.35% to 74.74%. The maximum reduction level of COD is 89.35%, which is better than the COD removal from tannery wastewater investigated in Ziati et al. (2018).

The maximum level of reduction was reached at a proportion of chrome tanning: neutralization (1:1). A further increase in the neutralization effluent is associated with a decrease in COD removal. The maximum percentages of TDS, turbidity, and conductivity removal were 91.37%, 94.30%, and 92.08%, respectively (at 1:1 chrome tanning-neutralization). As the neutralization dose increased, removal efficiency decreased significantly. Thus, chrome tanning at 1:1 neutralization yields better removal of COD, BOD, TDS, turbidity, and conductivity. Figure 7 (a), (b), (c), (d), (e) depict the change in the removal percentage of BOD, COD, conductivity, TDS, and turbidity, respectively, with the change in the proportion of liming effluent and chrome tanning effluent.

Table 9 also illustrates the effect of wastewater coagulation on chromium removal. After the addition of neutralization wastewater with chrome tanning effluent at a proportion of chrome tanning 1:1 neutralization, chrome tanning 1:2 neutralization, chrome tanning 1:3 neutralization, and chrome tanning 1:4 neutralization, the chromium concentration decreased by 83.32%-97.32%. The optimum level of chromium removal was achieved at a neutralization: chrome tanning ratio of 4:1. As the neutralization effluent dose increased, the reduction of chromium also increased. pH plays an important role in chromium removal. Approximately 97% of chromium was removed at pH 6.1 to 6.0, while 83% at pH 5.0. However, an increase in pH showed a more positive effect on chromium removal.

Table 9: Effects of mixture for different proportions of neutralizing and chrome tanning effluent.

Name of tannery	Parameter	Proportion 1:1 (50:50) mL	P ^H	Percentage of removal (%)	Proportion 2:1 (100 :50) mL	P ^H	Percentage of removal (%)	Proportion 3:1 (150 : 50) mL	P ^H	Percentage of removal (%)	Proportion 4:1 (200 : 50) mL	P ^H	Percentage of removal (%)
Ruma	BOD	1210	4.9	83.56%	1550	5.1	78.94%	2150	5.5	70.79%	2450	6.1	66.71%
	COD	2910	4.9	84.54%	3150	5.1	83.26%	4755	5.5	74.74%	4550	6.1	75.82%
	TDS	11500	4.9	89.15%	15110	5.1	85.75%	19550	5.5	81.56%	22500	6.1	78.77%
	Turbidity	107	4.9	94.48%	121	5.1	93.74%	155	5.5	91.99%	197	6.1	89.81%
	Conductivity	21500	4.9	89.95%	30150	5.1	85.91%	41550	5.5	80.59%	45150	6.1	78.90%
	Cr removal %	184.2	4.9	83.32%	120.1	5.1	89.12%	71.4	5.5	93.53%	27.4	6.1	97.52%
Samina	BOD	955	4.8	88.15%	1150	5.2	85.73%	1510	5.6	81.27%	1910	6.0	76.30%
	COD	2150	4.8	89.35%	2415	5.2	88.03%	3150	5.6	84.39%	3910	6.0	80.63%
	TDS	9723	4.8	91.37%	10510	5.2	90.67%	12510	5.6	88.90%	18150	6.0	83.89%
	Turbidity	101	4.8	94.30%	124	5.4	92.99%	174	5.6	90.18%	207	6.0	88.31%
	Conductivity	18150	4.8	92.08%	21500	5.4	90.61%	25100	5.6	89.04%	39150	6.0	82.91%
	Cr removal %	251.4	4.8	83.35%	174.1	5.2	88.47%	100.1	5.6	93.37%	44.4	6.0	97.06%

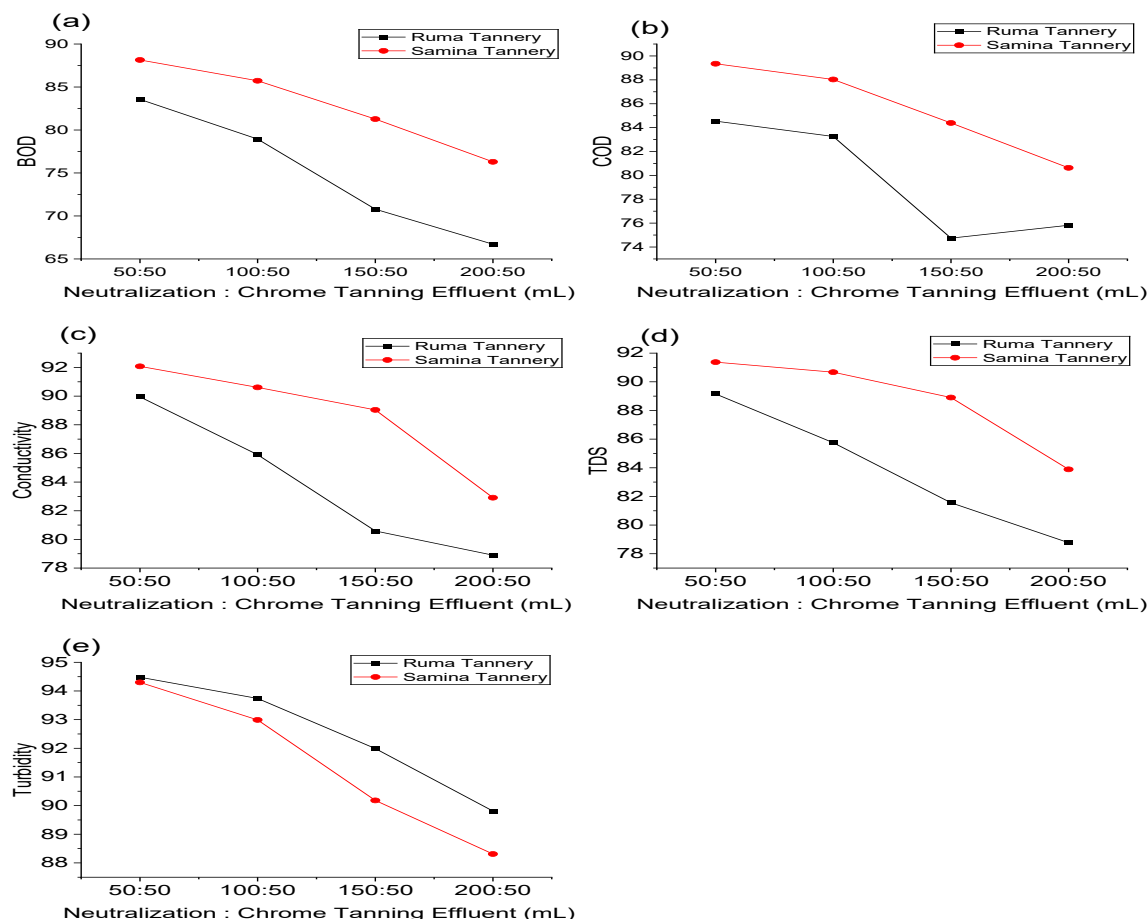


Figure 7. Changes in characteristics for the mixture of neutralization and chrome tanning effluent

3.3.1 Chemical reaction of the mixture of neutralization and chrome tanning effluent:

The neutralization process occurred following the acid wash phase in leather tanning. Oxalic and acetic acids were utilized in the acid wash process. Thus, the pH was reduced. The neutralization method was used to raise the pH level. Sodium formate, sodium bicarbonate, and neutralizing agents are used to neutralize pH (R. M. Ali et al., 2024). The technique uses a simple acid-base neutralization reaction. After mixing the neutralization effluent containing sodium bicarbonate with chrome tanning wastewater, bicarbonate ions raise the solution's pH via hydrolysis equilibria. The elevated pH promotes the precipitation of chromium (III) as insoluble chromium hydroxide via hydrolysis. The overall mechanism is influenced by pH-induced hydroxide precipitation rather than a simple stoichiometric reaction between chromium sulfate and sodium bicarbonate. The formed $\text{Cr}(\text{OH})_3$ flocs similarly enhance turbidity reduction and facilitate co-precipitation and adsorption of organic matter, contributing to decreases in BOD and COD, as previously observed with the other 2 mixing processes. The reduction in TDS and conductivity is primarily governed by the

precipitation of multivalent chromium species and subsequent co-precipitation of associated ions and organic matter. The removal of highly charged Cr^{3+} ions significantly lowers the ionic strength, resulting in measurable decreases in conductivity. The following are the reactions of the neutralization-chrome tanning process

Bi-carbonate dissociation: $\text{NaHCO}_3 \rightarrow \text{Na}^+ + \text{HCO}_3^-$

Bi-carbonate equilibrium: $\text{HCO}_3^- \rightleftharpoons \text{CO}_2 + \text{OH}^-$

Cr precipitation: $\text{Cr}^{3+} + 3\text{OH}^- \rightarrow \text{Cr}(\text{OH})_3 \downarrow$

Soluble salts formation: $\text{Ca}^{2+} + \text{SO}_4^{2-} \rightarrow \text{CaSO}_4 \downarrow$

3.3.2 Kinetic modeling of Cr removal in neutralization-chrome tanning system

The pseudo-first-order kinetic model was applied to evaluate chromium removal in the neutralization–chrome tanning system, and excellent linearity was observed for all mixing ratios, with correlation coefficients of 0.9623 for Ruma tannery and 0.9708 for Samina tannery (Figure 8). The apparent rate constants (k_1) increased progressively with increasing neutralization-to-chrome tanning ratio, ranging from 0.0373 to 0.0770 h^{-1} and 0.0374 to 0.0735 h^{-1} for Ruma and Samina tanneries, respectively. The high correlation coefficients indicate that chromium removal during neutralization–chrome tanning follows apparent pseudo-first-order kinetics. Unlike the liming–chrome tanning system, where instantaneous precipitation dominates, neutralization provides a buffered pH environment that promotes gradual chromium hydrolysis and controlled formation of $\text{Cr}(\text{OH})_3$. The observed increase in k_1 values with neutralization ratio reflects increased hydroxyl-ion availability while maintaining conditions favorable for time-dependent precipitation.

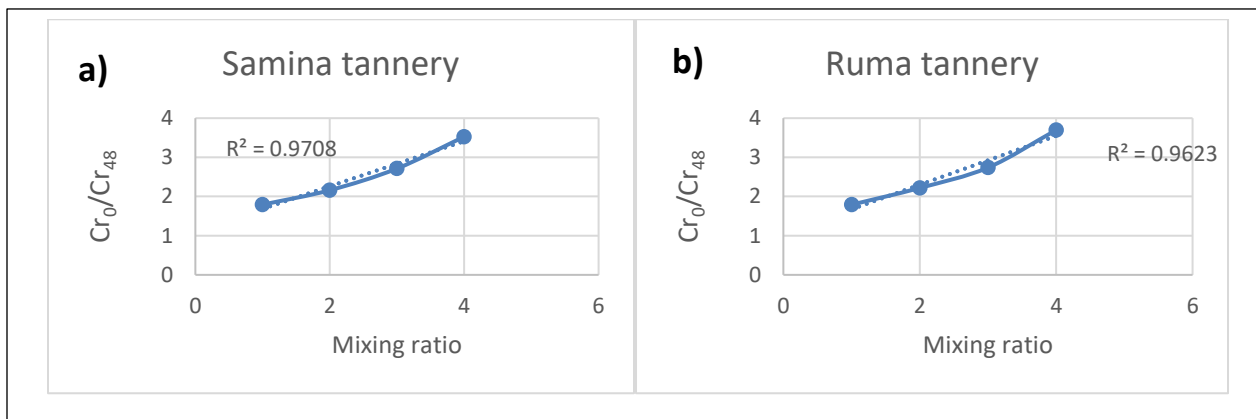


Figure 8. Pseudo-first-order kinetic model graph for neutralization-chrome tanning process

3.3.3 Linear regression model analysis

Table 10 summarizes the linear regression parameters obtained for the neutralization–chrome process across different water quality parameters and tanneries. For both Ruma and Samina tanneries, all regression slopes were negative, indicating a consistent decrease in removal efficiency as the treatment ratio increased. The coefficients of determination (R^2) were high for most parameters, ranging from 0.79 to 0.99 for Ruma and from 0.86 to 0.98 for Samina, suggesting a strong linear relationship between ratio and treatment performance. Among the parameters,

BOD, TDS, turbidity, and conductivity exhibited particularly strong linearity with R^2 values above 0.95 in most cases. The magnitude of the regression slopes reflects the sensitivity of pollutant removal efficiency to changes in treatment ratio. BOD exhibited the highest slope magnitude for both tanneries (-5.87 for Ruma and -4.00 for Samina), indicating that organic matter removal was most sensitive to variation in the ratio. In contrast, turbidity showed a comparatively lower slope, suggesting greater robustness of particulate removal across varying ratios. The high coefficients of determination obtained for most parameters confirm the suitability of linear regression for modeling the neutralization–chrome process. The strong agreement between experimental data and fitted regression lines indicates that variation in the ratio is a dominant controlling factor governing treatment efficiency in this process.

Table 10: Linear regression parameters describing the relationship between treatment ratio and pollutant removal efficiency in the neutralization–chrome process

Name of Tannery	Parameter	Slope	Intercept	R^2 value
Ruma	BOD	-5.87	89.67	0.983
	COD	-3.46	88.26	0.794
	TDS	-3.53	92.64	0.994
	Turbidity	-1.57	96.44	0.958
	Conductivity	-3.84	93.45	0.966
Samina	BOD	-4.00	92.86	0.978
	COD	-2.98	93.05	0.962
	TDS	-2.42	94.76	0.857
	Turbidity	-2.07	96.64	0.982
	Conductivity	-2.90	95.93	0.868

3.3.4 Correlation analysis

Table 11: Pearson correlation coefficients between treatment ratio and pollutant removal efficiency for the neutralization-chrome process

Name of tannery	Parameter	r value	r
Ruma	BOD	-0.99	0.99
	COD	-0.89	0.89
	TDS	-0.99	0.99
	Turbidity	-0.97	0.97
	Conductivity	-0.98	0.98
Samina	BOD	-0.98	0.98
	COD	-0.98	0.98
	TDS	-0.92	0.92
	Turbidity	-0.99	0.99
	Conductivity	-0.93	0.93

Note: absolute value of r (0.70-0.89=strong, 0.90-1.00=very strong)

Table 11 presents the Pearson correlation coefficients (r) between the treatment ratio and the removal efficiency of different water quality parameters in the neutralization–chrome process. For both Ruma and Samina tanneries, all parameters exhibited strong to very strong negative correlations with treatment ratio ($r = -0.89$ to -0.99). BOD, TDS, turbidity, and conductivity showed very strong correlations ($|r| \geq 0.92$), while COD also demonstrated a strong negative correlation with increasing ratio. The strong-to-very-strong negative correlation coefficients indicate that increasing

the treatment ratio consistently reduced pollutant removal efficiency during the neutralization–chrome process. The very high correlation values observed between BOD and turbidity suggest that organic matter and particulate removal are particularly sensitive to variations in the BOD-to-turbidity ratio. These findings are consistent with the linear regression results and confirm the suitability of linear modeling and slope-based sensitivity analysis for this process.

3.4 Effect of pH on the percentage of removal of chromium:

pH has a significant impact on the proportion of chromium removed. It was noted that the pH of the solution affected the amount of chromium removed from the mixture of deliming and chrome tanning effluent. Figure 9(a) showed that more chromium was extracted from the effluent as the solution's pH rose. As pH rises, a higher percentage of chromium is removed across all deliming effluent dosages. At pH 6.9–7.4, 99% of the chromium was eliminated. The concentration of chromium fell by 98.58% to 99.98% following the addition of the deliming effluent in the following proportions: delime 1:1 chrome, delime 2:1 chrome, and delime 3:1 chrome. This occurred because adding more deliming effluent raised the pH and brought it closer to neutrality. The pH of the mixture of deliming effluent and chrome tanning effluent at the ratio of (deliming 1:1 chrome tanning effluent) was 5.7–5.9. The best way to remove chromium from effluent is to lower the pH to 7, as chromium concentration decreases with increasing pH.

The extraction of chromium from the mixture of liming and chrome tanning effluent was depicted in Fig 9(b). At a pH of 8.0–8.4, the ideal percentage of chromium elimination was attained. On the other hand, a rise in pH from 6 to 8.4 indicated a better chromium elimination. The content of chromium dropped by 98.31% to 99.99% following the addition of liming effluent with waste water that had been chrome-tanned at a ratio of (lime 1:1, lime 2:1, and lime 1:2). The mixture's pH was 6.4–6.7 at the lime–chrome tanning ratio of 1:1. The pH rose further following the addition of additional liming dose, and the maximum percentage of chromium elimination was attained at a ratio of (lime 2:1 chrome). When the lime dosage was reduced to the ratio of (lime 1:2 chrome), a decrease in the elimination of chromium was noted. The outcome made the impact of pH very evident.

Fig. 9(c) shows the effect of pH on the mixture of neutralization and chrome tanning effluents. Neutralization, a crucial step in the leather tanning process, removes acidity from the leather, allowing dye and fat liquoring to permeate uniformly and fully while also neutralizing the leather to a pH of around 5.5-6. Substances such as bicarbonate, borax, neutralizing agent, sodium acetate, and sodium formate are utilized. These compounds increased the fluid pH. As a result, the pH of the neutralization effluent-chrome tanning effluent mixture increased as the fraction of neutralization effluent increased. Chromium removal was more effective as pH increased. At pH 6.1 to 6.0, approximately 97% of chromium was eliminated, while at pH 5.0, it was 83%.

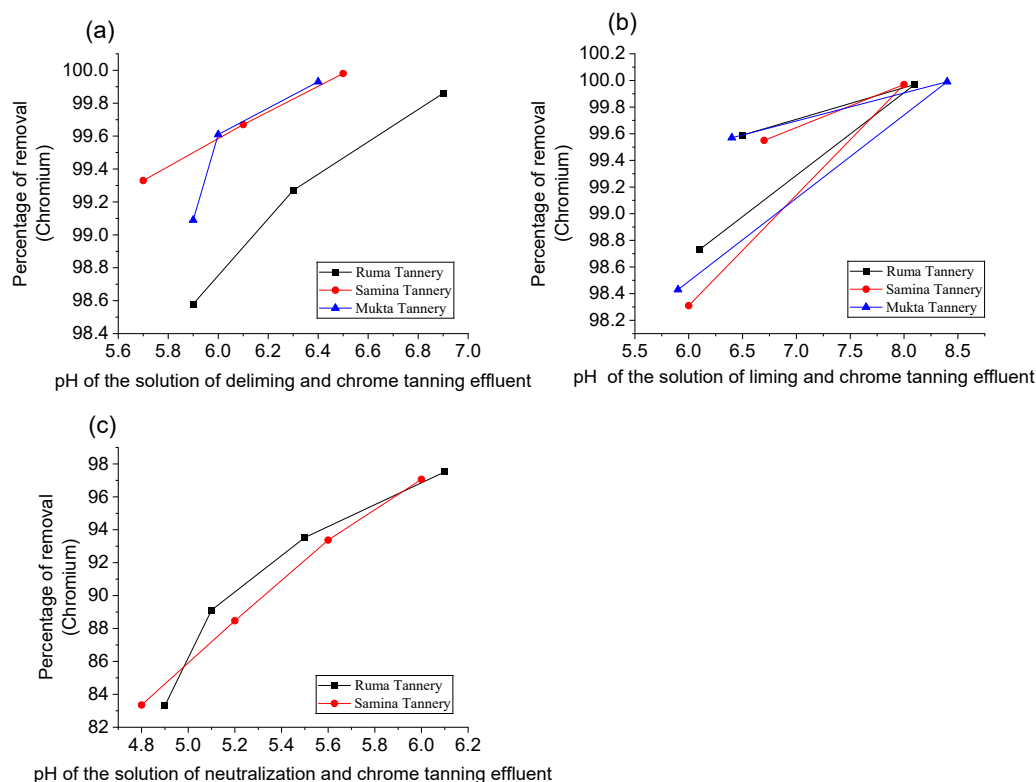


Figure 9. pH impact on the removal of chromium

4. Conclusion

In this study, tannery wastewater was treated using a mixture of wastewater from deliming, liming, neutralization, and the chrome tanning process, without the addition of reagents or adsorbents. Removal of chromium (III), BOD, COD, TDS, turbidity, and conductivity from tannery wastewater is possible using a mixture of deliming, liming, and neutralization of wastewater with chrome tanning effluent at a definite proportion. The deliming and liming mixture removed more than 99% chromium (III), while the neutralized wastewater mixture removed 97% chromium from tanning liquor. The optimum pH for chromium removal was found at 8 to 8.5 using liming liquor. Chromium removal increased with increasing pH and with increasing volumes of liming, deliming, and neutralization liquor in the solution. Other parameters, such as BOD, COD, TDS, turbidity, and conductivity, were also significantly reduced. The deliming–chrome and neutralization–chrome processes followed apparent pseudo-first-order kinetics, with treatment ratio identified as the dominant controlling factor governing chromium and pollutant removal performance. In both systems, BOD was the most ratio-sensitive parameter, whereas COD showed comparatively lower sensitivity, as evidenced by strong linear regression and correlation results. In contrast, the liming–chrome process was thermodynamically controlled, exhibiting spontaneous, equilibrium-driven chromium precipitation ($\Delta G^\circ = -10.10$ to $-22.19 \text{ kJ}\cdot\text{mol}^{-1}$) and nonlinear behavior with an optimal mixing ratio. Overall, treatment ratio critically influences process efficiency, though the governing mechanism varies between kinetic control (deliming and neutralization) and

thermodynamic equilibrium control (liming). Using delime, lime, and neutralization wastewater is beneficial: it neutralizes the acidic medium without reagent cost and produces lower sludge volume. The results indicate that the large volume of wastewater released into the environment by the leather industry can be treated using a sustainable effluent-mixing method without chemical or biological treatment.

Statements and Declarations

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Data Availability: Data will be made available on request.

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