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Comparative Analysis of Conventional Treatment and Advanced Oxidation Applied to Effluent from Stabilization Ponds in Terms of Subsequent Reuse of Treated Water

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Abstract: The possibility of reusing the effluent from Cuenca's wastewater treatment plant WWTP is analyzed through the application of two treatments: conventional physical-chemical (coagulation, flocculation, sedimentation and filtration, and disinfection) and advanced oxidation with a combination of hydrogen peroxide/ozone. The results show that neither treatment method independently resolves all the limitations of the effluent for reuse, especially regarding organic matter, nutrients, and turbidity. Therefore, the compatibility of the quality of the treated water quality is evaluated for three potential reuses such as unrestricted urban use, recreational use with primary contact, and agricultural irrigation, referencing EPA and Ecuadorian TULSMA standards. This study highlights the need to establish a legal and regulatory framework for water reuse in Ecuador to enable decision-makers to implement sustainable water reuse practices and manage scarcity effectively.

Keywords: advance oxidation; conventional treatment; wastewater reuse; water quality



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1. Introduction

According to reports from the United Nations (UN), around 500 million people live in areas where water consumption exceeds supply, resulting in water scarcity in those regions [1,2]. In Ecuador, where the average water access triples the international average, the scarcity situation might not seem as concerning. However, in the face of imminent climate change that generates water scarcity, it is necessary to analyze opportunities for water reuse [3]. Water reuse is fundamentally supported by three critical pillars: (1) ensuring that the treated water consistently meets rigorous quality standards tailored to its specific use, (2) protecting public health by implementing safeguards that prevent potential health risks, and (3) fostering a positive societal perception of water reuse through education and awareness, transforming it into an accepted and valued practice rather than a source of concern [4–8].

Globally, data on water reuse reveals that only 4% of all consumed water is reused. Israel, facing significant water scarcity, has high percentages of wastewater reuse, with 90% of its wastewater repurposed primarily for agricultural, industrial, and urban green area irrigation. In contrast, Latin America shows limited reuse, with the available records estimating that only 2% of produced wastewater is reused. In Ecuador, the situation is even more challenging, as there are no reports indicating any significant reuse of wastewater [9–17]. Regulatory, financial, and technological barriers contribute to the slow uptake of water reuse practices globally [18]. Specifically, achieving compliance with strict water quality standards, as seen in European food industry practices, highlights the need for advanced technologies and legislative harmonization to support reuse initiatives. Additionally, as wastewater reuse expands, managing the concentrated byproducts, especially

from processes like reverse osmosis, is critical. This complexity underscores the need for comprehensive regulations and sustainable management practices for treated wastewater and its byproducts [19].

Given this variability in experience and regulation across regions, it becomes evident that places with limited or nonexistent water reuse practices, like Ecuador, would greatly benefit from establishing clear and relevant regulations. In Ecuador, while wastewater treatment is widely used, potential applications for treated wastewater remain underexplored. One promising alternative to address these gaps is the reuse of effluents from domestic wastewater treatment plants (PTARs). However, implementing this solution requires careful consideration of factors such as the availability of treated wastewater, existing treatment technologies for the specific type of effluent, and ultimately, the feasible uses of treated water [20–22]. According to some authors, water reuse should be approached with a circular economy perspective. Explicitly, it should be used again and again, just as it happens in the natural cycle [6,16,23–27].

In Ecuador and other large Latin American cities, most PTARs generate significant amounts of flow intended for discharge into receiving bodies according to their country's regulations. However, these regulations are not always fully met. In Ecuador, the Ministry of Environment, Water, and Ecological Transition (MAATE) serves as the regulatory authority, with their guidelines established in the Unified Text of Secondary Environmental Legislation (TULSMA). However, in terms of the reuse of treated wastewater, there is still a significant lack of policies and guidelines that allow the systematization of this process and its establishment as a sustainable public policy. As a result, large volumes of treated water are discharged without being reused, leading to unnecessary resource wastage. An example of this is the WWTP effluent in the city of Cuenca, Ecuador. This WWTP, based on an integrated stabilization pond system, discharges around $1 \text{ m}^3/\text{s}$ into the Cuenca River without any further use. This leads to the waste of a resource that could be very useful, especially in times of scarcity, since its flow does not depend on rainfall or regional water balance [28–31].

The objective of this study is to evaluate two treatments applied to the effluent of the Cuenca, Ecuador PTAR in terms of reuse purposes [32–35]: first, a physical–chemical treatment through a conventional coagulation–flocculation–sedimentation–filtration–disinfection system [36–49], then, advanced oxidation using a hydrogen peroxide/ozone combination [50–66]. The selection of these methods was based on effluent characterization data, which presents limitations for direct reuse [67,68] such as the water color caused by algae presence (270 UC Pt-Co), the total suspended solids (55 mg/L), the organic matter measured as BOD and COD (42 mg/L and 150 mg/L) and, fundamentally, the coliform bacteria level above $1 \times 10^3 \text{ MPN}/100 \text{ mL}$. This last parameter is common in most lagoon systems and restricts nearly all subsequent uses. Therefore, this study seeks to provide an initial assessment of the feasibility of treated effluent reuse, aiming to stimulate interest in this research area and offering alternatives for eco-efficient municipalities to consider in their management.

2. Methodology

The present study was conducted in the Sanitary Laboratory of the Faculty of Engineering at the University of Cuenca, from August 2022 to January 2023. The proposed treatments were applied to the effluent from the Ucubamba WWTP, which treats 95% of the Cuenca wastewater through stabilization ponds, with a surface area of 18.2 Ha and a mean flow rate of $1 \text{ m}^3/\text{s}$ [69]. This effluent is discharged into the Cuenca River. In Figure 1, the scheme of the procedure applied in the present study is shown.

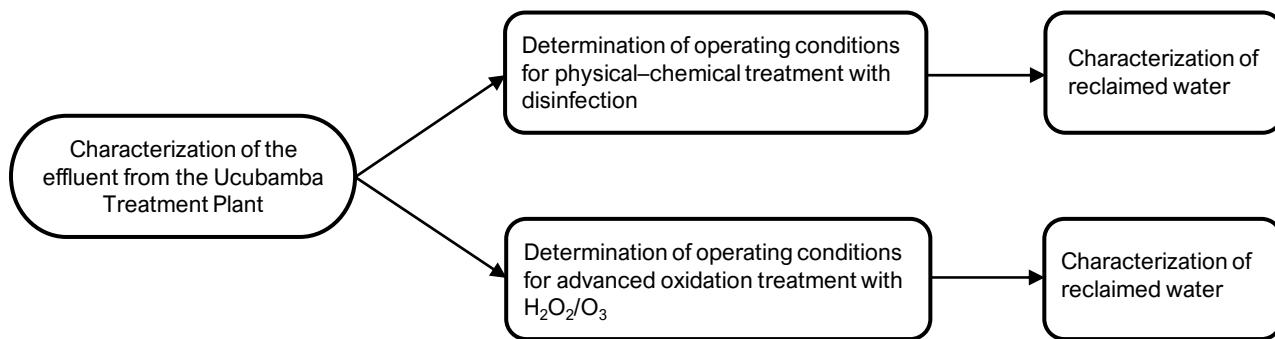


Figure 1. Outline of the procedure used.

2.1. Characterization of the Effluent from the Ucubamba WWTP

To characterize the Ucubamba WWTP effluent, a composite sample was prepared from 24 grab samples of 500 mL each, collected during a day of monitoring using an auto-sampler with refrigeration. The analytical methods used were those established in “Standard Methods for the Examination of Water and Wastewater, 23rd edition” [70] and the Mexican Norm NMX-AA-113-SCFI for helminth egg counting via microscopic observation [71].

2.2. Operating Conditions of the Physical–Chemical Treatment with Disinfection

The applied process consisted of five defined operational stages. The first was coagulation, wherein a jar-test apparatus with 6 jars of 2 L capacity was used with aluminum sulfate at 1% (*w/v*) as the coagulant, and hydrochloric acid 1 mol/L for the pH adjustment. The rapid mixing time was 1 min at 300 rpm. Then, flocculation was performed, which was optimized with the addition of the cationic polymer Praestol 650TR (slightly cationic) prepared at 0.05% [72]. Then, the sedimentation of the formed flocs occurred in a standard time of 20 min. Since no modifiable variables were identified, the sedimentation rate was not included in the statistical analysis. The next process was the filtration through a membrane filter with a pore size of 45 μm . The control parameters for the coagulation and flocculation included the color and turbidity of the filtered water, with which the corresponding removal percentage was calculated. Finally, disinfection was performed using calcium hypochlorite at 0.1% and using the jar-test apparatus. As a control parameter, the level of coliform bacteria was measured, expressed in MPN/100 mL [42,73–77].

The maximum and minimum values of the operating variables were set based on previous experiences, as indicated in Table 1.

Table 1. Values for experimental design of the physical–chemical process.

| Process | Variable | Minimum | Maximum | Reference |
|--------------|--------------------------|---------|---------|-----------|
| Coagulation | Coagulating dose (mg/L) | 30 | 100 | [78] |
| | pH | 6 | 8 | [79] |
| Flocculation | Flocculant dose (mg/L) | 0.0125 | 0.1 | [78] |
| | Stirring speed (rpm) | 20 | 80 | [80] |
| | Stirring time (min) | 10 | 35 | |
| Desinfection | Disinfectant dose (mg/L) | 1.5 | 5 | [81] |
| | Operation time (min) | 10 | 30 | |

2.3. Operating Conditions for Advanced Disinfection Treatment POA O_3/H_2O_2

For ozone dosing, an OEL/ozone brand generator with a capacity of 5 mg O_3 /min was used. The ozone concentration in the ozonized air was confirmed using the Standard Methods SM 2350 E technique [70]. The gasification of the samples was carried out in 500 mL screw-cap bottles equipped with a special cork to prevent losses. The operating variables are summarized in Table 2.

Table 2. Values for experimental design of AOPs.

| Process | Variable | Minimum | Maximum | Reference |
|---------------|--------------------------|---------|---------|-----------|
| POA Ozonation | Disinfectant dose (mg/L) | 50 | 150 | [82] |
| | Contact time (min) | 30 | 60 | |
| POA Peroxide | Disinfectant dose (mL/L) | 0.75 | 4.5 | [83] |
| | Contact time (min) | 30 | 60 | |

2.4. Characterization of Reclaimed Water

The data for the characterization of the reclaimed water were the average of ten repetitions of the proposed treatments in the study, with conditions established in the experimental design. Random samples were taken up to a total of ten processing runs and the removal calculation was based on the average value found [84–86].

2.5. Research Methodology—Statistical Analysis

The experimental design was based on the treatment stages, each with a set of dependent and independent variables. The independent variables were the coagulant dose, the flocculant dose, the disinfectant dose, the ozone dose, the hydrogen peroxide dose, the process times, the velocity gradients, and the pH. The dependent or response variables were turbidity, color, and coliforms.

The Design Expert 13v software uses a random matrix of experimental data for each proposed treatment stage with spaces for analyzing the response variables. To optimize the number of experiments, it summarized the variables involved in the experimental processes, which were based on previous experiences (see Tables 1 and 2). The experiments were conducted following the proposed order of the 2^k factorial design, as shown in Table 3, where K represents the number of independent variables involved in the process.

All the data obtained by the 2^k factorial design was analyzed via an Analysis of Variance (ANOVA), and for all the comparisons between the factor levels. The Tukey pos-hoc test was used with a 0.05 significance level. In general, for the graphs, the use of a profile plot was important and for the normality assumption test, the Shapiro–Wilk test was applied to the residuals of the model. Finally, for all the plots, tables and tests, the SPSS [87] was used.

Table 3. “Experiment Matrix for Full Factorial 2^k Design” [88].

| Experiments | X_1 | X_2 | X_3 | Outcomes |
|-------------|-------|-------|-------|----------|
| 1 | — | — | — | y_1 |
| 2 | + | — | — | y_2 |
| 3 | — | + | — | y_3 |
| 4 | + | + | — | y_4 |
| 5 | — | — | + | y_5 |
| 6 | + | — | + | y_6 |
| 7 | — | + | + | y_7 |
| 8 | + | + | + | y_8 |

2.6. Comparative Analysis of Compliance with Selected Reference Standards

Compliance with the legal framework that permits the reuse of reclaimed wastewater must be verified directly against the standards of each country. In the absence of Ecuadorian regulations, reference is made to the guidelines established by the EPA [89]. Additionally, Ecuadorian TULSMA (Ministerial Agreement 097-A Annex 1) [90] sets limits for various uses. However, specific values for recycled water are not defined. Nevertheless, the comparison is valid because if any treatment applied to an effluent meets the quality requirements for a certain use, then the reclaimed water is suitable for that secondary use.

3. Results and Discussion

In Table 4, the data on the characterization of the effluent is presented. Then, an analysis of the data obtained at each treatment stage, exploring the variables that improved the water quality was performed. Finally, the data on the characterization of the reclaimed water were presented and compared against the current regulations to define their potential reuse. To strengthen the analysis, all the results were compared with experiences from other investigations.

Table 4. Characterization of the Ucubamba WWTP effluent; average of 10 samples.

| Parameters | Ucubamba WWTP Effluent | Units |
|-------------------------------|------------------------|------------|
| Physical | | |
| Apparent Color | 270 | UC |
| Actual Color | 190 | UC |
| Turbidity | 27.71 | NTU |
| Sedimentable Suspended Solids | 1 | mg/L |
| Total Solids | 410 | mg/L |
| Total Fixed Solids | 249 | mg/L |
| Total Volatile Solids | 161 | mg/L |
| Total Suspended Solids | 55 | mg/L |
| Fixed Suspended Solids | 8 | mg/L |
| Volatile Suspended Solids | 47 | mg/L |
| Total Dissolved Solids | 355 | mg/L |
| Fixed Dissolved Solids | 241 | mg/L |
| Volatile Dissolved Solids | 114 | mg/L |
| Floating Material | Absence | |
| Chemical | | |
| pH | 8.2 | |
| Conductivity | 603 | us/cm |
| Bicarbonate | 190 | mg/L |
| Calcium | 42.72 | mg/L |
| Magnesium | 5.19 | mg/L |
| Chlorides | 41.2 | mg/L |
| Sulfates | 34.38 | mg/L |
| Iron | 0.884 | mg/L |
| Manganese | 0.375 | mg/L |
| Sodium | 4.5 | mg/L |
| Potassium | 3 | mg/L |
| Copper | 0.08 | mg/L |
| Aluminum | 0.019 | mg/L |
| Nickel | 0.54 | mg/L |
| Chromium | 0.223 | mg/L |
| Zinc | 0.63 | mg/L |
| Arsenic | 0.01 | mg/L |
| Fluorides | 1.2 | mg/L |
| Ammonium Nitrogen | 19.21 | mg/L |
| Organic Nitrogen | 4.21 | mg/L |
| Kjeldahl Nitrogen | 23.41 | mg/L |
| Nitrite Nitrogen | 0.017 | mg/L |
| Nitrate Nitrogen | 0.471 | mg/L |
| Inorganic Phosphorus | 1.52 | mg/L |
| Total Phosphorus | 3.88 | mg/L |
| Biochemical Oxygen Demand | 42 | mg/L |
| Chemical Oxygen Demand | 150 | mg/L |
| Hexane Soluble Substances | 8 | mg/L |
| Microbiological | | |
| Total Coliforms | 160,000 | NMP/100 mL |
| Fecal Coliforms | 95,000 | NMP/100 mL |
| Helminth Eggs | 6 | H/L |

3.1. Treatment of the Effluent from the Ucubamba WWTP via a Physical–Chemical Process

3.1.1. Coagulation

The variables considered were the coagulant dose and the pH. Five replicates were performed for each combination, giving a total of 20 experiments. Turbidity and color were the response variables. For flocculation, the standard test values, 45 rpm and 15 min, were used. For sedimentation, a time of 20 min was used. Finally, the samples were passed through the filter paper. The results of the percentage of turbidity and color removal obtained with each of the combinations of the coagulant dose (30 and 100 mg/L, respectively) and the pH (6 and 8, respectively) are presented in Table 5.

Table 5. Evaluation of % removal of turbidity and color, based on pH and coagulant dose (mg/L).

| Coagulant dose (mg/L) | 30 | | 30 | | 100 | | 100 | |
|-----------------------|---------|------|---------|------|---------|------|---------|------|
| pH | 6 | | 8 | | 6 | | 8 | |
| | Mean | SE | Mean | SE | Mean | SE | Mean | SE |
| % Turbidity removal | 78.40 b | 2.69 | 63.80 c | 2.20 | 89.80 a | 1.85 | 79.20 b | 2.65 |
| % Color removal | 67.20 b | 2.80 | 46.80 c | 2.82 | 86.60 a | 2.04 | 69.00 b | 5.03 |

Note: Different letters (a, b, c) indicate statistical significance ($p < 0.05$), according to the Bonferroni test.

There were statistical differences between the coagulant dosage (mg/L) and the pH level. Specifically, for both the turbidity and color removal percentages, a dosage of 100 mg/L and a pH of 6 yielded the highest averages ($p < 0.05$). The goal was always to achieve the lowest possible turbidity values, as demonstrated by [86,91], which report values similar to those obtained in the present study. Ref. [91] is highlighted, where the best results were achieved with a pH of 6 and a coagulant dose of 120 mg/L, slightly higher than the value obtained in the present work.

3.1.2. Flocculation

Variables considered are flocculant dosage (0.0125 and 0.10 mg/L), agitation speed (20 and 80 rpm), and flocculation time (10 and 35 min). The conditions were subjected to the design, performing five replicates for the two response variables proposed (% turbidity and color removal), obtaining a total of 40 experiments. The test was conducted using the variables that favored coagulation, i.e., 100 mg/L dosage and a pH of 6. For sedimentation, the standard test value of 20 min was used, followed by filtration through filter paper. The statistical analysis of the results is presented in Table 6.

Table 6. Evaluation of % turbidity and color removal, according to flocculant dosage (mg/L), speed (rpm), and time (minutes).

| Flocculant dose (mg/L) | 0.0125 | | 0.0125 | | 0.0125 | | 0.1 | | 0.1 | | 0.1 | |
|------------------------|--------|------|--------|------|--------|------|--------|------|--------|------|--------|------|
| Stirring speed (rpm) | 20 | 20 | 80 | 80 | 20 | 20 | 80 | 80 | 20 | 20 | 80 | 80 |
| Stirring time (min) | 10 | 35 | 10 | 35 | 10 | 35 | 10 | 35 | 10 | 35 | 10 | 35 |
| | Mean | SE |
| % Turbidity removal | 66.3 a | 2.93 | 91.1 b | 1.17 | 70.4 a | 1.68 | 95.3 b | 0.55 | 65.8 a | 3.29 | 91.7 b | 0.45 |
| % Color removal | 79.7 a | 0.41 | 79.5 a | 0.47 | 83.7 b | 0.41 | 84.1 b | 0.45 | 80.3 a | 0.45 | 80 a | 0.42 |

Note: Different letters (a, b) indicate statistical significance ($p < 0.05$) according to the Bonferroni test.

Statistical differences were also determined between the flocculant dosage (mg/L), the speed (rpm), and the time (minutes). For the turbidity removal percentage, all the averages related to the 35 min time showed statistical significance compared to the 10 min time ($p < 0.05$). On the other hand, for color removal percentage, combinations using a speed of 80 rpm statistically determined the highest removal averages ($p < 0.05$). This may indicate that for turbidity removal, neither the flocculant dosage nor the speed gradient was influential; only the time was, with better results at 35 min. This is obviously because

a longer time allows for greater particle aggregation and thus higher turbidity removal. In the case of color, neither dosage nor time were highly influential. However, there was the relationship of the velocity gradient with a higher gradient leading to greater color removal. This dosage might be somewhat important, and time had almost no influence. The influence of the velocity gradient might be due to the nature of the color since it required “force for the disruption of colloids”, possibly indicating that coagulation continued.

Some previous research concludes that successful results in the flocculation of wastewater are achieved with high agitation speeds and contact times, regardless of the flocculant dosage added [57,92,93]. Additionally, the experience developed by [94] revealed that the flocculant dosage positively influenced the physical-chemical treatment of wastewater, as observed in some experiments in this work. Ref. [95] also reached this conclusion, further indicating that a longer flocculation time results in a floc with better sedimentation characteristics.

3.1.3. Disinfection

The variables considered include disinfectant dose (1.5 and 5 mg/L) and contact time (10 and 30 min). Five replicates were performed with a total of 20 experiments. Coliform removal was determined as the response variable. The test was conducted on filtered water after passing through all the previous stages. The statistical analysis of the results is presented in Table 7.

Table 7. Evaluation of coliforms (MPN/100 mL), according to disinfectant dosage (mg/L) and time (minutes).

| Disinfectant dose (mg/L) | 1.5 | 1.5 | 5 | 5 | | | | |
|--------------------------|---------|------|---------|------|---------|------|---------|------|
| Time (min) | 10 | 30 | 10 | 30 | | | | |
| | Mean | SE | Mean | SE | Mean | SE | | |
| Coliforms (NMP/100 mL) | 37.00 a | 5.87 | 37.67 a | 3.36 | 99.90 b | 0.05 | 98.10 b | 1.89 |

Note: Different letters (a, b) indicate statistical significance ($p < 0.05$), according to the Bonferroni test.

Statistical differences were found between the disinfectant levels and time. For the coliforms (MPN/100 mL) variable, all the averages related to the disinfectant dose of 5 mg/L, regardless of time, determined the highest statistical averages ($p < 0.05$). Statistics show that the optimal dosage is 5 mg/L of chlorine, and the contact time does not influence the process. Significant coliform removals were achieved with both 10 and 30 min. However, a detailed analysis of the data shows that total removal (100%) was achieved only at 30 min. The percentage of coliforms not removed at 10 min still represents very high figures, especially for potential reuse. 5 mg/L might be seen as an excessive dose. A new experimental run with a dosage range higher than 1.5 but less than 5 mg/L, would highlight the influence of time.

The technological proposal by [96] for wastewater disinfection concludes that both the chlorine dose and contact time are critical for the removal of coliforms from the effluent. A dose of 2 ppm of chlorine and a minimum time of 30 min were effective. Current research has established that disinfection is defined by dosage. A dosage of 6 ppm (similar to this study) has been proven to be successful. However, most studies emphasize that a disinfection process is successful if the preceding stages, such as coagulation, flocculation, sedimentation, and filtration, are properly defined [97–99].

3.2. Treatment of the Ucubamba WWTP Effluent Using Advanced Oxidation

For the present study, the experimentation was carried out in two stages to analyze the influence of the oxidizing agents individually and subject each of them to the respective analysis.

3.2.1. Ozonation

The variables considered were oxidant dosage (50 and 150 mg/L) and contact time (30 and 60 min). Five experiment replicates were performed, giving a total of 20 experiments.

The percentages of the coliform, color, and turbidity removal from the treated water were measured to establish the treatment efficiency. The statistical analyses of the results are presented in Tables 8 and 9. Statistical differences were found between the ozone dose (mg/L) and the contact time (minutes). For the coliforms (MPN/100 mL), all the averages related to the ozone level of 150 mg/L, where time did not matter, statistically determined the highest averages ($p < 0.05$). However, the literature shows that contact time also has an influence, though to a lesser extent [100]. Similarly, some studies establish that the dose is more important than the time for bacterial removal, since for doses lower than the optimum established by experimentation, the time factor has no influence regardless of its value, as demonstrated in this research [101,102].

Table 8. Evaluation of % of removal of coliforms (MPN/100 mL), according to ozone dose (mg/L) and time (minutes).

| Oxidant Dose (mg/L) | 50 | 50 | 150 | 150 | | | | |
|------------------------|---------|------|---------|------|---------|------|---------|------|
| Time (min) | 30 | 60 | 30 | 60 | | | | |
| | Mean | SE | Mean | SE | Mean | SE | | |
| Coliforms (NMP/100 mL) | 95.65 a | 0.16 | 96.74 a | 0.55 | 98.94 b | 0.26 | 99.20 b | 0.26 |

Note: Different letters (a, b) indicated statistical significance ($p < 0.05$), according to the Bonferroni Test.

Table 9. Evaluation of % turbidity and % color, according to ozone dose (mg/L) and time (minutes).

| Ozone dose (mg/L) | 50 | 50 | 150 | 150 | | | | |
|-------------------|--------|------|--------|------|---------|------|---------|------|
| Time (min) | 30 | 60 | 30 | 60 | | | | |
| | Mean | SE | Mean | SE | Mean | SE | | |
| % Turbidity | 5.97 a | 1.30 | 8.72 a | 1.39 | 12.89 a | 1.72 | 27.91 b | 4.39 |
| % Color | 5.45 a | 1.04 | 7.47 a | 1.87 | 10.46 a | 0.89 | 17.59 b | 2.35 |

Note: Different letters (a, b) indicate statistical significance ($p < 0.05$), according to the Bonferroni test.

Although color removal by ozonation appears promising for highly colored waters [103–105], it is inefficient for effluents like the ones studied. These effluents contain small amounts of organic matter and dissolved minerals that, when in contact with the oxidant, generated new color compounds, as stated by [106,107]. Ozonation is efficient, but does not meet the discharge limits for organic matter, pH, color, and turbidity.

3.2.2. Hydrogen Peroxide

The variables considered include the dose of the oxidizing agent (0.75 and 4.5 mL/L) and the contact time (30 and 6 min). The experiments with each parameter were repeated five times giving a total of 20 experiments. The percentage of coliform removal and the percentage of the color and turbidity removal of the treated water were considered as response variables. The results are presented in Tables 10 and 11. A statistical difference was noted between the combinations of the H_2O_2 levels (mL/L) and the contact time (min). For the coliform level (MPN/100 mL), all the H_2O_2 averages, except for the contact time of 30 min, showed the highest statistical averages, with 100% or close to it ($p < 0.05$). However, a more detailed analysis of the data showed the efficiency of the highest dose at any time. Therefore, this variable would be crucial when conducting a new run with doses greater than 0.75 but less than 4.5 mL/L. It is possible that 4.5 mL/L is an excessive dose and may be detrimental, as it may trigger competitive reactions that produce an inhibitory effect on the degradation of COD due to the undesirable consumption of $HO\bullet$ radicals [67].

The research by [106] also demonstrated that the dose and contact time of peroxide with wastewater directly influenced the removal of coliforms. However, Ref. [87] showed that peroxide is inefficient in removing color, as in the results in the present study.

Table 10. Evaluation of coliforms (MPN/100 mL) according to H₂O₂ dose (mL/L) and contact time (minutes).

| | | | | |
|-----------------------------------------------|-------|------|-------|------|
| Oxidant: H ₂ O ₂ (mL/L) | 0.75 | 0.75 | 4.5 | 1.5 |
| Time (min) | 30 | 60 | 30 | 60 |
| | Mean | SE | Mean | SE |
| Coliforms | 100 b | 0.00 | 100 b | 0.00 |

Note: Different letters (a, b) indicate statistical significance ($p < 0.05$), according to the Bonferroni test.

Table 11. Evaluation of % turbidity and % color according to H₂O₂ dose (mL/L) and contact time (minutes).

| | | | | |
|----------------------------------------------|---------|------|---------|------|
| Oxidant H ₂ O ₂ (mL/L) | 0.75 | 0.75 | 4.5 | 4.5 |
| Time (min) | 30 | 60 | 30 | 60 |
| | Mean | SE | Mean | SE |
| % Turbidez | 13.77 a | 2.03 | 8.16 a | 1.56 |
| % de Color | 8.83 a | 0.64 | 13.11 a | 1.36 |

Note: Different letters (a, b) indicate statistical significance ($p < 0.05$), according to the Bonferroni test.

Ref. [83]’s experience with the treatment of effluent from the urban wastewater plant in Pinares, Colombia, showed that peroxide is inefficient in color removal, as in this study. However, coliform removal is effective with any dose within this tested range (from 0.3 to 8 mL/L). These values are comparable to the influential value of this research. Ref. [83] also noted that time does not interfere with coliform removal, questioning the importance of application time in defining the combined process.

Once individual experimentation was completed, the oxidative processes were combined and applied simultaneously to the same sample: 4.5 mL/L of hydrogen peroxide, plus 150 mg/L of ozone, with a contact time of 30 min for characterization; the experimental design did not consider time as a determining variable.

3.3. Comparison with Previous Studies

The results obtained in the present study were compared with two studies that address wastewater treatment and reuse in different contexts, showing both the advances and specific challenges. The present study evaluates the effluent from the Cuenca, Ecuador WWTP using physical-chemical and advanced oxidation treatments (H₂O₂/O₃), finding that neither of these methods alone meets the reference quality standards required for urban, recreational, and agricultural reuse, highlighting the need for a regulatory framework in Ecuador. In contrast, ref. [18] (study on the food industry) demonstrates high efficiency in contaminant reduction through technologies like reverse osmosis and anaerobic-aerobic treatment, supported by strict European regulations that facilitate reuse in industrial contexts. Meanwhile, ref. [19] discusses the reuse of treated municipal wastewater, emphasizing the challenge of managing the concentrated waste generated by reverse osmosis (RO), which contains high levels of dissolved solids and microparticles, necessitating specific concentrate management strategies. The main idea obtained from this comparison analysis is that, although approaches and technologies can vary, all underscore the importance of regulatory frameworks and appropriate technological solutions to ensure treated water quality and enable its safe and sustainable reuse across different sectors.

A relevant point of the present study, compared to the others, lies in its specific focus on effluent reuse in a local context (Cuenca, Ecuador), where regulatory frameworks and water reuse policies are limited or nonexistent. Additionally, it explores accessible and applicable alternatives in a setting where resources and infrastructure may be more limited. In addition, this study offers a less complex solution in terms of technological investment by applying advanced oxidation (H₂O₂/O₃) and physical-chemical methods that could be more feasible in similar Latin American settings. Furthermore, this research contributes to the development of a framework to establish water reuse in Ecuador, providing local data that could support policy formulation in the country for safe and efficient treated water reuse.

3.4. Comparison with Regulations

The comparison analysis is presented in Tables 12–14.

Table 12. Comparative analysis for water required for unrestricted urban reuse EPA.

| Parameters | Units | Ucubamba | Regenerated Water | Regenerated Water | Water Quality Required for Unrestricted Urban Reuse | Complies | |
|------------------------|------------|---------------|-------------------------|----------------------------------------------------------|-----------------------------------------------------|---------------|------------------------------------------------|
| | | WWTP Effluent | Treatment FQ + CHLORINE | Treatment O ₃ + H ₂ O ₂ | | FQ + CHLORINE | O ₃ + H ₂ O ₂ |
| Physical | | | | | | | |
| Turbidity | NTU | 27.71 | 1.55 | 25.6 | <2 | YES | NO |
| Total dissolved solids | mg/L | 355 | 360 | 380 | 200–500 | YES | YES |
| Floating material | | Absence | Absence | Absence | Absence | YES | YES |
| Chemical | | | | | | | |
| Ph | | 8.2 | 6 | 8.8 | 6–9 | YES | YES |
| Iron | mg/L | 0.884 | 0.312 | 0.212 | 5.0 | YES | YES |
| Manganese | mg/L | 0.375 | 0.105 | 0.205 | 0.2 | YES | YES |
| Copper | mg/L | 0.08 | 0.03 | 0.01 | 0.2 | YES | YES |
| Aluminum | mg/L | 0.019 | 0.0 | 0.0 | 5 | YES | YES |
| Nickel | mg/L | 0.54 | 0.20 | 0.12 | 0.2 | YES | YES |
| Chrome | mg/L | 0.223 | 0.154 | 0.011 | 0.1 | YES | YES |
| Zinc | mg/L | 0.63 | 0.15 | 0.16 | 2.0 | YES | YES |
| Arsenic | mg/L | 0.01 | 0.0 | 0.0 | 0.1 | YES | YES |
| Fluorides | mg/L | 1.2 | 0.07 | 0.03 | 1.0 | YES | YES |
| Bod ₅ | mg/L | 42 | 39.8 | 9.7 | <10 | NO | YES |
| Oils and fats | mg/L | 8 | 2.0 | 1.0 | Absence | YES | YES |
| Microbiological | | | | | | | |
| Fecal coliforms | NMP/100 mL | 95,000 | <1.8 | <1.8 | Not detectable | YES | YES |
| Helminth eggs | H/L | 6 | Absence | Absence | Absence | YES | YES |

Table 13. Comparative analysis of water for recreational purposes by primary contact TULSMA.

| Parameters | Units | Ucubamba | Regenerated Water | Regenerated Water | Water Quality Required for Unrestricted Urban Reuse | Complies | |
|------------------------|------------|---------------|-------------------------|----------------------------------------------------------|-----------------------------------------------------|---------------|------------------------------------------------|
| | | WWTP Effluent | Treatment FQ + CHLORINE | Treatment O ₃ + H ₂ O ₂ | | FQ + CHLORINE | O ₃ + H ₂ O ₂ |
| Physical | | | | | | | |
| Floating material | | Absence | Absence | Absence | Absence | YES | YES |
| Chemical | | | | | | | |
| Ph | | 8.2 | 6 | 8.8 | 6.5–8.3 | YES | NO |
| Ammoniacal nitrogen | mg/L | 19.21 | 19.1 | 7.2 | | NO | YES |
| Organic nitrogen | mg/L | 4.21 | 4.41 | 1.2 | | NO | YES |
| Kjeldahl nitrogen | mg/L | 23.41 | 23.54 | 8.4 | RELATION N:P 15:1 | NO | YES |
| Nitrite nitrogen | mg/L | 0.017 | 0.011 | 0.009 | | NO | YES |
| Nitrate nitrogen | mg/L | 0.471 | 0.101 | 0.45 | | NO | YES |
| Inorganic phosphorus | mg/L | 1.52 | 0.505 | 0.433 | | NO | YES |
| Total phosphorus | mg/L | 3.88 | 2.31 | 1.1 | | NO | YES |
| Microbiological | | | | | | | |
| Total coliforms | NMP/100 mL | 160,000 | <1.8 | <1.8 | 2000 | YES | YES |
| Fecal coliforms | NMP/100 mL | 95,000 | <1.8 | <1.8 | 200 | YES | YES |
| Helminth eggs | H/L | 6 | Absence | Absence | Absence | YES | YES |

Table 14. Comparative analysis of water for agricultural use plus degree of restriction in irrigation TULSMA.

| Parameters | Units | Ucubamba WWTP Effluent | Regenerated Water Treatment FQ + CHLORINE | Regenerated Water Treatment O ₃ + H ₂ O ₂ | Water Quality Required for Unrestricted Urban Reuse | Complies | |
|------------------------|------------|------------------------|-------------------------------------------|----------------------------------------------------------------------------|-----------------------------------------------------|---------------|------------------------------------------------|
| | | | | | | FQ + CHLORINE | O ₃ + H ₂ O ₂ |
| Total dissolved solids | mg/L | 355 | 360 | 380 | 450/450–2000/2000 | NONE | NONE |
| Visible matter | | Absence | Absence | Absence | Absence | YES | YES |
| Ph | | 8.2 | 6 | 8.8 | 6–9/6.5–8.4 | YES/LIGHT | YES/LIGHT |
| Conductivity | us/cm | 603 | 621 | 581 | 700/700–3000/3000 | NONE | NONE |
| Bicarbonate | meq/L | 3.76 | 0.15 | 0.09 | 1.5/1.5–8.0/8.0 | NONE | NONE |
| Sodium | meq/L | 0.95 | 0.43 | 0.22 | 3/3–9/9 | NONE | NONE |
| Calcium | meq/L | 2.136 | 1.6 | 1.0 | RAS = 0–3 y CE = 0.7/0.7–0.2 <0.2 | NONE | NONE |
| Magnesium | meq/L | 0.63 | 0.18 | 0.07 | | | |
| Ras | | 0.81 | 0.45 | 0.30 | | | |
| Chlorides | mg/L | 41.2 | 45.1 | 9.5 | 4/4–10/10 | SEVERE | MODERATE |
| Iron | mg/L | 0.884 | 0.312 | 0.212 | 5.0 | YES | YES |
| Manganese | mg/L | 0.375 | 0.105 | 0.20 | 0.2 | YES | YES |
| Copper | mg/L | 0.08 | 0.03 | 0.01 | 0.2 | YES | YES |
| Aluminum | mg/L | 0.019 | 0.0 | 0.0 | 5 | YES | YES |
| Nickel | mg/L | 0.54 | 0.20 | 0.12 | 0.2 | YES | YES |
| Chromium | mg/L | 0.223 | 0.154 | 0.011 | 0.1 | YES | YES |
| Zinc | mg/L | 0.63 | 0.15 | 0.16 | 2.0 | YES | YES |
| Arsenic | mg/L | 0.01 | 0.0 | 0.0 | 0.1 | YES | YES |
| Fluorides | mg/L | 1.2 | 0.07 | 0.03 | 1.0 | YES | YES |
| Nitrogen from nitrates | mg/L | 0.471 | 0.101 | 0.45 | 5/5–30/30 | NONE | NONE |
| Oils and fats | mg/L | 8 | 2.0 | 1.0 | Absence | YES | YES |
| Fecal coliforms | NMP/100 mL | 95,000 | <1.8 | <1.8 | 1000 | YES | YES |
| Helminth eggs | H/L | 6 | Absence | Absence | Absence | YES | YES |

3.5. Reuse Possibilities

3.5.1. Water for Unrestricted Urban Reuse

Table 12 shows that BOD₅ is the limiting parameter in physical–chemical treatment. This aspect would restrict this type of reuse, as it is a direct indicator of quality. This reveals that oxygen is still required to decompose biologically degradable organic matter, which will continue to decompose during reuse, eliminating unknown degradation compounds. As mentioned by [107], biological treatments are the ones that remove this contaminant. Although the consulted literature does not specify a particular risk in using water with high BOD₅, this restriction is because organic matter can increase soil acidity, facilitating contaminant absorption processes.

In advanced oxidation treatment, on the other hand, turbidity is the questioned parameter. A whitish turbidity is produced when oxidants are added due to the formation of insoluble compounds with low sedimentation rates, a condition that persists even after two or three days of the test, leaving a clear supernatant and a precipitate at the bottom. However, from a practical standpoint, such a prolonged contact time cannot be established. Therefore, subsequent filtration may be necessary. Besides the esthetic aspect, turbidity is very important because it has a sanitary meaning. It causes user rejection and constitutes a potential risk due to the growth of pathogenic microorganisms that hide in turbidity particles. They can continue to consume disinfectant agents until their total exhaustion, leading the water into conditions of vulnerability, as it may re-contaminate [108–110]. According to Mexican Regulation NOM-003 SEMARN AT-1997 [111], in New Mexico,

Arizona, and California, which only establish two parameters of interest (fecal coliforms and helminth eggs), the quality for this reuse is met [112,113]

3.5.2. Water for Recreational Purposes Through Primary Contact

It is evident from Table 13 that physical–chemical treatment does not allow this type of reuse. Nitrogen and phosphorus compounds exceed the limits set by MAAE [90], which are attributed to the major problem of the eutrophication of water bodies as stated by [114]. The treatment failure to meet the required levels is due to particle size. Therefore, another procedure will be necessary, such as nanofiltration, ultrafiltration, or precipitation, which are no longer applicable due to their high costs [115–117]. However, the removal percentage achieved is significant, and the remaining fraction is probably organic in nature, contributing to the residual BOD.

Advanced oxidation treatment shows pH as the only objection. A value above 8.3 could generate precipitates, affecting use. Although several authors approve a wider range of 6 to 9 for recreational water, as stated by [118]. According to EPA regulations, it does not meet the quality requirements for either primary or secondary contact, primarily due to turbidity and BOD_5 values [119].

3.5.3. Water for Agricultural Use + Degree of Restriction in Irrigation

Most studies on the reuse of regenerated wastewater aim to use these domestic effluents for agricultural tasks, mainly irrigation and, so far, achieving this goal may have seemed impossible. In both treatments, as shown in Table 14, the limiting factor is the chloride content, restricted for causing plant chlorosis. These anions accumulate in plant leaves, hinder development due to poor photosynthesis, and may even cause plant death [120]. Finally, more recent research like that by [121] considers the reuse of regenerated wastewater as a direct threat to food security if “emerging contaminants” are not included in its characterization, which increase their presence each year. Another concern is “emerging pathogens” which are the main restriction for water reuse [122,123].

According to EPA regulations [89], agricultural use is also not possible due to the presence of organic matter measured as BOD_5 and turbidity. However, when treated wastewater is reused for crop irrigation for human consumption, the main goal should be the removal of pathogenic microorganisms to protect the health of producers and consumers. The removal of organic matter containing valuable nutrients for agriculture is neither necessary nor desirable [124–126].

Finally, comparing the results of this study with Indian Standards IS and Spanish Legislation in three possible reuses, urban, industrial and recreational, the same limitations described before are detected. The physical–chemical parameters are partially met, but the microbiological parameters are fully met. This highlights the limited scope of the procedures applied [18,127–129].

The present study of the treatability of a lagoon effluent for reuse purposes by two procedures stands out as an achievement of the research of the conventional and/or “traditional” one, which allows optimizing the design parameters for the treatment units and the “novel” advanced oxidation system POA, by combining two oxidizing agents. There are no previous studies with this objective and a path of special interest is opened for the reuse of wastewater in general. This study discusses the benefits and limitations of each procedure based on the results obtained. Therefore, the information obtained here fills a gap in knowledge at the local level and constitutes the baseline for future research on the topic of reuse, which is a very current interest due to the growing scarcity of the resource.

4. Conclusions and Recommendations

4.1. Conclusions

Both of the treatment methods analyzed, the conventional physical–chemical process and advanced oxidation, proved effective in improving certain quality parameters of the effluent from Cuenca’s WWTP. The physical–chemical treatment including coagulation,

flocculation, sedimentation, filtration, and disinfection achieved significant reductions in suspended solids and color but had limitations to achieving the required standards for some reuse applications, particularly in reducing organic matter (BOD) and nutrients. On the other hand, the advanced oxidation process using hydrogen peroxide and ozone was highly effective in microbiological disinfection. However, it was not effective in reducing turbidity and controlling pH, which are critical for certain recreational and agricultural applications. The findings indicate that the treated effluent from both methods could be suitable for certain unrestricted urban uses and agricultural irrigation under specific conditions. However, additional optimization in reducing turbidity and organic matter would be necessary for applications involving recreational contact or the irrigation of crops for human consumption to meet stricter quality standards.

This research highlights the lack of specific regulations in Ecuador for the reuse of treated wastewater, representing a significant barrier to the implementation of sustainable water reuse practices. Establishing a regulatory framework would allow for the setting of quality standards for various reuse applications and would maximize the environmental and economic benefits of water management in the country.

This study provides a valuable foundation for future research focused on optimizing advanced effluent treatment processes. Developing technologies adapted to local contexts and continually improving these processes will expand the possibilities for wastewater reuse, promoting more efficient and sustainable water management in Ecuador and other regions facing similar challenges.

4.2. Recommendations

A more detailed analysis of the potential for wastewater reuse is needed, considering not only international reference regulations but also local conditions of availability and use. This would facilitate the formulation of regulations that respond to the specific needs of the local context and enable extreme situations of water scarcity to be addressed with adapted and effective solutions.

From the agricultural production perspective, the simultaneous availability of water and nutrients in the effluents of treatment plants represents a valuable resource that must be exploited. These effluents concentrate both elements optimally for use in the generation of agricultural products, helping to reduce input costs and promoting sustainable agricultural practices [130,131].

Regulations for water reuse must be effective and include incentives that encourage its implementation. Considering treated wastewater as a public good allows for the creation of a management model that, in addition to requiring financial investment from the public sector, promotes restrictions on the use of potable water and encourages its replacement with treated water in various activities. This strategy would help institutionalize reuse as a common and sustainable practice in multiple sectors.

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