

# Optimization of chloride removal from tannery soaking wastewater by lime alum process

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## Article info

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## Abstract

Chloride removal from tannery-soaking wastewater has been a significant issue due to the presence of high levels of chloride in the wastewater produced by the tanning industry. High levels of chloride ions are harmful to human health as well as the environment if the water is not properly treated. Traditional methods like ion exchange, reverse osmosis, demineralization, coagulation, electrodialysis, precipitation, and adsorption are costly and often ineffective. The lime-alum process offers a promising alternative. This method involves adding lime and alum to the wastewater, forming hydroxide and aluminum hydroxide flocs that precipitate and remove chloride ions. Our research identified the optimal conditions for this process: a pH of 10, reaction time of 25 minutes, temperature of 25°C, and alum dosage of 0.5 grams. Under these conditions, chloride removal reached 635 mg/L. The lime-alum process is cost-effective, using inexpensive chemicals and low energy, and it can be easily integrated into existing wastewater treatment systems. These findings highlight its potential as an efficient solution for chloride removal in the tanning industry.

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## 1. Introduction

Leather has become one of the most commonly traded markets in the world, with a leather industry and a demand for completed leather products like shoes, clothing, and bags in every country (Mpofu, Oyekola, & Welz, 2021; Zhao, Wu, Tang, Zhou, & Guo, 2022). With an estimated  $1.67 \times 10^9 \text{m}^2$  of

leather produced annually and a global trade value of US\$100×10<sup>9</sup>/year, the leather tanning and leather products business play a significant part in the developing world's economy (Dixit, Yadav, Dwivedi, & Das, 2015; Masciana, 2015). Given the abundance of a low-cost labour force, lower treatment, less severe environmental regulations and disposal expenditures of industrial wastewater, the developing world holds the largest share and supplies (>60%) of the world's largest skins/hides industry (TWW)(Mottalib, Somoal, Islam, & Alam, 2015; Shaibur, Tanzania, Nishi, Nahar, Parvin, & Adjadeh, 2022; Swartz, Jackson-Moss, Rowswell, Mpfu, & Welz, 2017).

Bangladesh is a highly populated nation and its growth, industrialization, and unplanned urbanization near river banks have caused severe strain on water resources (Das, Rani, Mamun, Howlader, & Shaibur, 2021; Shaibur, Parvin, Ahmed, Rahaman, Das, & Sarwar, 2021). Industrial waste, particularly tannery effluent, is one of the most significant pollutants globally and presents a serious environmental challenge in Bangladesh (Mizan, Zohra, Ahmed, Nurnabi, & Alam, 2016; Samet & Valiyaveetil, 2018). TDS, BOD<sub>5</sub>, COD and chromic oxide content of polluted water were reduced significantly. Bangladesh J. Sci. Ind. Res. 51(3). The concentration of Cr (VI) in tannery effluent from Hazaribagh in Bangladesh is high, with an average of 374.19 mg/L (Asaduzzaman, Hasan, Rajia, Khan, & Kabir, 2016). The highest concentration of 939.8 mg/L was found in the surface water near Hazaribagh in Dhaka, but it was much lower at 27.65 mg/L in Nowapara in Jashore (Shaibur, Tanzania, Nishi, Nahar, Parvin, & Adjadeh, 2022). Discharging untreated tannery effluent into rivers leads to pollution of aquatic ecosystems and fish contamination, leading to bio-accumulation of Cr (VI) in humans (Hossain, Chowdhury, Jahan, Zzaman, & Islam, 2021; Shaibur, Hossain, Khatun, & Tanzania, 2021). Bangladesh. A total of 35 water samples were collected from different tea stalls, street side fast food stalls, normal restaurants and well-furnished restaurants. The water quality was evaluated by determining the distinct physical, chemical and biological parameters. The results revealed that the water used in the food stalls and restaurants for drinking purpose was in desired quality in terms of turbidity, electrical conductivity, pH, total dissolved solids, nitrate (NO<sub>3</sub><sup>-</sup>). Tanners are striving to minimize their water usage, encourage the better chemical acquisition, reuse and/or reuse processed liquid, industrial effluent, and/or solid waste, decrease substance, and/or eliminate the widespread use of certain contaminants, following international attempts for pollution control (Younas et al., 2022). However, the majority of tanneries in the poor countries have found it difficult to employ these procedures due to the associated extra or capital expenditures, as well as the fear of jeopardizing

leather quality. (Mpofu, Oyekola, & Welz, 2019).

Chloride removal from tannery-soaking wastewater is an important step in the treatment of wastewater generated by the tanning industry. Chloride ions are a major component of dissolved salts in wastewater and are one of the main contributors to the total dissolved solids (TDS) in the water. High levels of chloride ions can cause environmental problems and can also be harmful to human health if the water is not properly treated.

There are several methods that can be used to remove chloride ions from tannery-soaking wastewater, including:

1. Lime-Alum process: This process involves adding lime ( $\text{Ca}(\text{OH})_2$ ) and alum ( $\text{Al}(\text{OH})_3$ ) to the wastewater. The lime reacts with the chloride ions to form calcium chloride ( $\text{CaCl}_2$ ), which is a white solid that precipitates out of the water. Alum reacts with the hydroxide ions ( $\text{OH}^-$ ) to form aluminum hydroxide ( $\text{Al}(\text{OH})_3$ ), which also precipitates out of the water. This process is highly efficient and cost-effective for chloride removal (Ayoub, Hamzeh, & Semerjian, 2011; Mottalib, Somoal, Islam, & Alam, 2015; Selvaraj, Aravind, George, & Sundaram, 2020)20, 25 mA/cm<sup>2</sup> with cylindrical electrodes (MMO and Ti sheet).
2. Reverse osmosis: This process involves forcing the wastewater through a membrane under high pressure, which effectively removes the chloride ions and other dissolved salts from the water.
3. Ion exchange: This process involves passing the wastewater through a resin bed that selectively removes the chloride ions from the water (Payel, Hashem, & Hasan, 2021)unhairing and liming (termed as liming).
4. Electro chlorination: This process involves passing an electric current through the wastewater, which generates chlorine gas. The chlorine gas reacts with the chloride ions in the water to form chloride ions, which can then be removed by precipitation or filtration (Mustafa, 2014; Mustapha, Ndamitso, Abdulkareem, Tijani, Mohammed, & Shuaib, 2019).

Lime-Alum process is only effective for removing chloride ions, other dissolved salts such as sodium and sulfates will remain in the water and will not be removed by this process, so this process should be used in combination with other technologies to achieve the desired results. Indeed, the price per m<sup>3</sup> of treated water could be prohibitive. Installation and running costs are expensive once the rates are large (tens or even hundreds of m<sup>3</sup> of water per hour). The technique is determined by the water's final destination, and everything hinges on the findings of the scoping study. The issue is the cost of desalinated water.

The available chloride removal technologies are costly and time-consuming (Barman, Juel, & Hashem, 2016; Zhao, Wu, Tang, Zhou, &

Guo, 2022) on the other hand Lime-alum process is easy and cost-efficient (Selvaraj, Aravind, George, & Sundaram, 2020). Chlorides react with Calcium Hydroxide and Aluminum sulfate then produce Calcium Chloroaluminate which is insoluble and precipitated. By taking this mechanism, it has been found maximum time saving, temperature, pH. and amount of alum in which maximum chloride is removed from soaking water (Mpofu, Oyekola, & Welz, 2021).

## 2. Methodology

A brief description of the methodology to be applied in this study has been given in this chapter. This includes sample and material collection, wastewater preparation, characterization, and process optimization of the lime alum process. A comparison of the raw and final treated water has also been incorporated here.

### 2.1. Materials

The collection of raw materials, of sufficient amount and quality, is a fundamental factor in the nanocomposite manufacturing process. Raw materials are the primary production components, playing an important role in synthesis and testing. In this study, Soaking Wastewater, Alam and Lime has been used. Soaking wastewater collected from a renowned tannery in Jessore Bangladesh. Alam and Lime have been purchased from Scientific & Chemical Mart, Khulna, Bangladesh. Figure 1 illustrated the materials used in this study whereas Table I represents the characteristics of raw soaking wastewater.

**Table I**

*The characteristics of raw soaking wastewater and reference water*

Parameters	pH	Chloride mg/L	TDS g/L	Salinity ppt	Conductivity Ms	COD mg/L
soaking wastewater	7.8	12396	7.1	8.7	11.76	8352
reference water	7.2	635	5.72	6.8	11.3	1560



**Figure 1**

*Raw materials used in this study are Soaking Wastewater, Alum and Lime*

## 2.2. Experimental procedure

The whole set of experiments was done with both the tannery-soaking wastewater and synthetic distilled water made in the laboratory. The distilled water was named reference water. At first, six beakers were taken with 100 mL soaking wastewater each. Then pHs for all the beakers were adjusted from 8 to 13 by adding the appropriate amount of lime. Then 1gm alum was added to each beaker and stirred in a magnetic stirring machine for 30 minutes. After that, the beakers were kept undisturbed for 30 minutes for gravity settling. The decantation from the top of the beakers was done carefully and the decanted samples were taken for chloride determination. The same experiments were done with the reference saline water by keeping the parameters (temperature, time, amount of alum) unchanged.

This procedure was repeated for different parameters. For the parameter temperature, it was kept undisturbed setting for 30 min at 20°C, 25°C, 30°C, 35°C, and 40°C and recorded the effect of temperature on chloride.

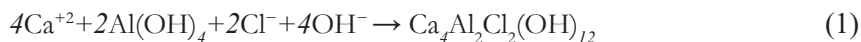
With varying time from 5 minutes to 35 minutes by 5-minute intervals, the effect of time was also observed when other parameters remain unchanged. Lastly, the effect of alum dosages was documented.

## 2.3. Chloride removal mechanism by Lime-Alum process

Chlorides easily react with Calcium Hydroxide and Aluminum sulfate then

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produce calcium Chloroaluminate which is an insoluble and precipitated reaction. So, Chlorides can be easily removed from the wastewater. The mechanism has been present by equation 1.



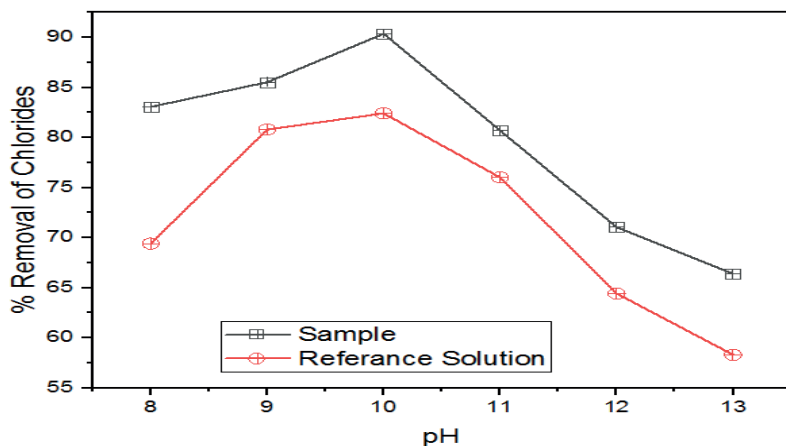
Equation 1 describes the mechanism of chloride removal from tannery soaking wastewater using the Lime-Alum process. The equation shows the chemical reaction that takes place when lime ( $\text{Ca}(\text{OH})_2$ ) and alum ( $\text{Al}(\text{OH})_3$ ) are added to wastewater containing chloride ions ( $\text{Cl}^-$ ). The lime and alum react with the chloride ions and hydroxide ions ( $\text{OH}^-$ ) in the wastewater to form a complex compound called calcium aluminum chloride hydroxide hydrate ( $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ ). This compound is a white solid that precipitates out of the water, effectively removing the chloride ions thus reduces the salinity of the wastewater.

It's worth noting that the Lime-Alum process is only effective for removing chloride ions, other dissolved salts such as sodium and sulphates will remain in the water and will not be removed by this process, so this process should be used in combination with other technologies to achieve the desired results. Additionally, care should be taken in the disposal of the generated sludge and monitoring of pH in the treated water to minimize negative environmental impacts.

### 3. Results and discussion

#### 3.1. Effect of pH on the removal of Chloride

By adding Alum and Lime the value of the pH varies from 8 to 13 along with chloride removal. Table II and figure 2 enlisted and illustrated the effect of pH on chloride removal. pH value plotted in the X-axis and the percentage of chloride removal in the Y-axis of figure 2. From the graph and table II, it is observed that Chloride removal increase with increasing pH from 8 to 10 but Chloride removal decreases with increasing pH from 11 to 13 for a sample and reference water. It was seen that Chloride removal was maximum at pH 10 for a sample and reference water. Salinity for the sample and reference water were measured it showed a higher value for sample water than reference water. Salinity is also affected by the pH of the water enlisted in table II. The sample water salinity was similar to the reference water for pH 11.



**Figure 2**  
Chloride removal vs pH (dose, time, temp= constant)

**Table II**  
Effect of pH on chlorides removal and salinity for sample and reference solution

SL. No.	pH	Chloride content, mg/L (for sample)	% Removal of chlorides for sample	Chloride content, mg/L (for reference solution)	% Removal of chlorides for reference solution	Salinity(ppt) for the sample water	Salinity(ppt) for reference solution
1	8	2098	83.07	3823	69.41	6.8	5.6
2	9	1794	85.53	2398	80.81	6.2	2.9
3	10	1194	90.37	2198	82.42	4	2
4	11	2392	80.71	2998	76.02	2.1	3.8
5	12	3588	71.05	4448	64.42	6.9	4
6	13	4176	66.41	5211	58.31	7.1	5.7

pH in the X-axis and the percentage of chloride removal in the Y-axis are plotted in a graph. The graph is shown in figure 2. The pH of the raw samples examined ranged from 8 to 13, with maximum chloride removal of 90.37% and minimum chloride removal of 66.41%. Following the addition of various amounts of lime to raise the pH to around 11, a progressive fall in pH was observed. This progressive increase was attributed to the creation of  $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$  by the addition of alum and lime at an increased pH, with concentrations increasing with higher dosages of lime and alum. Increasing the concentration of hydroxyl  $(\text{OH})^-$  ions which leads to increased pH values. After pH value 11 the concentration of  $(\text{OH})^-$  was higher, which protested chloride removal.

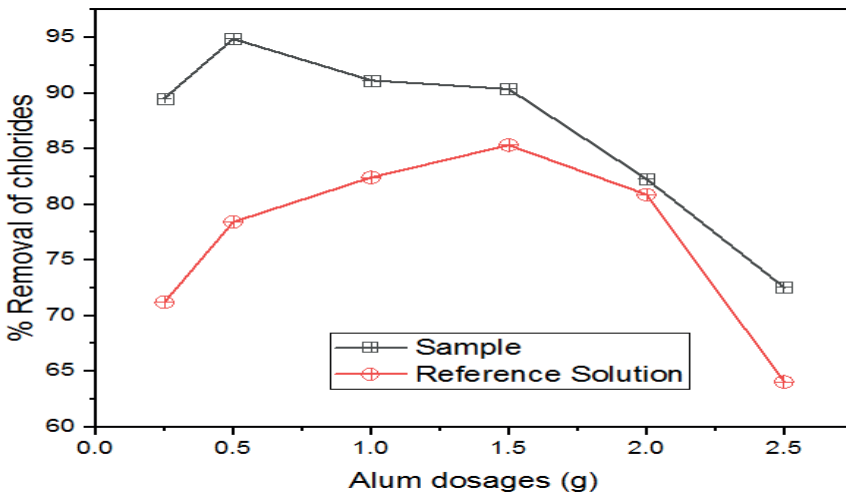
### 3.2. Effect of alum dosage on Chloride removal

The concentration of alum played a key role to remove chloride from wastewater. Due to the increase in alum dosage, pH also increases, and the phenomenon is common as before. Table III and figure 3 have listed and plotted the characteristic of chloride removal.

**Table III**

*Effect of alum dosage on chloride removal and salinity for sample and reference solution.*

SL. No.	Amount of alum	Chloride content, mg/L (for sample)	% Removal of chlorides for sample	Chloride content, mg/L (for reference water)	% Removal of chlorides for reference water	Salinity(ppt) for sample water	Salinity(ppt) for reference water
1	0.25	1297	89.54	3598	71.21	4.8	3.7
2	0.5	635	94.88	2697	78.42	1.2	2.6
3	1.0	1194	90.37	2198	80.88	4	2
4	1.5	1097	91.15	2198	85.53	6.1	1.9
5	2	2197	82.28	2389	80.88	6.45	4
6	2.5	3404	72.54	4495	64.04	7.5	5.6



**Figure 3**

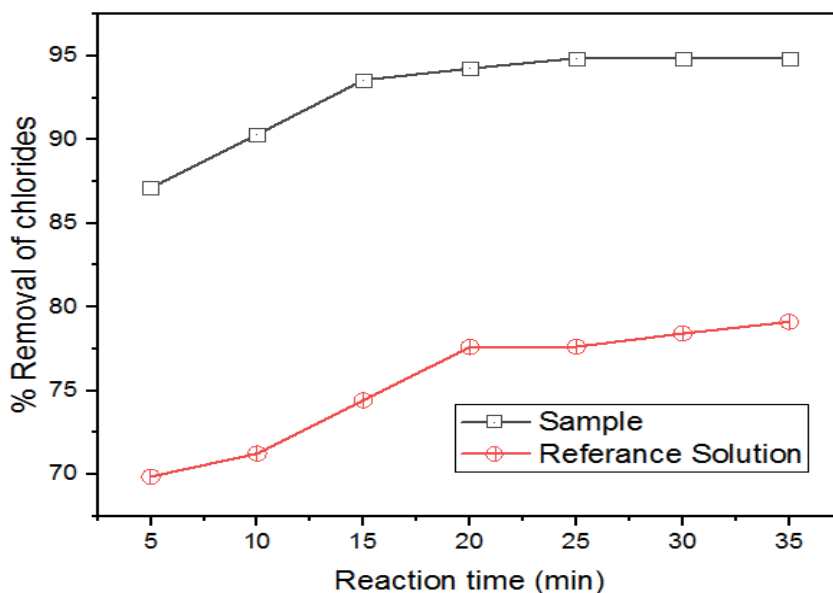
*Chloride removal vs Alum dosage (pH =, time=, temp= constant)*

Alum dosage on the X-axis and the percentage of chloride removal on the Y-axis are plotted in a graph. The graph is shown in fig 3. It was observed that Chloride removal increased with increasing Alum dosage from 0.25gm to 0.5gm but Chloride removal decreased with increasing Alum dosage from 1gm to 2.5gm for sample water. On the other hand, for reference water Chloride removal increase with increasing Alum dosage from 0.25 gm to

1.5gm but Chloride removal decrease with increasing Alum dosage from 2gm to 2.5 gm. It was decided that Chloride removal was maximum at Alum dosage 0.5 gm for sample water and 1.5gm alum dosage for reference water.

### 3.3. Effect of reaction time on Chloride removal

The interaction period was kept at 25 minutes in the experiment because of the approach used. However, because the rate of reaction is time-dependent, an experiment was conducted to assess the rate of reaction at various contact times, as shown in figure 4. The contact duration between the biomass and the test solution was varied while the other parameters were kept constant (Apte, Apte, Kore, & Kore, 2011). Reaction time in the X-axis and percentage of chloride removal in the Y-axis is plotted in figure 4. It was observed that Chloride removal increased with increasing Reaction time from 5 minutes to 30 minutes, but Chloride removal decreased with increasing reaction time from 30 minutes for sample water. On the other hand, for reference water Chloride removal increase with increasing reaction time from 5 minutes to 20 minutes but decrease for 25minute then increase with increasing reaction time from 30 minutes. It was decided that Chloride removal was maximum at a reaction time of 25 minutes for sample water and a reaction time of 35 minutes for reference water.



**Figure 4**  
Chloride removal vs Reaction time (pH =, temp and alum dosage 0.5gm for the sample and 1.5 gm for reference water)

**Table IV***Effect of time on chloride removal and salinity for sample and reference solution.*

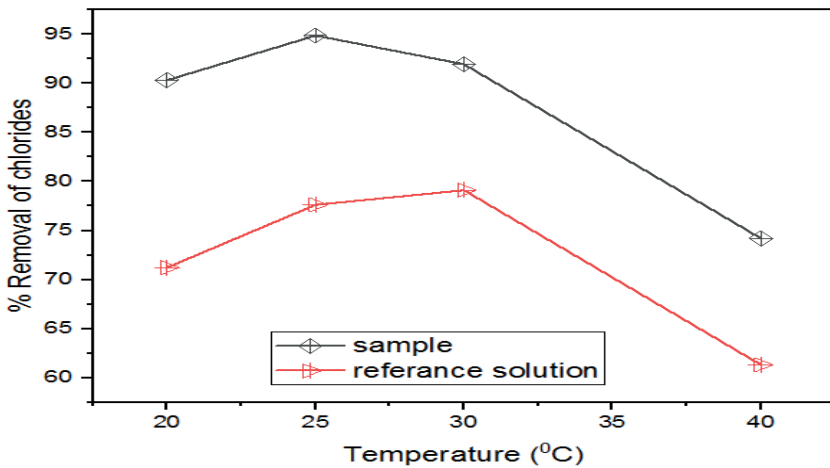
SL. No.	Time (minute)	Chloride content, mg/L (for sample)	% Removal of chlorides for sample	Chloride content, mg/L (for reference water)	% Removal of chlorides (for reference water)	Salinity(ppt) for sample water	Salinity(ppt) for reference water
1	5	1596	87.12	3767	69.86	6.1	6
2	10	1199	90.32	3594	80.88	5.8	5.7
3	15	797	93.57	3196	90.37	4.6	4
4	20	711	94.26	2796	77.61	4	4.4
5	25	635	94.88	2697	93.42	3.1	2.6
6	30	635	93.57	2611	69.86	1.2	2.1
7	35	635	93.57	2528	79.77	1.1	2

### 3.4. Effect of temperature on Chloride removal

The effect of temperature is shown in fig 5. From the figure, it was studied that Chloride removal increase with increasing temperature from 20°C to 25°C then decreases with raising the temperature for the sample and reference water. It was decided from the graph maximum chloride was removed at 25°C.

**Table V***Effect of temperature on chloride removal and salinity for sample and reference solution.*

SL. No.	Temperature (°C)	Chloride content, mg/L (for sample)	% Removal of chlorides for sample	Chloride content, mg/L (for reference water)	% Removal of chlorides (for reference water)	Salinity(ppt) for sample water	Salinity(ppt) for reference solution
1	20	1199	72.54	3596	71.23	3.8	2.8
2	25	635	94.88	2796	90.32	1.2	2.6
3	30	997	82.28	2610	79.12	2.8	3.6
4	40	3196	74.21	4836	61.31	4.6	5.1



**Figure 5**  
*Chloride removal vs Temperature (°C) [PH=10, time=25 for sample and 35 for reference, alum .5gm for sample and 1.5 gm for reference]*

### 3.5. Result analysis

The effect of pH, alum dosage, reaction time, and temperature on chloride removal from wastewater was studied. The results showed that chloride removal was maximum at a pH of 10 for a sample water and at a pH of 11 for reference water. The chloride removal increased with increasing alum dosage from 0.25 gm to 0.5 gm for sample water and from 0.25 gm to 1.5 gm for reference water. The chloride removal increased with increasing reaction time from 5 minutes to 25 minutes for sample water and from 5 minutes to 35 minutes for reference water. Finally, the chloride removal was maximum at a temperature of 25°C for both sample and reference water.

## 4. Conclusion

In conclusion, the optimization of the Lime Alum process for chloride removal from tannery soaking wastewater was successfully carried out in this investigation. The optimum conditions for the process were found to be pH 10, a reaction time of 25 minutes, a temperature of 25°C, and an alum dosage of 0.5gm. These conditions resulted in excellent chloride removal of (94.88%), with a final chloride concentration of 635 mg/L. The study also found that the Lime Alum process is cost-effective, as it uses inexpensive chemicals and requires low energy consumption. These findings suggest that the Lime Alum process is a promising solution for chloride removal from tannery-soaking wastewater and similar industries. The optimized conditions can be recommended for future implementation in the treatment of

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tannery-soaking wastewater. Additionally, care should be taken in the disposal of the generated sludge and monitoring of pH in the treated water to minimize negative environmental impacts.

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