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Optimization and evaluation of the process variable's effect on color and turbidity removal from coffee processing wastewater: Using a photoelectrochemical oxidation process

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Abstract

Background: Coffee is the foundation of Ethiopia's economy, but the wastewater generated by coffee processing cannot be properly treated, therefore, causing various environmental problems.

Methods: In this research, electrochemical oxidation(ECO) and photo electrochemical oxidation(PECO) are combined with UV and hydrogen peroxide (UV/H_2O_2) to reduce organic compounds in coffee processing effluent with color and turbidity effect. The effects of various experimental parameters such as hydrogen solubility (pH), sodium chloride and calcium chloride (NaCl and $CaCl_2$) concentrations, current and electrolysis time, and H_2O_2 dose were investigated.

Results: The results were investigated and analyzed using response surface methodology (RSM) and Microsoft Excel. The color (99.6%) and turbidity (99.4%) were removed by combining ECO with UV/ H_2O_2, which produces high amounts of hydroxyl ions (OH^-), oxidizes large amounts of contaminants, and increases efficiency. These results were obtained at pH 7, current of 0.40 AMP, and 1.5 g $CaCl_2$ after 40 minutes of electrolysis. The operating factors were pH, electrolyte dosage, time, current and H_2O_2, which plays a major role in increasing the removal capacity of photoelectrochemical oxidation for coffee processing waste water treatment. $CaCl_2$ was once more wonderful in the removal of organic compounds from coffee processing effluents.

Conclusion: Therefore, the introduction of this ultraviolet light is a powerful oxidant with H_2O_2, which can improve pollution control. An analysis of variance (ANOVA) with a 95% confidence interval can be used to determine the magnitude of the independent variable.

Keywords: Coffee, Wastewater, Water purification, Ethiopia

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Introduction

Water pollutants are one of the largest troubles in our civilization today. Pesticides utilized in acid rain, sewage, agriculture, commercial methods, industrial and home sewage, etc. circulate rivers (1). This is a chief hassle in each evolved nation because of the quantity and form of pollution produced, and in growing nations, because of insufficient water purification and wastewater recycling technology (2). Treatment structures may be primarily based totally on conventional techniques, which include physical, organic, and chemical approaches (3). In addition to standard strategies, choosing remedy strategies is primarily based totally on the self-cleaning ability of the stream. The use of an increasing number of applied superior technology includes membrane separation methods, opposite osmosis, ultrafiltration, and superior oxidation methods (4). Wastewater remedy is a vital part of commercial manufacturing operations within the manufacturing sector (5). A huge sort of additives is frequently infected (6). Appropriate treatment is required to discharge this wastewater into the frame of water. Failure to achieve this goal will have a terrible effect on the surroundings and human life (7). The use of poisonous insecticides to manipulate pest troubles has come to be a not unusual place exercise across the world. Pesticides also are observed in air, food, soil, water, or even breast milk (8). Recently, electrochemical advanced oxidation processes (AOPs) have been developed as a promising technology for the removal of contaminants (9). The research of electrochemical oxidation for wastewater remedies dates once more to the nineteenth century (10). The electrochemical

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method has been successfully tested in various industrial wastewater treatment plants (11). For more than 30 years, studies have investigated the oxidation performance and electrochemical balance of electrode materials, elements affecting manner performance, and the mechanism and kinetics of contaminant decomposition (12). The manner of electrochemical oxidation is known as one of the most useful strategies for decomposing contaminants in fiber effluents, landfill leachates, simulated effluents, olive mill effluents, paper mill effluents, and commercial paint effluents (13). The most common activation techniques are alkaline activation, electron transfer between transition metal ions, heat activation, and radiation (UV, visible light) (14-18).

The addition of hydrogen peroxide (H_2O_2) to the electrochemical oxidation (ECO) and photo electrochemical oxidation (PECO) barely progressed the performance of pollutant elimination (19). Many superior oxidation methods had been formerly achieved by the use of electrochemical oxidation; however, these methods are achieved in aggregate with ECO (electrochemical oxidation with ultraviolet and hydrogen peroxide (UV/H_2O_2). The coffee remedy could boost the performance of elimination from wastewater and different wastewater (20). The electrochemical remedy approach is simple to apply, can be done at a low value and in a quick time. In addition, electrochemistry is normally easy and clean, rather cost-effective, and eco-friendly than conventional chemical AOPs (21). In addition, research carried out up to this point has related to electrochemical wastewater remedy or UV/H_2O_2 for untreated wastewater (22). Treatment with H_2O_2 is organic and reduces toxicity (23). Based on preceding findings, this examination mixed each strategy to enhance the performance of waste dealt with water from the espresso processing enterprise (24). Coupling generation chemical oxidation (CO)/UV/H_2O_2 may be utilized in quite a few methods as a selective separation generation and/or decomposition manner, permitting chemical-loose wastewater remedy, and as a result, making contributions notably to this challenge. In addition, electrochemical methods have currently skilled a tremendous boom in new developments (25). Second, many research is being performed on the cafeteria, commercial, and pharmaceutical wastewater, alternatively, this research was conducted on espresso-processed wastewater with structured variables consisting of nutritional vitamins and chemical oxygen demand (COD) (25).

Based on different literature reviews, the performance of electrochemical oxidation and UV/H_2O_2 methods was used for the removal of contaminants from wastewater. However, in this research, the maximum amount of turbidity and color was removed by a combination of ECO with UV/H_2O_2, which produces high amounts of hydroxyl ions (OH^-), which oxidize large amounts of contaminants and increase efficiency. It additionally contributes notably to fixing troubles in this area and might be useful after publication.

Materials and Methods

Materials and chemicals used

The equipment's used for this study were beaker, magnetic stirrer (model RHB2), desiccator, Drying oven, filter paper, COD reactor (Hatch 45600-02), COD kit, electrode (Al-Al), DC-power supply (WYJ-o-15V/5A), spectrophotometer (model 6700), vacuum pump, multimeter, Heaters, conical flasks, standard flasks, Erlenmeyer flasks, measuring cylinder, plastic bottles, burettes, thermometer, funnel, suction flask, wash bottle, porcelain dish, weighing balance (model Pw 124), filtration apparatus, graduated cylinder, turbidity meter (Wag WT3020), pH meter (pH 3310), conductivity meter (Cond 3110), and ultraviolet (UV) lamp (PUV-1022 Heraeus).

Study design and sample size

This laboratory-based study (experimental) was conducted at Jimma University, with the focus on the evaluation of the performance of the electrooxidation of integrated UV. The samples were collected at various time intervals using simple sampling method to obtain the best representation of coffee processing effluent. In addition, depending on the number of experiments, approximately 156 L of coffee treatment wastewater was collected for investigation, as shown in Figure S1-S4. This sample quantity was obtained as a function of the number of analyses (N), according to equation 3. The test was run 156 times, which corresponds to the sample size. Due to the character of the wastewater sampled, a composite sampling method was used in this study. Wastewater was taken from an espresso remedy plant in Jimma city. In the study period, approximately 200 L of wastewater samples were collected. The cans were soaked in 10% HCl for 24 hours, then, washed very well and rinsed with distilled water. The lab guide serves as a manual for pattern transportation. The samples were prepared to analyze the performance of UV/H_2O_2 and electrochemical oxidation processes individually or in combination. The samples were stored by observing the maximum storage time to the start of the laboratory measurement procedure for each parameter. The maximum residence time was observed and implemented based on the 2004 WHO/UNEP standard protocol and laboratory water quality manuals.

Experimental setup

The system consists of electrochemical oxidation, UV/H_2O_2, and an integrated UV/H_2O_2 oxidation process. The experimental device includes an electrochemical reactor and a UV lamp. Wastewater was analyzed for pH, EC, color, turbidity, and wastewater temperature. The working electrode, reference electrode, counter electrode Al electrode, and pipette (for blow) were inserted into the hole of the rubber stopper, as shown in Figure 1.

Method of data analysis and presentation

After data collection, the collected data were analyzed and interpreted using Microsoft Excel Office and response surface methodology (RSM) software. The optimization and evaluation were performed using qualitative and quantitative statistics evaluation technique. All outcomes were compared with the limits presented by the WHO in 2004. Process overall performance changed into evaluated primarily based on the reaction of color and haze elimination performance to electricity consumption. Color and turbidity elimination quotes were calculated primarily according to on equations 1 and 2.

Percentage color turbidity removal

$$\%\ \text{Color removal} = \frac{Abs_i - Abs_t}{Abs_i} * 100 \quad (1)$$

Where, Abs_i and Abs_t are the absorbance of samples for the corresponding wavelength (λ = 420 nm) at the initial (t = 0) and at any reaction time (t), respectively.

$$\%\ \text{Turbidity removal} = \frac{Tur_i - Tur_t}{Tur_i} * 100 \quad (2)$$

Where, Tur_i and Tur_t are the turbidity of the sample (NTU) at initial (t = 0) and at any reaction time (t), respectively. In this study, pH, turbidity, color, electrical conductivity, and temperature were measured using pH meter, nephelometer, spectrophotometer, conductivity meter, and thermometer, respectively.

Experimental design and statistical analysis

The RSM is a sequence of experimental techniques for locating the optimum running conditions. This usually involves conducting multiple experiments and using the results of one experiment to guide how to proceed (26). In this study, using a photoelectrochemical oxidation process was done at pH of 5-9, electrolyte concentration of 0.5-2.5 g NaCl/$CaCl_2$, current of 0.2-0, 6 A, and response time of 20-50 minutes. Therefore, as shown in Tables 1 and 2, these entries show the number of experiments run, pH range, time, current, and electrolytes generated using RSM software.

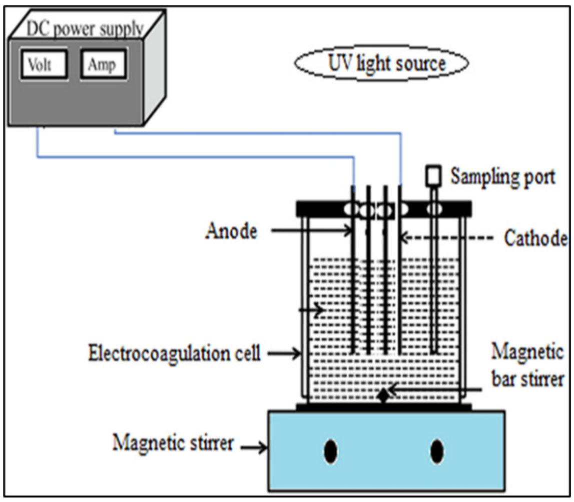

Figure 1. Experimental set up for photoelectrochemical oxidation

The parameters were taken into account to determine the removal efficiency of color and haze associated with energy consumption. The order of the experiments was randomized. In the laboratory, a total of 156 experiments using a combination of aluminum and aluminum electrodes (60 for electrochemical oxidation with NaCl/$CaCl_2$, 96 with the combination of NaCl/$CaCl_2$ and UV/H_2O_2 electrochemically oxidized) were carried out. Among the independent variables of the process, color and haze removal were analyzed according to the response, and electrolyte concentration, H_2O_2, current, electrolysis time, and pH were measured. The rotatable layout became finished with 4 unbiased variables at 3 coded levels (1, 0, + 1), as shown in Table 3. The real cost is the unique cost given to the diverse factors, and the code cost is likewise given to the element stage (27). In this study, a 4-element central composite design (CCD) version was implemented to optimize the parameters. The layout of the experiments was primarily based on a two-stage factorial design with the addition of middle and big-name points. The overall wide variety of experiments (N) was calculated using Eq. (3).

$$N = N_a + N_o + N_c \quad (3)$$

Where *Na* represents the number of two-step experiments with a complete factorial design or factorial point of doubling, and N_0 is the experiment at the midpoint (6x) to evaluate the network error, N_c represents the number. The number of overlaps of axis (star) points (2*4 = 8) using factorial points of Alpha = 2.24 (16 + 8 = 24) and a total of 6 midpoints 30 tests provided by the software out of execution. This means experimental electrochemical oxidation (EO) 60 (30 for NaCl, 30 for $CaCl_2$), and a combination of photo electrochemically oxidized NaCl, $CaCl_2$, and UV/H_2O_2 (25 + 12 + 6 = 48). This is because H_2O_2 is an additional factor, and experiments were performed using 48 * 2 (96) $CaCl_2$ and NaCl. The experimental effects were analyzed using the RSM set of rules and suited for an expected quadratic polynomial function. The quadratic version of the equation for predicting the ultimate situations may be expressed via the following Equation.

$$Y_i = \beta_0 + \sum_{i=1}^{4} \beta_i X_i + \sum_{i \le j}^{4} \sum_{j}^{4} \beta_{ij} X_i X_j + \sum_{i=1}^{4} \beta_{ii} X_i^2 + e \quad (4)$$

Where Y_i is the response variable, β_0 is the model (regression) constant, β_i is the linear term, βii is the square (secondary) term, β_{ij} is the interaction term, X_i and X_j are the independent variables, and *e* is random. The error and

Table 1. Experimental design for electrochemical oxidation using NaCl/$CaCl_2$

Factor	Name	Units	Type	Minimum	Maximum	Coded low	Coded high	Mean	Standard deviation
A	pH		Numeric	5.00	9.00	-1 ↔ 5.00	+1 ↔ 9.00	7.13	1.57
B	Time	min	Numeric	20.00	50.00	-1 ↔ 30.00	+1 ↔ 50.00	40.00	10.50
C	Current	amp	Numeric	0.2000	0.6000	-1 ↔ 0.30	+1 ↔ 0.50	0.4033	0.0928
D	Electrolyte	g	Numeric	0.5000	2.50	-1 ↔ 1.00	+1 ↔ 2.00	1.50	0.4549

Table 2. Experimental design for electrochemical oxidation in combination with UV/H_2O_2

Factor	Name	Units	Type	Minimum	Maximum	Coded low	Coded high	Mean	Standard deviation
A	pH		Numeric	5.00	9.00	-1 ↔ 5.00	+1 ↔ 9.00	7.00	1.65
B	Time	min	Numeric	20.00	50.00	-1 ↔ 30.00	+1 ↔ 50.00	40.00	10.11
C	Current	amp	Numeric	0.2000	0.6000	-1 ↔ 0.30	+1 ↔ 0.50	0.4021	0.093
D	Electrolyte	g	Numeric	0.5000	2.50	-1 ↔ 1.00	+1 ↔ 2.00	1.50	0.461
E	H_2O_2	ml	Numeric	1.0000	5.00	-1 ↔ 2.00	+1 ↔ 4.00	3.04	0.966

Table 3. The optimum value of pollutant removed by photo-electrochemical oxidation

Major pollutants	Coffee wastewater before treatment	Coffee wastewater after treatment	Removal efficiency (%)	Permissible WHO standard for effluents
Color (abs)	2.95	0.261	91.165	50 TCU
Turbidity (NTU)	144.5	5.966	95.871	300NTU
Color (abs)	2.95	0.122	95.856	50 TCU
Turbidity (NTU)	144.5	3.565	97.533	300 NTU
Color (abs)	2.95	0.049	98.339	50 TCU
Turbidity (NTU)	144.5	2.789	99.454	300NTU
Color (abs)	2.95	0.003	99.898	50 TCU
Turbidity (NTU)	144.5	1.11	99.923	300 NTU

k = 4 are the numbers of parameters (28).

Response surface plots offer a manner to be expecting wastewater elimination efficiency. In addition, the contour strains of the plot assist to the perception of the character of the interplay among those variables. The most anticipated yield is received and displayed inside the vicinity surrounded through the minimal curve of the contour map. Each graph suggests the variant of the goal reaction because of the variant of the running parameter level.

Results

The removal efficiency of photo-electrochemical oxidation process for coffee processing wastewater

Coffee processing wastewater is one of the industrial wastewaters containing pollutants that can affect the ecosystem after being released into the environment. Therefore, wastewater from an inexperienced espresso processing plant has the subsequent water pleasant parameters: Physical parameters include color, temperature, and turbidity. According to the analysis, the color of 2.95 abs, temperature of 43°C, very odor, turbidity of 144.5 NTU, and pH 5.31, COD of 7680 mg/L, and very black were obtained.

The removal efficiency of electrochemical oxidation using different electrolytes

Sodium chloride (NaCl) is a chemical used as an electrolyte, and as proven in Table S1, it will increase the conductivity by forming $Na^+$and Cl^{-1} at some points of the remedy procedure, and the voltage provided to the wastewater. Used to lessen the quantity of calcium chloride ($CaCl_2$) is a chemical substance used as an electrolyte, and as proven in Table S1 and S2. It will increase conductivity via way of means of forming Ca^{+2} and Cl^{-1} at some point in the remedy procedure to boom elimination performance and wastewater. In this phase, an aggregate of electrolyte NaCl and UV/H_2O_2 was used to boost the performance of hydroxyl ion destruction and contaminant elimination. In this phase, as proven in Tables S3 and S4, the electrolytes $CaCl_2$ and UV/H_2O_2 were used to boost the destruction of hydroxyl ions and the performance of contaminant elimination. An aggregate was required.

Effect of operating parameters on % removal efficiency

In this study, the operating parameters that strongly affect EO and UV/EO processes, such as solution pH, electrolyte concentration (NaCl/$CaCl_2$), current, and response time, in terms of power consumption-related color and haze removal were investigated.

Effect of pH

pH is a term used to describe the strength of an acidic or alkaline state of a liquid. Highly alkaline water has a high pH value. In EO and UV/H_2O_2 processes, the pH of the solution plays a fundamental role in the removal of impurities. Therefore, integrate NaOH or H_2SO_4 solutions and adjust to a range of 5-9 to investigate the effect of pH on the process performance. Neutral conditions are promising for nitrate, phosphate reduction, and color and turbidity removal. More oxidants are produced in the neutral medium, decreased in the basic medium, and the H^{+1} redox potential is significantly reduced, resulting in a decrease in pH. Using aluminum electrodes, the best color and turbidity removal at neutral pH was achieved, which is consistent with the results of a study by Khemila et al. Figure 2 shows the effect of pH on the pollutant removal rate.

Effect of electrolysis time

Long electrolysis instances can regulate sludge structure, regulate contaminant elimination performance, and regulate floc sedimentation and buoyancy characteristics. Studies show that the longer the reaction time, the lower the elimination rate. This can be because of the separation of metallic hydroxides on the electrode level, which is consistent with the results of other studies (29-32). Coffee treatment in the case of wastewater treatment, the elimination performance is low for the long term and a brief time. For this study, 40 minutes is the most suitable elimination time. The impact of the % pollutant removal capability parameter is shown in Figure 3.

Effect of electric current

The current turned into at once proportional to the voltage. As the current increased, the melting of aluminum increased. Therefore, the formation of hydroxide Al(OH)3 will increase all through the manner. Higher voltages generate oxygen and decrease the performance of natural oxidation. The impact of modern-day pollutant % removal efficiency is shown in Figure 4.

Effect of electrolyte concentration

Table salt is generally used to boost the conductivity of the dealt water or wastewater. In addition to the ions' contribution to charge, chloride ions have been observed as a good way to notably lessen the unfavorable consequences of diverse anions including HCO_3 and SO_4. The life of carbonate or sulfate can result in the precipitation of Ca^{2+}or Mg^{2+}ions, which shape an insulating layer beneath the electrode. The AO and AO/H_2O_2 approaches remove and mineralize natural compounds faster in the presence of NaCl or $CaCl_2$ (24) compared to Na_2SO_4 (33-35). This insulating layer can significantly improve the performance of electrodes, and significantly, reduce their efficiency today. In addition, the addition of NaCl and $CaCl_2$ can reduce current consumption due to

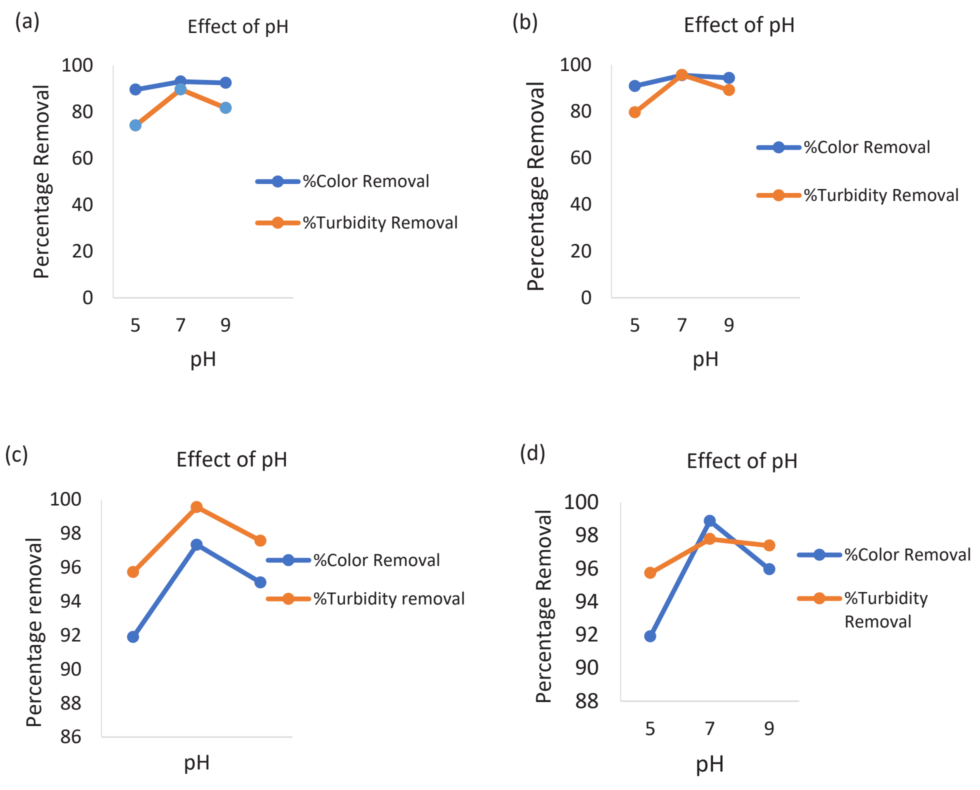

Figure 2. (a) Effect of pH on removal efficiency using NaCl as an electrolyte; (b) Effect of pH on removal efficiency using $CaCl_2$; (c) Effect of pH on removal efficiency using UV/H_2O_2 and NaCl; (d) Effect of pH on removal efficiency using UV/H_2O_2 and $CaCl_2$

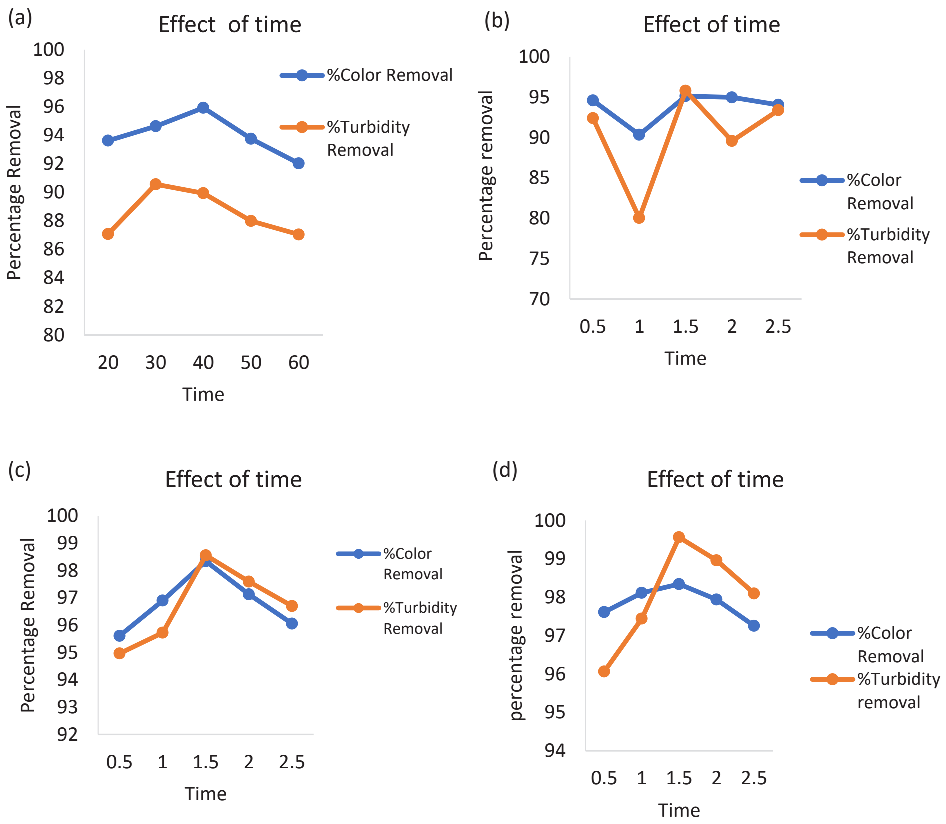

Figure 3. (a) Effect of time on removal efficiency using NaCl; (b) Effect of time on removal efficiency using $CaCl_2$; (c) Effect of time on removal efficiency using UV/H_2O_2 and NaCl; (d) Effect of time on removal efficiency using UV/H_2O_2 and $CaCl_2$

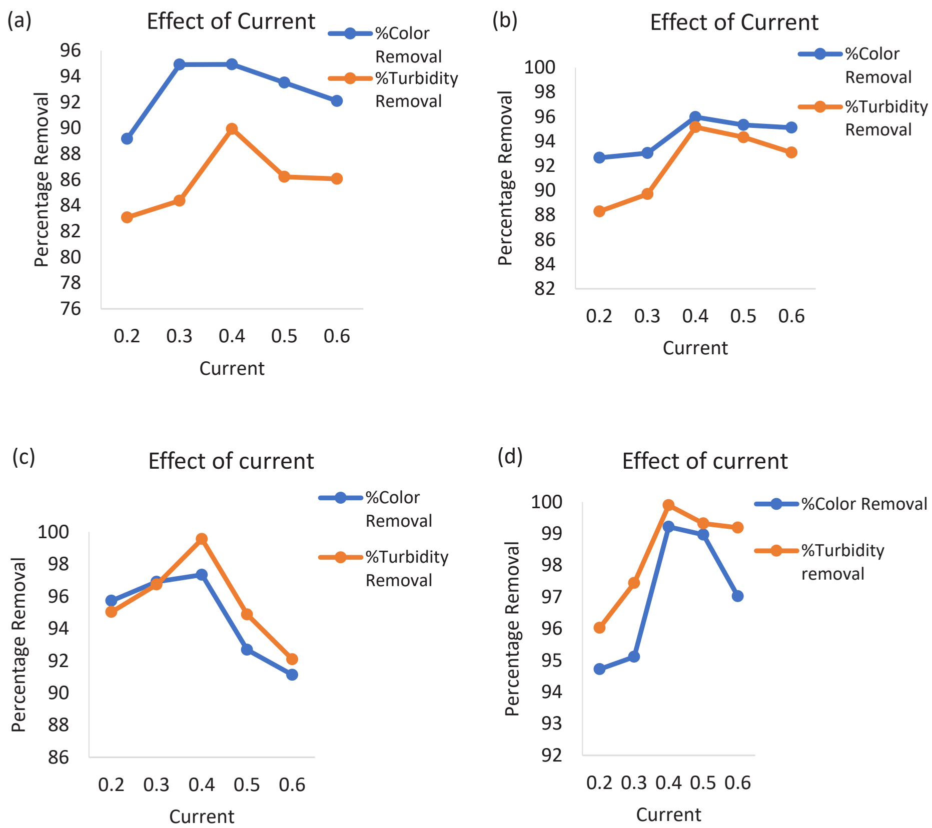

Figure 4. (a) Effect of current on removal efficiency using NaCl; (b) Effect of current on removal efficiency using $CaCl_2$; (c) Effect of current on removal efficiency using UV/H_2O_2 and NaCl; (d) Effect of current on removal efficiency using UV/H_2O_2 and $CaCl_2$

the conductivity boom. In addition, electrochemically produced chlorine is effective in disinfecting water (36). Therefore, in this study, 0.52.5 g/L NaCl and $CaCl_2$ concentrations were chosen for the experiment. The amount of electrolyte factor has a significant effect on the response compared to other factors. NaCl/$CaCl_2$ increases the conductivity of the EO system and improves the removal rate of color, COD, nitrates, phosphates, and turbidity. $CaCl_2$ gives more efficient results than NaCl because the ions increase from + 1 (NaCl) to + 2 ($CaCl_2$). The purpose of adding the supporting electrolyte (NaCl or $CaCl_2$) was to increase the conductivity of the solution (37). Using NaCl, the maximum COD removal rate was 95.2%, while using $CaCl_2$, it was reported 96.4%. The conductivity of the wastewater turned into adjusted by including the right quantity of electrolyte. If the anode capability is excessive enough including direct oxidation of natural compounds and Cl ions aggregated inside the wastewater may additionally occur. Among the effective and superior oxidation techniques, the oblique electro-oxidation system is a powerful opportunity for the destruction of excessive-molecular-weight substances, mainly the elimination of COD, and is mainly exciting for the treatment of tremendously conducive wastewater (38). Within those processes, the natural load is broken down via a fine oxidant as active chlorine species (ACS). ACS is developed from chloride observed in water via an electron switch to the anode (response 1), and the anode reacts with water to generate hypochlorous acid (response 2). According to the properties of chlorine in water, the balance of hypochlorous acid and hypochlorite ion depends on the interest and pH of the solution. After response 3, besides these energetic species, chloride radicals are generated via direct oxidation (response) on the anode.

$$2Cl^- \rightarrow Cl_{2(aq)+}\left(2e^-\right) \tag{R1}$$

$$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+ \tag{R2}$$

$$HClO \leftrightarrow ClO^- + H^+ \tag{R3}$$

$$Cl^- \rightarrow Cl + e^- \tag{R4}$$

Therefore, the generated chlorine gas can oxidize pollutants. It is clear that aluminum consumes more energy and consumes fewer electrodes. It was found that the greater the conductivity, the higher the procedure efficiency. The effect of the electrolyte on the pollutant elimination cost is shown in Figure 5.

The rate of color, COD, nitrate, and phosphate removal that increases with increasing electrolyte dose (g/L) and maximum electrolyte mass is no longer important to removal efficiency. At current amperes, this is due to the oxidation of organic compounds that occurred directly on the surface of the electrode.

Effect of ultraviolet light/hydrogen peroxide (UV/H_2O_2)

The ECO performance can be improved by combining H_2O_2 and UVC light. These combined technologies can have a synergistic impact on the elimination of natural count numbers (39). The APT was once carried out using each batch reactor and a system in which the sample used to be processed with UV mild/H_2O_2 variables (40). With respect to turbidity and color removal, a high dosage of H_2O_2 creates dark color, which may prevent the penetration of UV light through wastewater during the oxidation experiments, as a result, this formation of black color reduces the removal efficiency of color and turbidity (40). In particular, studies noted that at high concentrations, H_2O_2 itself may act as a free-radical scavenger in secondary reactions, causing a decrease in the hydroxyl radical concentration, which reduces the removal efficiency (41). Since both turbidity and color were both physical properties of wastewater and the presence of one impurity is directly related to the other, as a result, removal of turbidity and color were interrelated. The results of more than a few electrolyte parameters with percentages of pollutant elimination capacity are shown in Figure 6.

In the photoelectrochemical experiment, a reactor with a maximum capacity of 1 L of coffee treatment effluent was used. This reactor was equipped with a UV lamp (Model PUV1022 Heraeus) with 40 cm long, and an emission spectrum of 200-460 nm, 60 W, 220 V, 11.4 amps of current. The photo-reactor has a demineralized coffee processing waste. Therefore, as the dosage of H_2O_2 increases removal of organic substance after the optimum value of dosage reached.

The interaction effects

The interplay effect of the input variables used was investigated through more than a few mixtures of two or three independent variables and experimental parameters that had a good impact on the analytical and experimental parameters statistically designed using the CCD method. The results evaluated the usage of a range of descriptive facts such as *P* value, f-value, and degree of freedom (df). The coefficient of variation (R^2) for each coefficient was determined using Fisher's F test. A small likelihood value of p (P-value) is the probability that the located F cost will appear if the null hypothesis is true. If the probability value is small, the null speculation is rejected. The greater the value of F and the smaller the cost of p, the more important the corresponding coefficient.

Synergistic effect

Four different preliminary tests were performed to assess the simultaneous effects of UV/H_2O_2 and electrochemical processes on removal efficiency. In all experiments, solution pH, reaction time, electrolyte concentration, and current values were used as operating parameters. In all experiments, solution pH, reaction time, electrolyte concentration, and current values were used as operating parameters. In electrochemical reactors, oxidation occurs

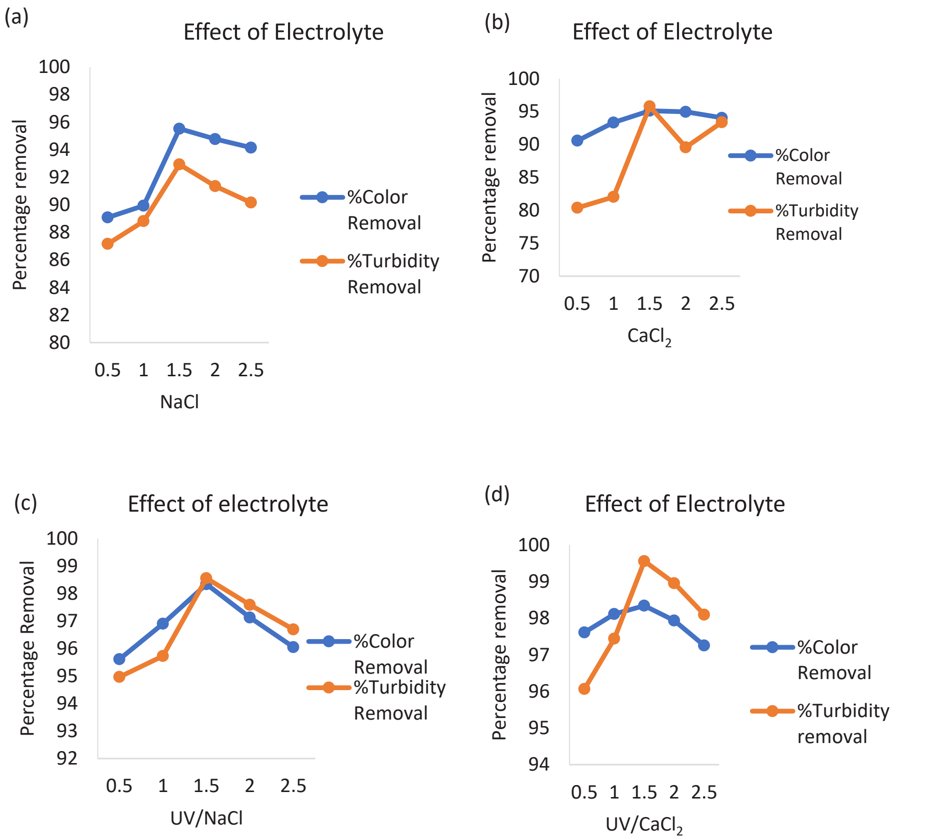

Figure 5. (a) Effect of electrolyte concentration on removal efficiency using NaCl; (b) Effect of electrolyte concentration on removal efficiency using $CaCl_2$; (c) Effect of electrolyte on removal efficiency using UV/H_2O_2 and NaCl; (d) Effect of electrolyte on removal efficiency using UV/H_2O_2 and $CaCl_2$

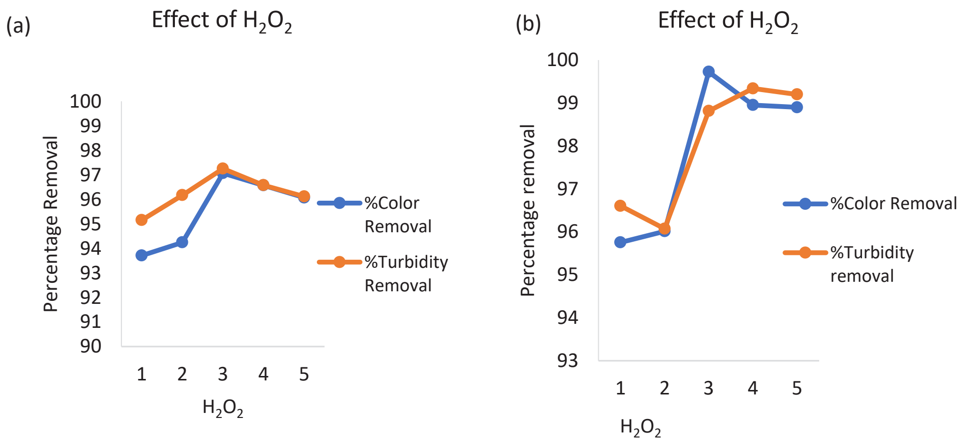

Figure 6. (a) Effect of hydrogen peroxide on removal efficiency using UV/H_2O_2 and NaCl; (b) effect of hydrogen peroxide on removal efficiency using UV/H_2O_2 and $CaCl_2$

at the anode, and reduction occurs at the cathode. This study focused on an overview of electrochemical reactors in water and wastewater treatment. The electrochemical system consists of at least two electrodes as an anode and a cathode and an intermediate space filled with electrolytes. For electrochemical properties, the system can be further extended with a reference electrode (41). This limit electro-oxidation to the removal rate rather than minimizing the contaminant in terms of color and turbidity. The removal rate is improved by applying UV/H_2O_2 to the electrochemical oxidation. According to the study of Nadais et al (42), to clarify the results, some concepts of photoelectrochemical oxidation for higher removal efficiency than electrochemical oxidation are as follows: The hydroxyl radicals can be generated by photochemical systems such as UV/H_2O_2 (43). Factors that affect H_2O_2 processing include pH, temperature, contact time, application rate, and reactivity of the compound.

Inorganic substances generally react with H_2O_2 more rapidly than organic substances and because of mass transfer limitations, the reaction of trace organic substances has the slowest rate. The oxidation with H_2O_2 alone is not effective in some refractory materials at high concentrations. H_2O_2 is also used in the surface treatment industry where cleanliness is an issue. Ultraviolet rays can activate H_2O_2 to form hydroxyl radicals, which are strong oxidizing agents. The oxidation that is used in the formation of hydroxyl radical intermediates is often referred to as AOP. Aluminum electrodes can be completely oxidized, they also have strong corrosion resistance and operating current density of the electrode. The ionic conductivity of the reaction medium is a very important parameter in an electrochemical cell for the energy-saving process. The conductivity of the solution affects the output current applied battery voltage and power consumption. If the ionic conductivity of the solution is low, more energy is required to overcome the high resistance between the anode and the cathode. The most common way to increase the conductivity of a solution is to add a small amount of conductive salt. This reduces energy consumption during electrolytic machining. This behavior of decreasing energy consumption with increasing electrolyte concentration is due to the increase in energy consumption with increasing applied cell voltage, which directly affects the current and increases the ionic conductivity and electrical resistance of the reaction medium. Significant interactions between experimental factors that may be due to the reduced applied cell voltage were confirmed by surface plots, interaction plots, and analysis of variance (ANOVA).

Discussion

Optimization by response surface methodology

The electrochemical parameters of the study were statistically optimized using RSM. The RSM is a regression analysis designed to predict the value of a dependent variable based on the control value of an independent variable. To optimize experimental parameters for other processes including AOPs, RSM is a reaction surface that enables the prediction and discovery of the optimal operating conditions for maximizing system performance. This is a very efficient technique for generating a model. In addition, it shows the relative magnitude and impact of various factors on the reactions and their interactions. This has led to its use in modeling various water and wastewater treatment systems or processes (44).

Influential parameters and color absorption were measured at wavelength of 450 nm; the wave length was read by spectrophotometers and turbidity meters. The main purpose of this study was to determine the optimum operating parameters for efficient treatment conditions of coffee treatment wastewater. The estimation model performed response optimization to determine the points optimized for the operating conditions and achieve the maximum percentage of distance. The maximum removal rates for color and turbidity were selected to achieve the best removal performance under the operating conditions of the independent variables. Target values for four independent variables, including reaction time, solution pH, current, salt, and H_2O_2, were selected within the range of conditions. The optimum values for the independent variables were obtained as follows: pH = 7, reaction time of 40 minutes, current 0.4 amps, and salt concentration of 1.5 g/L. Under these conditions, the model's desirability level was 1, and the color and turbidity removal rates are shown in Table 3.

The efficiency of photoelectric oxidation depends on many factors such as pH, electrolyte concentration, electrolysis time, current density, and turbulence. Optimizing these operating parameters is a key to maximizing pollution control with relatively low power consumption. The problem in electrical oxidation can provide improved oxidation while consuming less power. The creation of turbulence in electro-oxidation can also reduce the time it takes to reach the maximum oxidation.

Comparison of the obtained result with previously investigated similar research

In this research, the maximum amount of turbidity and color was removed by the combination of ECO with UV/H_2O_2, which produces large amounts of OH^-, which oxidize large amounts of contaminants and increase removal efficiency as compared with previous studies, which is shown in Table 4.

Table 4. Comparison of the obtained result with previous studies (45-49)

Major pollutants	Coffee wastewater before treatment	Coffee wastewater after treatment	Removal efficiency (%)	Permissible WHO standard for effluents	Previously investigated researches
Color (abs)	2.95	0.261	91.165	50 TCU	90%
Turbidity (NTU)	144.5	5.966	95.871	300 NTU	91%
Color (abs)	2.95	0.122	95.856	50 TCU	86.2%
Turbidity (NTU)	144.5	3.565	97.533	300 NTU	87.1%
Color (abs)	2.95	0.049	98.339	50 TCU	99%
Turbidity (NTU)	144.5	2.789	99.454	300 NTU	98.4%
Color (abs)	2.95	0.003	99.898	50 TCU	92%
Turbidity (NTU)	144.5	1.11	99.923	300 NTU	98.2%

Analysis of variance test

ANOVA was used for graphical data analysis to capture interactions between process and response variables. The quality of the adjusted polynomial model is expressed by the value of the correlation coefficient (R^2). The statistical significance of this coefficient was tested by the F test. The model formula was evaluated by *P* value (probability) with a 95% confidence level. The data were analyzed by the ANOVA. Descriptive statistics and test statistics are presented here. This trial was run to study the effects of all factors on the target response. Essentially ANOVA is a statistical technique that divides the total number of variations in a data set into components related to a particular source of variation and tests hypotheses about model parameters (50). The experiments were conducted randomly to avoid a systematic error. The coefficients of the quadratic model, which explains the degree of suppression of the studied parameters (response), act as the performance of the independent variables (factors). The 0.0500 quadratic model result obtained from ANOVA results with probability values p and is significant. The mean square was calculated by dividing the sum of squares of each source of variation by its degrees of freedom and using the 95% confidence level ($P < 0.05$). The results are shown in Table S5-S13.

ANOVA for the % removal of ECO quadratic model using NaCl

As shown in Table S5, the F value of the model is 103.21, which means that the model is significant. There is only a 0.01% chance that such a large f-number occurs due to noise. A *P* value less than 0.0500 indicates an important model term. In this case, A, B, C, D, AD, and A^2 are important model terms. The values greater than 0.1000 indicate that the model term is not important. If you have a lot of unrelated model terms (not counting those needed to support the hierarchy) you can improve your model by flattening it. The incompatibility with a F-number of 1.82 means that the incompatibility is not as significant as a pure error. There is a 26.6% chance that such a large F-number occurs due to mismatched noise.

ANOVA for the % removal of ECO quadratic model using $CaCl_2$

As shown in Table S6, the F-price of the model is 136.34, which means that the version is huge. There is the simplest 0.01% risk that noise can cause such a high F-price. In this situation, A, B, C, D, A^2, B^2, C^2, and D^2 are larger versions of the phrase. A value greater than 0.000 indicates that the version phrase is not very large. If you have a large number of unimportant version phrases (phrases needed to maintain the hierarchy will no longer be counted), you can also improve your version with a version discount. Lack of adjustment of F value of 2.36 means that the lack of adjustment is not always greater than the natural error. The risk of such a significant price shortage due to noise is 17.81%.

ANOVA for the % removal for a combination of UV/H_2O_2 and ECO (photoelectron chemical oxidation) quadratic model using $CaCl_2$

According to Table S7, the F value of the model is 44.66, which means that the model is significant. There is only a 0.01% chance that such a large f-number occurs due to noise. A *P* value less than 0.0500 indicates an important model term. In this case, A, B, C, D, E, AD, CE, and A^2 are important model terms. The values greater than 0.1000 indicate that the model term is not important. If you have a lot of unrelated model terms (not counting those needed to support the hierarchy), you can improve your model by flattening it. The incompatibility with an F-number of 2.27 means that the incompatibility is not as significant as a pure error. There is a 15.69% chance of such a F-number mismatch due to noise.

Fit statistics

The statistical significance of the model equations and model terms was evaluated by ANOVA. According to the study of Nair et al (51), the model's goodness-of-fit was tested using the coefficient of determination (adjusted R^2 and R^2), and statistical significance was tested by Fisher's exact test (F test). The final model verification was performed using predictive R-squared (R^2). It estimates the predictive power of the model using new observations based on the opt-out approach. The correlation between experimental correlation and the predictive response was evaluated quantitatively by the coefficient (R^2). The coefficient of determination (R^2), which represents the overall rate of change of the model's predicted response is the ratio of the sum of squares to the sum of squares. The size of R^2 should be close to 1 and should fit well with adjusted R^2. The fit of the quadratic polynomial model is represented by R^2. The fit of the model was also evaluated by R^2 (correlation coefficient) and adjusted R^2. The high value of the correlation coefficient ($R^2 = 0.986$) indicates that the model is more reliable in predicting the percentage gap and can explain 98.6% of the response variability. In this study, all R^2 values are greater than 0.9. According to the study of Mumecha et al (52), R^2 must be at least 0.8 for the model to fit. Many scientists have reported that a high R^2 value indicates a good agreement between the experimental data and the data estimated by the model. Therefore, the agreement between the high values of R^2 and adjusted R^2 in this study indicates that the model is very important. Reasonable accuracy (AP) is a measure of the "signal-to-noise ratio". In other words, the AP compares predicted values at the design point with the mean prediction error shown in Table S14-S20.

Effects of model parameters and their interactions

Three-dimensional (3-D) surfaces and 2D contour diagrams are graphical representations of regression equations for optimizing response situations and are the maximum beneficial technique for clarifying the situations of response systems. It is also used to investigate the impact of every variable at the reaction. In any such quadratic version plot, the reaction features of the 2 elements are plotted by converting them inside the experimental range, whilst maintaining all different elements consistent at their levels. The consequences display that all mixed technique variables have a large impact on caseation and haze elimination, in addition to electricity intake inside the processing technique. The optimal values for working conditions were predicted through 3-D response floor evaluation of unbiased and structured variables. Figures 6 and 7 show a sequence of 3-D response floor plots displaying the relation between elimination performance and elements.

Effects of interactions for the ECO combination with UV/H_2O_2

Effect of interaction is where more than two independent variables affect positively or negatively the efficiency of pollution removal in coffee processing wastewater. Some interaction effects are shown in the 3D diagram from Figures 7 and 8.

As shown in Figure 7, color removal efficiency was high at neutral pH, which is indicated by red color. Also, at H_2O_2 concentration of 3 mL, the interaction effect of pH and H_2O_2 positively affected the process.

The results of the interaction of the four independent variables with the color and turbidity of the dependent variables are shown in the panel (ad) for time and pH. Depending on the reaction, current, electrolysis time, solution pH, salt concentration, COD, color, turbidity, nitrate, phosphate removal, and power consumption, it has a positive or negative effect. As shown in the figure, the COD removal rate increases as pH increases from acidic to neutral. The maximum COD removal rates were identified in the pH of 7-8, an interval of 30 to 50 minutes, current of 0.4-0.6 amps, and $CaCl_2$ concentration of 1.52 g. Increasing the initial salt concentration will increase the decomposition of H_2O_2 and increase the decomposition rate. Previous studies have also reported maximum catalytic activity in coffee processing effluents close to the pH of 6.8 (53).

Regression equations

Regression analysis provides information about the relationship between a response variable (dependent) and one or more independent variables (predictor) when the information is contained in the data. The purpose of regression analysis is to plot response variables against predictors. The duality of fit and the accuracy of the conclusions depend on the data used (54-56). The optimal value for the final model was calculated using a numerical method. For this purpose, the experimental range predictors were divided into grids, and the final model was calculated for all possible combinations of predictors in the grid. Therefore, the experiments to select pH (A), reaction time (B), applied current (C), chemical concentration (D) (supporting electrolyte), and hydrogen were studied and the optimal values for maximum removal efficiency were performed. The operating conditions were fixed. In photoelectrochemical oxidation, all influencing factors are optimized to achieve high removal rates. It is based on a quadratic polynomial model. A UV/H_2O_2 response using $CaCl_2$ and an independent variable was obtained and could be approximated by a quadratic polynomial according to equations 5 and 6.

$$\text{Color}=99.15+0.6863A+0.2879B+0.2089C+0.2221D+0.3464+0.3502AB0.1109AC+0.0265AD-0.0037AE-0.0228BC+0.0122BD-0.0659BE-0.0977CD+0.0596CE+0.0424DE-1.63A^2-0.0766B^2-0.2196C^2-0.2796D^2-0.1387E^2 \quad (5)$$

$$\text{Turbidity}=99.09+1.12A-0.1593B+0.1459C+0.1926D+0.1392E+0.0105AB-0.0340AC-0.1346AD-0.0488AE+0.0117BC+0.0114BD+0.0925BE-0.0429CD+0.1458CE-0.1137DE-2.57A^2-0.0479B^2-0.1123C^2+0.0223D^2-0.0515E^2 \quad (6)$$

The equations associated with the coded factors can be used to make predictions about a particular response level for each factor. By default, high coefficient values are encoded as + 1 and low coefficient values are encoded as 1. According to the results, many model terms such as pH (A), reaction time (B), current (C), electrolyte (D), H_2O_2 (E), and pH (A^2) are important for the reaction. An interaction term for time (B^2), current (C^2), electrolyte (D^2), H_2O_2 (E^2), and AB, AC, AE, BE, BD BC, AD, CD, CE, DE. Model terminology is in encrypted form. Model suitability was checked using the ANOVA test. The validity of the model was confirmed by applying the nonconformity tests shown in Table 4. It was very significant in the regression model ($P = 0.05$). All results show that this model is in good agreement with the experimental data. These results show that the combination of ECO and UV/H_2O_2 is the best for treating wastewater in a short time due to the high removal values of color and turbidity, and high extraction yield; therefore, it is an effective method. Mean with different characters in the same line indicates a significant difference ($P \le 0.05$).

The prediction of the optimum condition of responses

The results show a good agreement between the optimal prediction and the experimental results, proving that the model has a high value. The predicted R^2 for the first model is 99.09%. Backward elimination was used to obtain a sparse model with significant predictors. The coefficient of determination obtained by the predictive model showed a quadratic relationship between the response and the parameters, and the regression coefficient was good. The optimal ECO and UV/H_2O_2 conditions were

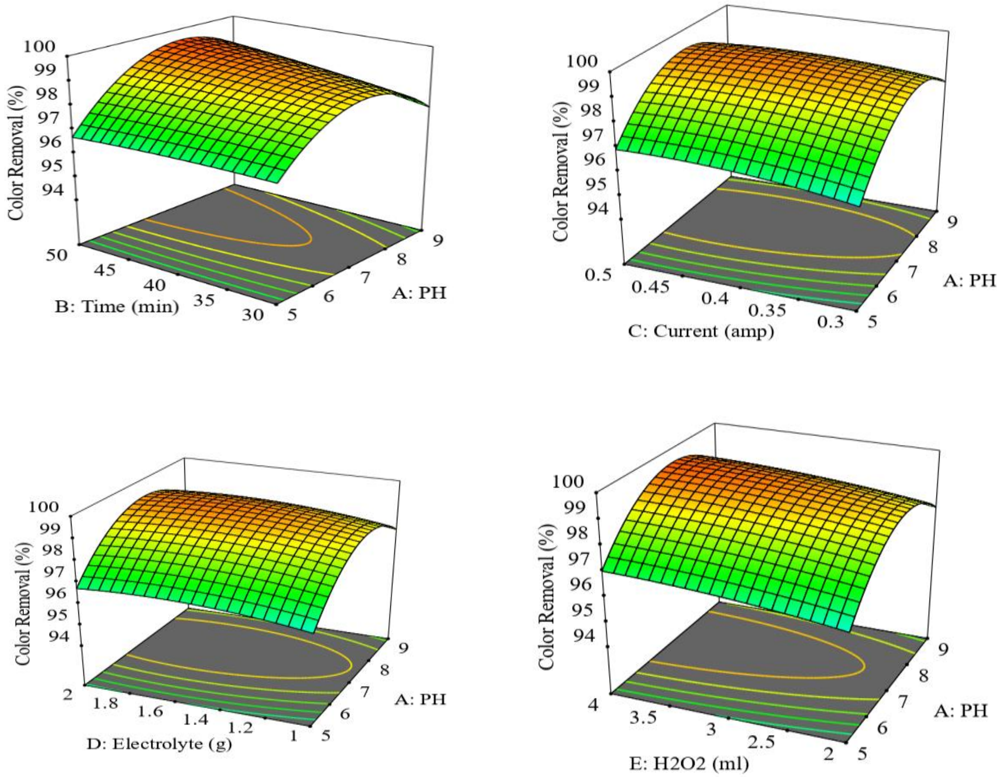

Figure 7. Interaction effect of independent variables response in surface 3D plots for % removal of color by a combination of ECO with UV/H_2O_2 using $CaCl_2$

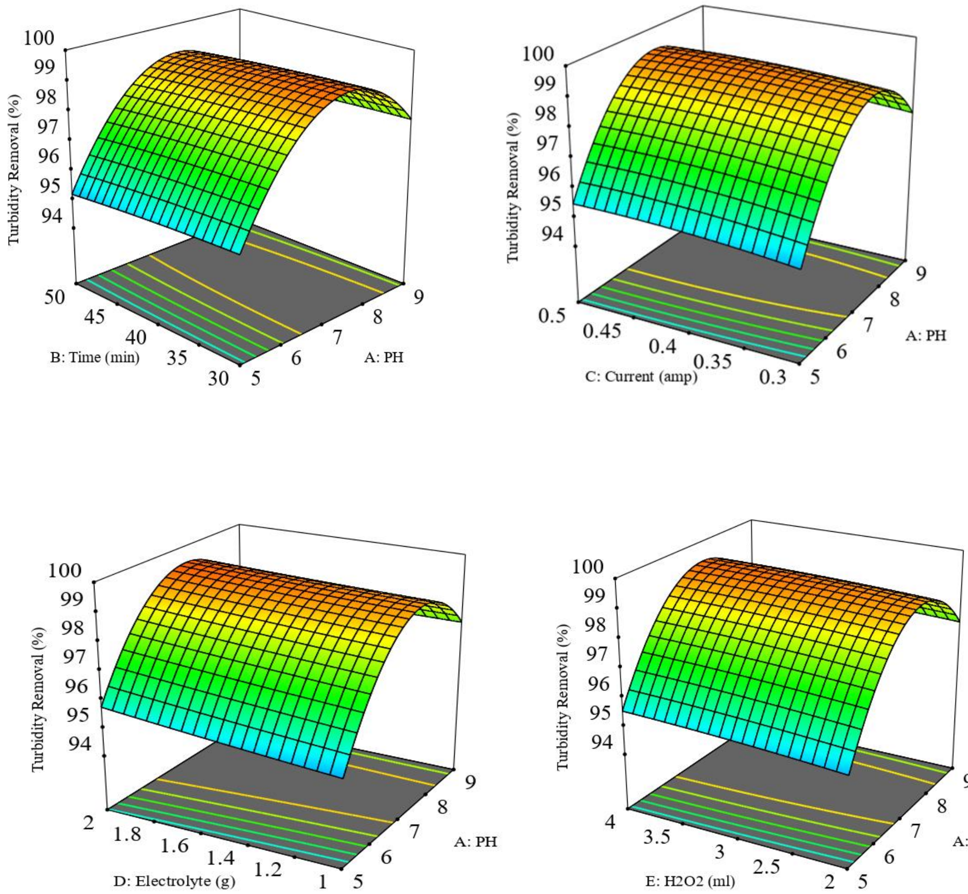

Figure 8. Interaction effect of independent variables in response surface 3D plots for % removal of turbidity by the combination of ECO with UV/H_2O_2 using $CaCl_2$

obtained using Design Expert 11.1.2.0 software and practical optimal values were determined. To further verify the reliability of the theoretical model predictions, under optimal conditions (electrolysis time of 60 minutes, UV lamp of 50 W, salt concentration of 1.5 g/L, pH 7), verification experiments were performed (n = 5). According to the results, the experimental results for removal efficiency were very close to the predicted values and there was no significant difference in the values ($P > 0.05$). Therefore, as shown in Table S21, it can be concluded that the established model is reasonable and valid in this study.

Conclusion

Photoelectrochemical oxidation procedures were used to deal with espresso processing effluents using NaCl and $CaCl_2$ as helping electrolytes and H_2O_2 as an oxidant separately. In all experiments, impartial (operational) variables including pH, response time, electrolyte concentration, and modern were investigated to limit power intake as a response function, even as effluent color and turbidity. The possibilities of those responses in the ECO and hybrid procedures were compared to determine the best running situations possible through the most ECO/UV/H_2O_2 elimination aggregate. In the system of electrochemical oxidation of wastewater remedy, impartial variables including pH, electrolytes, time, modern, and H_2O_2 have the best effect on enhancing the performance of pollutant elimination. Response floor methodology (RSM), primarily based totally on CCD, changed into a fantastic device used to assess and optimize the impact of operational parameters at the response. The importance of the impartial variables and their interactions were examined by the use of evaluation of variance (ANOVA) with a 95% self-assurance limit. The quadratic regression equation was proposed as an excellent version for predicting the performance of color and haze elimination. Combining the best elimination performance of electrochemical oxidation with UV/H_2O_2 the use of $CaCl_2$ to get rid of color and turbidity effects in most efficiencies of 99.6% and 99.4%, respectively. The best performance was obtained at pH = 7, electrolysis time of 40 minutes, modern 0.4 amps, $CaCl_2$ concentration of 1.5 g, and H_2O_2 concentration of 4 mL. This suggests that the combination of ECO and UV/H_2O_2 has an enormous synergistic impact on distance. As a synergetic electrolyte, $CaCl_2$ changed into green than NaCl in each ECO and UV/H_2O_2 procedure. For the treatment of wastewater from espresso remedy, the combination of ECO with UV/H_2O_2 was tested to be a greater green approach than ECO alone.

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Ethical issues

The authors hereby certify that all data collected in the field of study described in the manuscript and data from the study have been or will not be published separately elsewhere.

Competing interests

The authors declare that there are no conflicts of interest.

Authors' contributions

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Supplementary files

Supplementary file 1 contains Tables S1-S21 and Figure S1-S4.

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