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Electrochemical degradation of distillery spent wash using catalytic anode: Factorial design of experiments

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ABSTRACT

In the present study, electrochemical degradation experiments were conducted to degrade distillery spent wash. It was performed with ruthenium oxide coated titanium mesh acting as anode and stainless steel as cathode. The effects of current density, dilution, electrolysis time and pH on the degradation rate were investigated. Increasing the initial pH and dilution decreases the decolorization efficiency. At the same time, increasing the chloride concentration and increasing the current density increased the color removal. The combined effects of these factors were optimized using factorial design of experiments for color removal and chemical oxygen demand (COD) removal. Regression models were developed to study the interaction among the variables for both the color removal and COD reduction. The optimal removal of color of 83.31% and COD degradation of 39.66% was obtained for current density (14.285 mA/cm²), electrolysis time of 3 h and at dilution of 10% distillery spent wash at slightly acidic pH 5.5. The actual color removal and COD degradation at optimal conditions are 81% and 37%, respectively, which confirms close to factorial design results.

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1. Introduction

Industrial activity is responsible for generating a large volume of hazardous effluents. Color is one among the most important hazard in industrial effluent, which needs to be treated [1]. Molasses spent wash (MSW) contains nearly 2% of a dark brown recalcitrant pigment called melanoidin formed due to Maillard amino-carbonyl reaction [2,3]. The empirical formula of melanoidin is $C_{17-18}H_{26-27}O_{10}N$. The molecular weight distribution is between 5000 and 40,000. It is acidic, polymeric and composed of highly dispersed colloids, which are negatively charged due to the dissociation of carboxylic acids and phenolic groups [4,5]. Its highly colored components lead to reduction of sunlight penetration in rivers, lakes thereby reducing the photosynthetic activity and dissolved oxygen concentrations causing hazardous to aquatic life. Disposal on land cause reduction in soil alkalinity, manganese availability and inhibits seed germination [6,7].

Several studies have been carried out concerning the decolorization of waste water using Cyanobacterium [8], fungi such as Aspergillus fumigatus [9], Coriolus [10] and Phanerochaete chrysosporium [11] have shown to degrade melanoidin and anaerobic mass imparting color to spent wash. Basically being heterotrophs, these organisms tend to deplete oxygen in the effluent and further, higher fungi are not easily adopted for aquatic habitats. Biological treatment is unable to degrade the coloring compounds and is appropriate only for the waste water containing low content of biodegradable matter.

A large range of physico-chemical processes have been proposed: coagulation with alum, ferric chloride, magnesium chloride and lime [12–16], adsorption on sugarcane dust, peat, fly ash and biosorbents [17–20], evaporation process [21] and ozonation [22]. However recent studies have pointed out several serious drawbacks of using aluminum salts, such as Alzheimer's disease [23]. There is also the problem of reaction of alum with natural alkalinity present in the water leading to a reduction of pH [24].

The electrochemical treatment is widely used to remove the color from industrial effluent [25–27]. These processes use electron as main reagent, but also require the presence of supporting electrolytes. The latter exist in waste water to be treated, but not always in sufficient concentration. In the electrochemical process, the pollutants are destroyed by either the direct or indirect oxidation process. In a direct anodic oxidation process, the pollutants are first adsorbed on the anode surface and then destroyed by the anodic electron transfer reaction. In an indirect oxidation process, strong oxidants such as hypochlorite/chlorine, ozone, hydrogen peroxide are electrochemically generated. The pollutants are then destroyed in the bulk solution by oxidation reaction of the generated oxidant. All the oxidants are generated in-situ and are utilized





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immediately. Among the oxidants hypochlorite is cheaper and most of the effluents have a certain amount of chloride. The electrochemical method involves the application of electrical current to the effluent to convert chloride to chlorine/hypochlorite. The chlorine and hypochlorite oxidize the pollutants and are then reduced to chloride ions. Different anodes were used successfully to treat various industrial effluents [28–30]. Electro-catalytic anodes were used to achieve higher efficiency in effluent treatment. The titanium substrate insoluble anode material favored the oxidation of organics containing higher aromatic rings with the formation of carboxylic acids.

The following reactions take place during electrolysis of the effluent. Chlorine gas is formed at the anode according to:

$$2Cl^{-} \rightarrow Cl_{2} + 2e^{-} \tag{1}$$

At the cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
 (2)

In the electrochemical cell, chlorine formed at the anode and hydroxides formed at the cathode react to form chloride and hypochlorite.

$$Cl_2 + 2OH^- \rightarrow H_2O + OCI^- + CI^-$$
 (3)

Both hypochlorite and free chlorine are chemically reactive and oxidize organics in the effluent to carbon dioxide and water.

$$Organics + OCl^{-} \rightarrow CO_2 + Cl^{-} + H_2O$$
(4)

The choice of electrode material is of fundamental importance. Dimensionally stable anodes (DSA) materials have been widely studied for application of organic oxidation. DSA materials have relatively long lifetimes and do not necessarily undergo the same poisoning phenomena associated with traditional electrode materials such as platinum. DSA have been classified as active or non active depending on its chemical nature [31,32]. Active electrodes mediate the oxidation of organic species via the formation of higher oxidation states oxides of the metal (e.g., RuO₂ or IrO₂) leading to selective oxidation. Non active electrodes present no higher oxidation state available and the organic species is directly oxidized by an adsorbed hydroxyl radical, generally resulting in complete combustion of the organic molecule (e.g., SnO₂ or PbO₂). Commonly salts are added to the effluent in order to increase the conductivity and frequently sodium chloride is used. Several authors have reported that it is possible to obtain the almost complete mineralization of solutions containing model compounds with chlorine mediated electrolysis [33] and real waste water, including textile and tannery effluents [34,35] and car wash waste water [36]. The electrolysis of distillery effluent in a static electrochemical reactor using ruthenium oxide coated titanium anode between the current density 1.5 and 5.5 A/dm² results 98% decolorization [37]. A cylindrical electrochemical reactor utilizing ruthenium oxide coated titanium anode between current intensity 1 and 9A results decolorization of 92% of spent wash. The studies provide that presence of additives like hydrogen peroxide and sodium chloride enhances the decolorization [38].

The present study is focused on degradation studies of distillery spent wash for removal of color and chemical oxygen demand (COD) using electrochemical method. The various factors affecting the electrochemical degradation are studied using catalytic anode of titanium mesh coated with ruthenium oxide. The 2⁴ factorial design is employed for combined optimization of various factors.

Table 1

Physico-chemical characteristics of distillery spent wash (10% diluted)

Parameters	Magnitude
рН	4.2-4.3
Temperature (°C)	30
Color	Dark brown
Odor	Burnt sugar
Chemical oxygen demand (mg/L)	10,000-11,000
Biochemical oxygen demand (mg/L)	7000-7500
Total dissolved solids (mg/L)	5500-5700
Chloride (mg/L)	500-600
Potassium (mg/L)	1000-1300
Calcium (mg/L)	210-300

2. Materials and methods

2.1. Electrochemical studies

The distillery spent wash used for the study was collected from distillery unit near Tiruchi. The sample was diluted to desired dilution using deionized water. The pH of the sample was adjusted using $0.1M H_2SO_4$ or 0.1M NaOH as required. The physico-chemical characteristics of raw spent wash is given in Table 1.

Electrochemical reactor employed in the study consists of anodic material comprised of ruthenium oxide coated titanium mesh $(7 \text{ cm} \times 7 \text{ cm})$ and cathode consisting of stainless steel $(7 \text{ cm} \times 7 \text{ cm})$. The anode and cathode were positioned vertically and parallel to each other with an inter electrode gap of 3 cm. The experiments were done using 0.5 L of spent wash with constant stirring at 200 rpm using a magnetic stirrer to maintain uniformity throughout the system. The area of electrode exposed for the electrolysis was fixed to be 35 cm² and remaining area was prevented from exposure with lacquer. The temperature of the reactor was maintained constant using an external water re-circulation system. The analysis of sample was done after filtering it using Whatmann 42 filter paper. The absorbance of filtered sample was measured using UV-vis double beam spectrophotometer (Systronics 2201) at a maximum wavelength 475 nm [39]. Color removal efficiency was measured as a decrease in optical density measurement at 475 nm for the sample before and after electrolysis [40]. COD tests were also made according to standard methods [41]. The concentration of chloride was analyzed as described in standard methods [42].

2.2. Factorial design

The factorial design helps to develop a statistical model of a reaction by performing the minimum number of well chosen experiments and to determine the optimal values of process parameters. Factorial design is an empirical modeling technique used to evaluate the relationship between experimental variables and corresponding responses. The design of experiments chosen for this study was the 2^4 factorial design for four independent variables current density (X_1), dilution (X_2), time of electrolysis (X_3) and pH (X_4).

The behavior of the system is explained by the following quadratic equation [43,44].

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_4 X_4 + b_5 (X_1 X_2) + b_6 (X_1 X_3)$$

+ $b_7 (X_1 X_4) + b_8 X_2 X_3 + b_9 X_2 X_4 + b_{10} X_3 X_4 + b_{11} X_1 X_2 X_3$
+ $b_{12} X_1 X_2 X_4 + b_{13} X_1 X_3 X_4 + b_{14} X_2 X_3 X_4 + b_{15} X_1 X_2 X_3 X_4,$ (5)

where b_0 represents the global mean and b_i represents the regression coefficient corresponding to the main factors effects and interactions.



Fig. 1. Effect of sodium chloride concentration on electrochemical degradation of distillery spent wash. (Conditions: initial pH 4, dilution = 10%, reaction temperature = $30 \,^{\circ}$ C, current density = $28.571 \, \text{mA/cm}^2$, reactor volume = $0.5 \, \text{L}$).

The results of experimental design were studied and interpreted by MINITAB 14 statistical software to estimate the response of dependent variable (% color removal and % COD removal).

3. Results and discussion

3.1. Effect of sodium chloride on the degradation

Fig. 1 shows the color removal with different sodium chloride concentration at current density 28.571 mA/cm². It is clear that increasing the chloride concentration increases the color removal due to increased mass transport of chloride ions to the anode surface and also increased diffusion in the diffusion layer of the anode. As a result, more amount of chlorine/hypochlorite will be generated which results in increased rate of color removal. Hence further experiments were performed with addition of 1.5 g/L sodium chloride.

3.2. Effect of pH on the degradation

The color removal decreased with increase in the initial pH of the solution as shown in Fig. 2. The color removal decreased drastically if the initial pH was 10. The chlorine/hypochlorite generation was stable at given current density in the presence of sodium chloride as supporting electrolyte. However at higher pH the hypochlorous acid converts itself into chlorate or hypochlorate according to reactions mentioned in Eqs. (6) and (7). This result in reduced availability of hypochlorite at higher pH which causes reduction in



Fig. 2. Effect of pH on electrochemical degradation of distillery spent wash. (Conditions: current density = 28.571 mA/cm^2 , sodium chloride = 1.5 g/L, reaction temperature = $30 \degree$ C, dilution = 10%, reactor volume = 0.5 L).



Fig. 3. Effect of current density on electrochemical degradation of distillery spent wash. (Conditions: initial pH 4, sodium chloride = 1.5 g/L, reaction temperature = $30 \degree \text{C}$, dilution = 10%, reactor volume = 0.5 L).

decolorization.

 $6HOCl + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 12H^+ + 3/2O_2 + 6e^-$ (6)

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^-$$
 (7)

Another reason may be at acidic pH, the chlorine is present in the solution in the form of hypochlorous acid, which is having higher oxidation potential (1.49 V) than that of hypochlorite (0.94 V). The hypochlorite is prevalent in the alkaline condition [45].

3.3. Effect of current density on degradation

The current density was varied from 7.142 to 57.142 mA/cm² using 10% dilution and 1.5 g/L sodium chloride at pH 4.The results were presented in Fig. 3. Increasing the current density increases the over potential required for the generation of chlorine/hypochlorite. At the same time, the performance of the reactor will be affected under different current densities while altering the other operating conditions simultaneously because the generation of chlorine/hypochlorite depends on mass, charge or mixed control. Increasing the current resulted in a faster decolorization of the solution, due to a greater charge entering the cell and electrogenerating more active chlorine. The color removal rate was almost proportional to the current density. The color removal increased up to 28.571 mA/cm² and beyond this current density variation has no further significant contribution on decolorization rate of spent wash. The increase in current density results in increase of COD reduction as shown in Fig. 4.



Fig. 4. COD reduction during electrochemical degradation of distillery spent wash. (Conditions: initial pH 4, sodium chloride = 1.5 g/L, reaction temperature = $30 \circ \text{C}$, dilution = 10%, reactor volume = 0.5 L).



Fig. 5. Effect of dilution on electrochemical degradation of distillery spent wash. (Conditions: initial pH 4, sodium chloride = 1.5 g/L, reaction temperature = $30 \degree \text{C}$, current density = 28.571 mA/cm², reactor volume = 0.5 L).

3.4. Effect of dilution on degradation

The effect of dilution on the removal of color was studied in the range of 5–30% while the other conditions were fixed constant (Fig. 5). The color removal decreased with increase in dilution. This may be due to constant production rate of chlorine/hypochlorite at given conditions. The load of pollutants increases with increase in dilution and results in reduction in decolorization with increase in dilution.

3.5. Statistical analysis and modeling

The most important factors that affect the electrochemical process are current density (X_1) , dilution (X_2) , time of electrolysis (X_3) and pH (X_4) . In order to study the combined effect of these factors experiments were conducted at different combination of physical parameters. The results of experimental design were studied and interpreted by MINITAB 14 statistical software to estimate the response of dependent variable. The range of the four variables studied is shown in Table 2. The experimental results obtained for

Table 2

Experimental range and levels of independent process variables

Independent variables	Low level, -1	High level, +1
Current density (mA/cm ²)	14.285	42.857
Dilution (%)	10	30
Time of electrolysis (h)	2	5
рН	4	9

Tabl	le 3
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Experimental data, fits and residuals

Table 4

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Coefficients, t, P a	nd standard	deviation fo	r color removal
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Term	Effect	Coefficient	Standard deviation	t	Р
Constant		87.184	0.3318	262.78	0.000
X_1	3.889	1.945	0.3318	5.86	0.010
X2	-2.338	-1.169	0.3318	-3.52	0.039
X3	15.267	7.634	0.3318	23.01	0.000
X4	3.256	1.628	0.3318	4.91	0.016
X_1X_2	0.950	0.475	0.3318	1.43	0.247
X_1X_3	-3.044	-1.522	0.3318	-4.59	0.019
X_1X_4	1.385	0.693	0.3318	2.09	0.128
X_2X_3	1.258	0.629	0.3318	1.90	0.154
X_3X_4	1.466	0.733	0.3318	2.21	0.114
$X_1 X_2 X_4$	1.839	0.919	0.3318	2.77	0.069
$X_1 X_3 X_4$	-1.767	-0.884	0.3318	-2.66	0.076
$X_1 X_2 X_3 X_4$	-1.421	-0.711	0.3318	-2.14	0.122

R-Sq = 0.9954.

2⁴ full factorial designs and the corresponding fit and residuals are given in Table 3. Decolorization yield varied between 84% and 98% and COD degradation varied within 28% to 72%.

The decolorization yield (Y_1) can be predicted using the coefficients given in Table 4 [46,47].

$$Y_{1} = 87.184 + 1.945X_{1} - 1.169X_{2} + 7.634X_{3} + 1.628X_{4}$$

+0.475(X₁X₂) - 1.522(X₁X₃) + 0.693(X₁X₄) + 0.629(X₂X₃)
+0.733(X₃X₄) + 0.919(X₁X₂X₄) - 0.884(X₁X₃X₄)
-0.711(X₁X₂X₃X₄) (8)

The COD degradation rate (Y_2) can be predicted using the coefficients given in Table 5.

$$\begin{split} Y_2 &= 49.986 + 0.715X_1 + 1.305X_2 + 2.774X_3 + 16.131X_4 \\ &\quad -2.310(X_1X_4) - 0.648(X_2X_4) + 1.225(X_3X_4) - 1.045(X_1X_2X_3) \\ &\quad +0.889(X_1X_2X_4) - 0.498(X_1X_3X_4) - 0.501(X_1X_2X_3X_4) \end{split} \tag{9}$$

The students 't' test and Fischer 'F' test was used to determine the significance of the regression coefficients of the parameters. The P values were used as a tool to check the significance of each of the interaction among the variables. More significant the terms of coefficient if value of 't' is larger and value of 'P' is smaller [48,49]. The effects of current density and time of electrolysis on color removal are highly significant with P values close to zero. The effect of pH is more significant in color removal with P value 0.016 compared

Run	Current density $(mA/cm^2)X_1$	Dilution (%) X_2	Time (h) X_3	рН <i>X</i> 4	% Color removal y ₁	% COD removal Y ₂	Fit for color removal	Residuals for color removal	Fit for COD removal	Residual for COD removal
1	42.857	10	2	9	84.325	56.680	84.9528	-0.6278	57.2496	-0.5696
2	14.285	10	5	9	98.250	71.210	97.4018	0.8482	71.8482	-0.6382
3	14.285	10	5	4	92.450	28.265	92.6065	-0.1565	30.7828	-2.5178
4	14.285	30	2	4	75.265	32.230	73.7222	1.5428	31.2273	1.0027
5	42.857	10	5	4	93.265	38.560	94.1598	-0.8948	36.9929	1.5671
6	42.857	30	5	4	92.874	40.230	91.9792	0.8948	40.1368	0.0932
7	14.285	30	2	9	72.235	62.135	73.0860	-0.8510	64.3379	-2.2029
8	14.285	30	5	4	91.235	34.562	91.0785	0.1565	33.7045	0.8575
9	42.857	10	2	4	84.235	32.520	82.9154	1.3196	32.2268	0.2932
10	14.285	10	2	4	78.265	28.265	79.8078	-1.5428	27.6075	0.6575
11	42.857	10	5	9	97.465	68.720	97.2620	0.2030	68.9772	-0.2572
12	14.285	10	2	9	78.570	65.230	77.7190	0.8510	63.7650	1.4650
13	42.857	30	5	9	97.356	68.260	97.5590	-0.2030	68.7407	-0.4807
14	42.857	30	2	9	86.652	64.430	86.0242	0.6278	63.1225	1.3075
15	42.857	30	2	4	76.857	36.210	78.1766	-1.3196	38.1634	-1.9534
16	14.285	30	5	9	95.645	72.270	96.4932	-0.8482	70.8939	1.3761

Table 5

Coefficients, t, P and standard deviation for chemical oxygen demand removal

Term	Effect	Coefficient	Standard deviation	t	Р
Constant		49.986	0.3257	153.46	0.000
X_1	1.430	0.715	0.3257	2.20	0.093
X2	2.610	1.305	0.3257	4.01	0.016
X3	5.547	2.774	0.3257	8.52	0.001
X_4	32.262	16.131	0.3257	49.52	0.000
X_1X_4	-4.619	-2.310	0.3257	-7.09	0.002
X_2X_4	-1.296	-0.648	0.3257	-1.99	0.118
X_3X_4	2.449	1.225	0.3257	3.76	0.020
$X_1 X_2 X_3$	-2.090	-1.045	0.3257	-3.21	0.033
$X_1 X_2 X_4$	1.778	0.889	0.3257	2.73	0.052
$X_1 X_3 X_4$	-0.997	-0.498	0.3257	-1.53	0.201
$X_1 X_2 X_3 X_4$	-1.002	-0.501	0.3257	-1.54	0.199

R-Sq = 0.9985.

to individual effect of dilution with *P* value 0.039. In case of COD, removal time of electrolysis and pH play a significant role with *P* values close to zero.

The main effects were analyzed using main effects plot for color removal and COD removal as provided in Figs. 6 and 7. The color removal is found directly proportional to current density, time of electrolysis and pH while indirectly proportional to the dilution of spent wash. The COD removal was almost constant and was found not to vary widely with current density and dilution. The increase of time of electrolysis from 2 to 5 h increased the COD removal.

3.6. Interaction plots and analysis of variance test (ANOVA)

The interaction plot for color removal is shown in Fig. 8. In order to develop the regression model that is statistically significant the insignificant terms in the Eq. (8) is eliminated. The terms with P value more than 0.1 are insignificant and hence removed. The 2-way interactions between current density and dilution (P=0.247), current density and pH (P=0.128), dilution and time of electrolysis

Main Effects Plot for % Color Removal



Fig. 6. Main effects plot for % color removal.





Fig. 7. Main effects plot for % chemical oxygen demand removal.



Interaction Plot for % Color Removal

Fig. 8. Interaction plot for % color removal.

eliminated from Eq. (9).

(P=0.154), time of electrolysis and pH (P=0.114) and the 4-way interactions with *P* value 0.122 were eliminated to obtain statistically significant regression model.

$$Y_1 = 87.184 + 1.945X_1 - 1.169X_2 + 7.634X_3 + 1.628X_4$$

-1.522(X₁X₃) + 0.919(X₁X₂X₄) - 0.884(X₁X₃X₄) (10)

The mutual interactions among various variables for COD degradation are shown in Fig. 9. The statistically insignificant terms involving interaction between dilution and pH (P=0.118), the 3way interactions between current density, time of electrolysis and pH (P=0.201) and the 4-way interactions with P value 0.199 were

$$Y_{2} = 49.986 + 0.715X_{1} + 1.305X_{2} + 2.774X_{3} + 16.131X_{4}$$
$$- 2.310(X_{1}X_{4}) + 1.225(X_{3}X_{4}) - 1.045(X_{1}X_{2}X_{3})$$
$$+ 0.889(X_{1}X_{2}X_{4})$$
(11)

The statistical significance of ratio of mean square due to regression and mean square residual error was tested using ANOVA test. ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation for the purpose of testing hypotheses on the parameter of the model [50]. According to the ANOVA, *F* values for two, three and 4-way interactions tabulated is less than the



Interaction Plot for % COD Removal

Fig. 9. Interaction plot for % chemical oxygen demand removal.

Analysis of variance for % color removal

Source	DF	Seq SS	Adj SS	Adj MS	F	Р
Main effects	4	1057.12	1057.12	264.280	150.06	0.001
2-Way interactions	5	63.29	63.29	12.659	7.19	0.068
3-Way interactions	2	26.02	26.02	13.010	7.39	0.069
4-Way interactions	1	8.08	8.08	8.077	4.59	0.122
Residual error	3	5.28	5.28	1.761		
Total	15	1159.79				

Table 7

Analysis of variance for % chemical oxygen demand removal

Source	DF	Seq SS	Adj SS	Adj MS	F	Р
Main effects	4	4321.76	4321.76	1080.44	636.49	0.000
2-Way interactions	3	116.06	116.06	38.69	22.79	0.006
3-Way interactions	3	34.09	34.09	11.36	6.69	0.049
4-Way interactions	1	4.01	4.01	4.01	2.36	0.199
Residual error	4	6.79	6.79	1.70		
Total	15	4482.70				

corresponding value of *F* from statistical table of 5% upper point. This illustrates the fitness of data obtained to the regression model developed. The ANOVA chart for color removal and COD degradation were shown in Tables 6 and 7, respectively. The coefficient of determination for color removal ($R^2 = 0.9954$) and COD removal ($R^2 = 0.9985$). This implies that 99.54% and 99.85% of the sample variation for color removal and COD removal are explained by the independent variables and this also means that the model did not explain only about 0.46% and 0.15% of sample variation for color removal, respectively.

3.7. Response optimization for color removal

The optimization of color removal done for set target of 98% color removal and 65% COD removal. The optimal removal of color of 83.31% and COD degradation of 39.66% is obtained for current density (14.285 mA/cm²), electrolysis time of 3 h and effective result was found to be obtained at low dilution of 10% distillery spent wash at slightly acidic pH 5.5.The actual color removal and COD degradation at optimal conditions are 81% and 37%, respectively which confirms close to factorial design results.

4. Conclusion

The present study clearly demonstrated the usefulness of electrochemical treatment of distillery spent wash using titanium mesh coated with ruthenium oxide electrode for degradation of hazardous compounds in spent wash. The existence of interactions between the factors studied for the response of color removal and COD degradation. This study clearly shows that factorial design was one of the suitable methods to optimize the best operating conditions for target value of color removal. Satisfactory predicted equations were developed for both color removal and COD degradation using factorial design to optimize the process parameters.

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