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A STUDY ON TREATMENT OF DISTILLERY SPENTWASH USING ELECTRO CHEMICAL PROCESS

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ABSTRACT

Distillery spentwash is one of the most serious environmental problems since it is the undesirable residual liquid waste produced during the ethanol production process. The ever-increasing production of distillery spentwash and the strict regulations for its disposal have prompted the need for finding creative solutions to handle this effluent effectively and inexpensively. The present study suggested that electrochemical method as suitable substitutes for treating distillery spentwash. The experimental study was carried out using the electro-Fenton (EF) method to remove COD and colour from distillery spentwash. Experiments were also carried out to determine the effects of various process parameters, such as reaction time, pH, voltage, and various oxidant doses, on the removal effectiveness of COD and colour. The various affecting parameters were optimized using the RSM (Box-Behnken) model, and the outcomes were expressed as a percentage COD and colour reduction. The maximum COD and colour removal efficiency for the EF technique were 35.31% and 88.55%, respectively. The optimum conditions were a pH of 4, a dose of 25 ml/L of H_2O_2, a voltage of 3 volts, and a reaction period of 55 minutes. Following the application of EF, the GI values of radish and fenugreek were increased to 78.61% and 49.53% respectively. The results obtained showed a reduction in phytotoxicity of the treated effluents.

Keywords: Distillery Spentwash, Electro-Fenton, Phytotoxicity, COD Removal, Color Removal

I. INTRODUCTION

In Kanpur, India's first distillery was established in 1805 to provide rum for the soldiers. There are currently around 325 distilleries with a total production capacity of 3250 million liters of alcohol per year and 40.4 billion liters of effluents per year.[1] Due to vast industrial applications of alcohol, such as chemicals, medicines, cosmetics, drinks, fragrances, and the food industry, alcohol distilleries are rapidly expanding around the world. The majority of distilleries coexist with sugar mills, using molasses from cane sugar production as the raw ingredient for alcohol production. For the production of alcohol and other chemical products, distilleries also require raw materials such as sugarcane juice, syrup, and other agro products. [2] The distillation process produces a large amount of water and wastewater, which has a big influence on soil and aquatic bodies. The distillery industry is a major contributor to the Ministry of Environment and Forests' list of 17 extremely polluting industries. As a result, distillery effluent must be thoroughly treated before it may be discharged into bodies of water. [3]

In Distillery, approximately 12-15 liters of spentwash is produced per liter of alcohol production. Distillery spentwash contains impurities, nutrients added during molasses fermentation process. Spentwash is a dark brown, highly acidic, high ash content, inorganic, organic chemical, and dissolved salts and has a very high COD (80,000–120,000 mg/L) and BOD (35,000–50,000 mg/L). [3] Draining untreated spentwash into surface water streams has a negative impact on the ecosystem because it raises the temperature of the receiving water, lowering the amount of dissolved oxygen available. As a result, treating effluent before releasing it into the aquatic environment significantly improves the earth's and ecosystems overall health. [2]

In India, distilleries 88 percent of the raw materials used for the manufacture process are converted into waste and discharged into water bodies, which has become a major source of pollution. The improper treatment of large amounts of biodegradable distillery wastewater leads in significant environmental contamination [4]. The distilleries are being compelled to upgrade existing treatment technologies and seek alternate effluent management systems due to a growing scarcity of high quality freshwater and increasingly severe regulatory criteria [5]. In addition, the CPCB established a task force on Corporate Responsibility for Environmental Protection (CREP) in 2003, which mandated that distilleries achieve Zero Liquid Discharge (ZLD) in inland surface watercourses by the end of 2005. (CPCB, 2003).

Physical, chemical, and biological approaches are used to treat distillery spentwash, particularly for decolorization and COD removal. These conventional methods would reduce the colour and COD requirement of spentwash, on the other hand, produce a substantial amount of secondary sludge [6]. Biological processes are environmentally beneficial and eco-efficient; however they cannot completely breakdown organic molecules in hazardous wastewater [8]. As a result, it is critical to overcome the limits of current technologies and to develop integrated treatment methods that provide a comprehensive solution for the treatment of wastewater from molasses-based distilleries [7].

In this study electrochemical method was proposed for the treatment of distillery effluents. The effects of germination tests conducted with two species.

II. RELATED WORK

Eslami *et.al (2013)* examined and compared the treatment of real high strength textile wastewater using the Electrochemical Fenton (EF) and Chemical Fenton (CF) methods. The effluent having pH 3 and Iron electrodes were used for EF process. The EF procedure, which used 350 mA of electrical current, 1978 mg/L of hydrogen peroxide, and 60 minutes of reaction time, yielded the highest COD and colour removal efficiencies of 70.6 percent and 72.9 percent, respectively. Additionally, for each kilogram of COD eliminated, the EF and CF processes cost 17.56 and 8.6 US dollars to operate, respectively. Similarly, even though the EF process had greater operating costs than the CF process, it significantly reduced reaction time to achieve the best degrading efficiency. A similar study conducted (Reza Davarnejadet *et.al., 2014)* to compare, the effects of COD and colour removal from petrochemical wastewater by using the electro-Fenton method with aluminum and iron plate electrodes. The studies were carried out to determine effects of the reaction time (10–90 min), current density (25–80 mA/m^2), pH (2–5), H_2O_2/Fe^{2+} molar ratio, and H_2O_2 to petrochemical wastewater (PW) (ml/l) affected the processes performance. The outcomes demonstrate that the iron electrode's COD and colour removal (67.3% and 71.58%) efficiencies were higher than those of the aluminum electrode (53.94% and 67.3%) respectively. Experiments were carried out using hydrogen peroxide (H_2O_2) and potassium permanganate ($KMnO_4$) for the treatment of recalcitrant landfill leachate. The efficiency of the treatment was expressed in terms of colour, COD, and ammoniacal nitrogen (NH_4-N) reduction. The reduction of COD, Colour (30% and 42%) and ammoniacal nitrogen (19% and 24%) was fairly moderate at the optimum dosage (300 mg/L) conditions and pH 7, however the removal of colour was significantly lower (43%) for H_2O_2 compared to $KMnO_4$ (74%). Color removal was stronger at pH 3 for $KMnO_4$ and pH 4 for H_2O_2, but it was almost identical at pH higher than 5. The operating costs were calculated and compared for treating 1 m^3 of stabilized leachate with H_2O_2 (100 USD) and $KMnO_4$ (294 USD) respectively (Nabihah Abdullah *et.al.*2014). The both batch and continuous modes of operation for the electro-Fenton (EF) process were investigated (P.V Nidheesh *et.al, 2015)* for the treatment of textile effluent. In batch mode, the influence of operating parameters on the removal of colour and chemical oxygen demand (COD) from textile wastewater was investigated. The continuous flow mode was then operated using the best conditions determined from the batch studies. In batch mode under ideal circumstances, 57% of COD and 83% of colour from the wastewater were eliminated. A bubble column reactor was used in continuous mode to remove 67.7% of colour and 37% of COD. Additionally, after EF oxidation, the biodegradability of the textile effluents improved. Finally it can be concluded that, the EF method as a pretreatment has a great potential for removing colour and COD from textile wastewater. Nematollah Jaafarzadeh *et.al* (2016) performed the effective integrated processes of Permanganate (PM), electro-Fenton (EF), and Co_3O_4/PMS/UV (SR-AOP) to treat pulp and paper wastewater (PPW). The electro-Fenton process was pretreated with permanganate (PM) oxidation, and the EF effluent was fed into a sulfate radical (SR)-based process (Co_3O_4/PMS/UV). On the reduction of chemical oxygen demand (COD), the key operational parameters of each process were evaluated. After applying the integrated process, the COD value of the effluent was decreased by 95% and also after the EF and SR treatments, biodegradability was also improved. The sequence of these processes was evaluated, and it was discovered that the combination of PM+EF+SR was effective in removing COD and could meet discharge standards. The germination index was used to assess the phytotoxicity of the effluents generated in each process. Puspalatha M *et.al.* (2017) reviewed the treatment of various wastewaters using EF process. This review paper author focused on EF development, use, and advantages for the remediation of wastewater from various industries and some influencing factors like pH, Electrode distance & current, Fe^{2+} concentration, H_2O_2 concentration. Due to its effectiveness and cheap operating costs, it is an alternate approach for treating various wastewater and for removing COD, TOC, and colour. The review concludes that, when compared to other methods EF process is promising and efficient method for treatment and mineralization of inorganic and organic wastewater and also doesn't produce any harmful end products. The EF process used to evaluate the efficiency of COD reduction in ADSW for different variables such as current intensity, pH, reaction time and solution agitation speed (V. P. Patil *et.al.*2019*)*.The batch experiments were conducted using an electrochemical batch reactor and two parallel-connected iron electrodes. The electro-Fenton process was studied for optimization of power consumption, agitation speed and the reaction time under various pH conditions (3.0, 5.0 and 7.0). For Electro-Fenton process, 24.9% ADSW COD reduction was attained using Fe-Fe electrode in electrolysis treatment. The COD removal efficiency found more at low pH (3.00), agitation speed 500 rpm, treatment time 120 min and power consumption 15 W. Finally, it concluded that ADSW with a high organic content can be successfully treated using the Electro-Fenton process.

Table 1: General Characteristics of Spentwash

Sl. No	Parameters	Units	Effluent Values
1	Colour	-	Dark Brown
2	Odour	-	Unpleasant burn
3	pH	-	3.5-4.5
4	Total solids	mg/l	150000-160000
5	Total dissolved solids	mg/l	90000-150000
6	COD	mg/l	110000-190000
7	BOD	mg/l	50000-60000
8	Chlorides	mg/l	8000-8500
9	Sulfate	mg/l	7500-9000
10	Total Nitrogen	mg/l	5000-7000
11	Phosphorous	mg/l	2500-2700
*pH has no unit			
Source: Conditions for Fermentation Industry CPCB			

III. ISSUES AND CHALLENGES

The conventional approaches only treat spentwash to a limited extent. These technologies do, however, have some limitations that prevent full adherence to the specified standards. These restrictions are forced on by either the high cost of treatment or the inability of technology to safely and effectively reduce the pollutants, for discharge into water bodies or on lands. There is a need for an efficient, feasible, and economical treatment plan that can mineralize organic contaminants.

IV. OBJECTIVES

- The main objective of the present work is to examine and compare the removal of COD and colour of distillery effluent by using electrochemical method.
- To investigate the impact of different operating parameter such as concentration of H_2O_2, pH, optimum voltage, and reaction time on the removal efficiency of COD and colour of distillery effluent by batch process with aid of "Response Surface Methodology (RSM)" and also to optimize these operational parameters to achieve optimum efficiency.
- To assess the phytotoxicity of the effluents generated in EF process using the germination index.

V. MATERIALS

Table 2: Material Specifications

Materials	Specifications
Iron Electrodes	10 cm x 3 cm x 1 cm
Whatman Filter Paper	Diameter 125mm
Acrylic Box reactor (2.5L capacity)	10 cm x 15 cm x 16 cm

Chemicals

The chemicals used in this study were the entire analytical grade. Chemicals were procured from Bangalore-based Merck Company.

Table 3: General Properties of Chemical

Chemical Compound	Formula	Molar mass	Density
Hydrogen peroxide	H_2O_2	34.0147 g/mol	1.45 g/cm³
Sodium hydroxide	NaOH	39.997 g/mol	2.13 g/cm³
Potassium dichromate	$K2Cr_2O_7$	294.185 g/mol	2.68 g/cm³
Mercury(II) sulfate	$HgSO_4$	296.65 g/mol	6.47 g/cm³

Instruments

- ❖ Spectrophotometer is a device that counts the number of photons (light particles) absorbed after they pass through a sample solution.

Fig. 1 Spectrophotometer

- ❖ TOC-L Analyzer (Shimadzu) is a Total Organic Carbon analyzer that converts organic carbon into CO_2 by using a catalytic oxidation combustion process at high temperatures (up to 720 °C).

Fig. 2 TOC-L Analyzer (Shimadzu)

- ❖ Germination Chamber is closed chamber that provides an optimum humidity and temperature control to help start seedlings.

Fig. 3 Germination Chamber

- ❖ COD Digester is used to measure the chemical oxygen demand (COD) of sample.

Fig.4 COD Digester

VI. METHODOLOGY

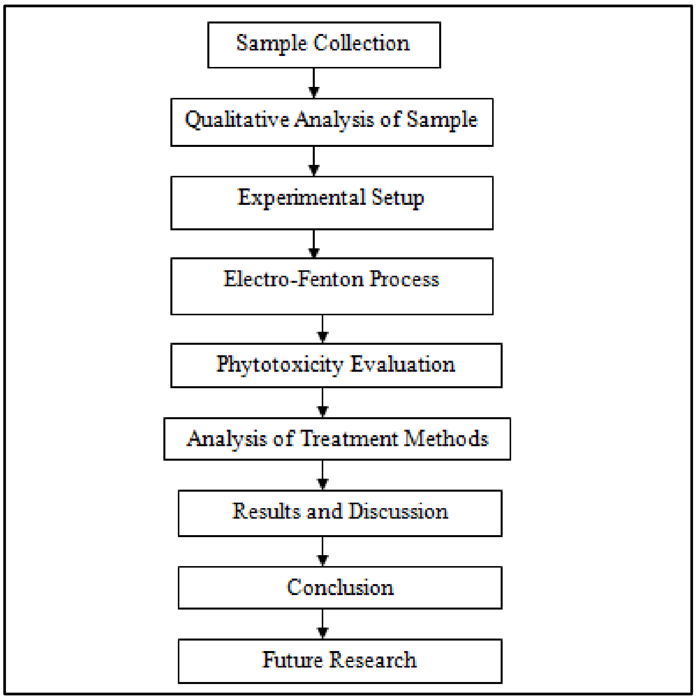


Fig. 5: Methodology for Distillery Spentwash Treatment

Sample Collection:

Spentwash was collected from a distillery near Vijaypur, Karnataka State, India. The collected grab samples were preserved and brought to the laboratory maintaining temperature below 4°C.

Qualitative Analysis of Sample

The characterization study (Table 4) was carried out right away in the lab using the 20th edition of the "Standard Methods for the Examination of Water and Wastewater".

Table 4 Characteristics of Spentwash

Sl. No	Parameters	Units	Value	Test Method
1	pH	-	3	pH Meter
2	Chemical Oxygen Demand	mg/L	110000	Open Reflux Method
3	Biochemical Oxygen Demand	mg/L	42000	Dilution Method
4	Conductivity	µS/cm	390	Conductivity Meter
5	Total Dissolved Solids	mg/L	92000	TDS Meter
6	Chloride	mg/L	10600	Argentometric Method
7	Nitrogen	mg/L	1460	Spectrophotometry Method
9	Total Suspended Solids	mg/L	26000	Gravimetric Method
10	Alkalinity	mg/L	600	Titrimetric Method
11	TOC	mg/L	58000	TOC analyzer

Experimental Set Up

Electro-Fenton (EF) Process:

The experiments were conducted at room temperature and atmospheric pressure in an open rectangular Acrylic Box with a capacity of 2.5 L (10 cm x 15 cm x 16 cm), while its effluent's working volume was 2.0 L. The pH of the sample taken is adjusted by 1M H_2SO_4 or 1M NaOH before conducting the experiments. For EF process, iron electrode (10 cm x 3 cm x 0.1 cm) pair was used. The electrodes were washed with 10% HCl solution before and after every experiment to remove dissolve matters on electrodes. A preferential quantity of hydrogen peroxide (H_2O_2) was added in each run. The electrodes were inserted into the reactor, and the current density will be adjusted accordingly. The electrodes were 3 cm apart, and the solution was mixed at 200rpm. To ensure adequate mixing, the solution was agitated with a magnetic bar. Electrical current was applied using a digital DC power supply. After each run, the samples will be allowed to settle for 30 minutes. A 10mL sample of the supernatant will be taken for COD and colour analysis. The supernatant of 10 mL was taken out for COD, and colour for phytotoxicity analysis.

Figure 6: Diagram of EF apparatus.

Response Surface Methodology (RSM) is used to optimize the operating parameters for this process. Parameters considered for the process; namely, H_2O_2 Dosage, reaction time, voltage and pH are taken as in the Box- Behnken statistical design with low and high values. The COD and Colour are represented by a response function. Tables 5, 6 and 7 provide the RSM build information, the coded upper and lower limits and experimental runs for EF process respectively.

Table 5 RSM Build Information

File Version	12.0.11.0		
Study Type	Response Surface	**Subtype**	Randomized
Design Type	Box-Behnken	**Runs**	27.00
Design Model	Quadratic	**Blocks**	No Blocks
Build Time (ms)	2.00		

Table 6 RSM Factors Information

Factor	Name	Units	Minimum	Maximum
A	pH	-	3.00	5.00
B	H_2O_2 Dosage	ml/L	5.00	45.00
C	Reaction Time	min	10.00	100.00
D	Voltage	V	1.00	5.00

Table 7 Experimental Runs for EF Process

	Factor 1	Factor 2	Factor 3	Factor 4
Run	**A:pH**	**B: H_2O_2 Dosage**	**C: Reaction Time**	**D:Voltage**
		ml/L	**min**	**V**
1	5	25	55	1
2	5	5	55	3
3	4	25	10	5
4	**4**	**25**	**55**	**3**
5	4	5	55	5
6	3	5	55	3
7	3	25	100	3
8	4	25	100	5
9	5	45	55	3
10	4	25	100	1
11	4	45	55	1
12	3	25	55	1
13	4	45	55	5
14	5	25	55	5
15	**4**	**25**	**55**	**3**
16	4	5	10	3
17	3	25	10	3
18	4	25	10	1
19	4	45	10	3
20	3	45	55	3
21	4	45	100	3
22	5	25	100	3
23	3	25	55	5
24	5	25	10	3
25	4	5	55	1
26	4	5	100	3
27	**4**	**25**	**55**	**3**

Phytotoxicity Evaluation

In the present study, the germination index (GI) was used to assess the phytotoxicity of untreated and treated wastewater. The radish (Raphanus sativus), Fenugreek (Trigonella foenum-graecum), were used to test phytotoxicity. The tests were conducted on untreated spentwash, EF treated spentwash. The 20 seeds from each species were evenly distributed in a Petri plates with a filter paper. After each phase of the treatment, 10 mL of sample which was placed in plastic Petri plates. To limit moisture loss, the Petri plates were sealed with nescofilm and incubated in germination chamber at 25 °C for 72 hours. The GI (percentage) was determined using below equation.

$$\text{GI (\%)} = 100 \text{ X } \frac{\text{Seed germination X root length of the sample}}{\text{Seed germination X root length of the control}}$$

Analysis of Treated Sample

After each run, COD and colour removal values are going determined by standard methods. The open reflux method will be used to determine the COD value, Colour removal values are determined by absorbance characteristics in UV-Vis range using UV-Vis Spectrophotometer. The wavelength for determination of absorbance value of spentwash was determined by the colour of the table of the sample and 475nm was used for analysis. TOC-L Analyzer will be used to determine the TOC values. The Whatmann 42 filter papers were used to filter out the treated samples.

The following calculation was used to determine percentage of colour removed from the effluent.

$$\text{\% Colour removal} = \frac{Abs_o - Abs_t}{Abs_o} \text{ X } 100$$

Where, Abs_o and Abs_t represent the absorbance values at initial time interval and at any time interval t for respectively, for similar wavelength $\lambda_{max.}$

The following calculation was used to determine percentage of COD removed from the effluent.

$$\text{\% COD removal} = \frac{COD_o - COD_t}{COD_o} \text{ X } 100$$

Where, COD_o, COD_t represent the chemical oxygen demand values at initial time interval and at any time interval t for respectively, are given mg/L.

VII. RESULTS AND DISCUSSION

The experiments were conducted using electro-Fenton method for the treatment of spentwash. In order to treat spentwash as effectively as possible, DOE was carried out using Design Expert (Trial Version) software, and RSM was used to study the various influencing parameters, including pH, oxidant dosage, reaction time, voltage. By using a Box-Behnken design with three variables and two levels, 27 experimental runs were obtained for EF process (Table 8). According to these trials, a pH of 4, a H_2O_2 dosage of 25 ml/L, voltage of 3V and a reaction duration of 55 minutes resulted in a higher COD and colour removal efficiency. The obtained results showed the maximum COD and colour removal efficiency of 35.31% and 88.55%, respectively.

Table 8 Experimental run of EF Process

	Response 1	Response 2
Run	**COD Removal**	**Colour Removal**
	%	**%**
1	18.05	35.16
2	17.01	32.07
3	16.15	30.24
4	**35.31**	**88.55**
5	14.36	27.41
6	14.32	28.34
7	23.68	48.52
8	25.2	56.3
9	25.04	55.06
10	17.27	30.22
11	15.36	29.39
12	17.86	32.46
13	20.09	39.24
14	28.89	63.41
15	**35.31**	**88.55**
16	12.32	22.56
17	13.26	25.83
18	13.36	26.89
19	15.31	29.86
20	20.24	38.29
21	25.31	56.32
22	25.6	58.48
23	24.78	50.32
24	18.36	37.12
25	11.28	20.36
26	13.21	25.63
27	**35.31**	**88.55**

Effects of pH on COD and Colour reduction

The acidic conditions were beneficial for electro-Fenton (EF) process for COD and colour removal from spentwash. Therefore, effects of pH in the range of 3–5 were examined, on the COD and colour removal by EF process and results were obtained. Fig. 7 and 8 show, pH from 3 to 4 the COD and colour reduction increased from 13.26% to 35.31% and 25.83% to 88.55% respectively. For pH value beyond 4, the reduction efficiency of COD and colour were reduced from 35.31% to 17.01% and 88.55% to 32.07% respectively. According to the results, pH of 4 was had the maximum COD and colour reduction efficiency of 35.31% and 88.55% respectively.

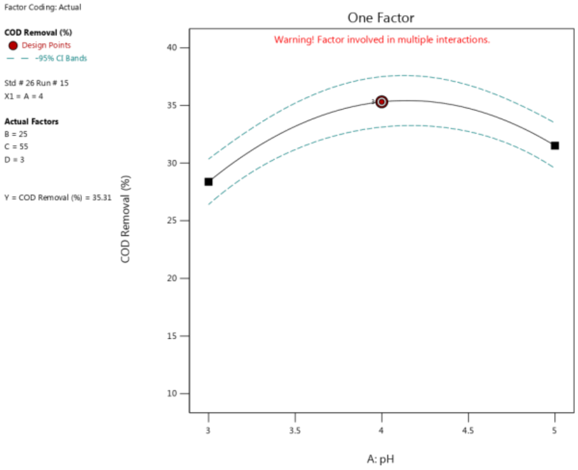


Fig.7 Influence of pH for COD reduction

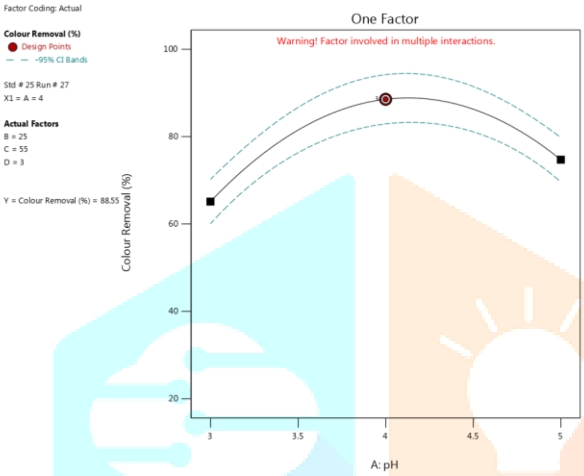


Fig. 8 Influence of pH for Colour reduction

Effects of H_2O_2 Dosage on COD and Colour reduction

The experiments were carried out by varying H_2O_2 dosage from 5 ml/L to 45 ml/L in order to assess the role of H_2O_2 dosage in the electro-Fenton process. Fig. 9 and 10 shows, H_2O_2 dosage from 5 ml/L to 25 ml/L the COD and colour reduction increased from 11.28% to 35.31% and 20.36% to 88.55% respectively. For H_2O_2 dosage beyond 25 ml/L, the COD and colour removal efficiency was reduced from 35.31% to 15.31% and 88.55% to 29.86% respectively. This may be caused by the recombination of OH^o radicals and the auto-decomposition of H_2O_2 to O_2 and H_2O. The results showed that, H_2O_2 dosage of 25 ml/L had the maximum COD and colour removal efficiency of 35.31% and 88.55% respectively.

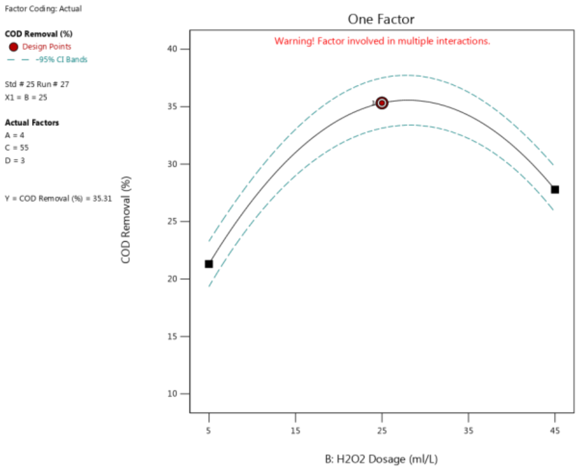


Fig. 9 Influence of H_2O_2 for COD reduction

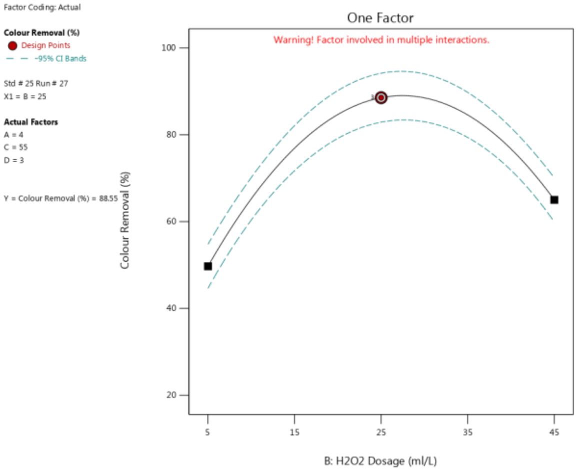


Fig. 10 Influence of H_2O_2 for Colour reduction

Effects of Reaction Time on COD and Colour reduction

The effects of reaction time on reduction of COD and colour were investigated. To minimize the power consumption during electro-Fenton process, the reaction time for treating the spentwash must be as short as possible. Fig. 11 and 12 show reaction time from 10 to 55 minutes the COD and colour reduction increased from 12.32% to 35.31% and 22.56% to 88.55% respectively. For reaction time beyond 55 minutes, the removal efficiency of COD and colour was reduced from 35.31% to 13.21% and 88.55% to 25.63% respectively. According to the results, reaction time of 55 minute had the maximum COD and colour removal efficiency of 35.31% and 88.55% respectively.

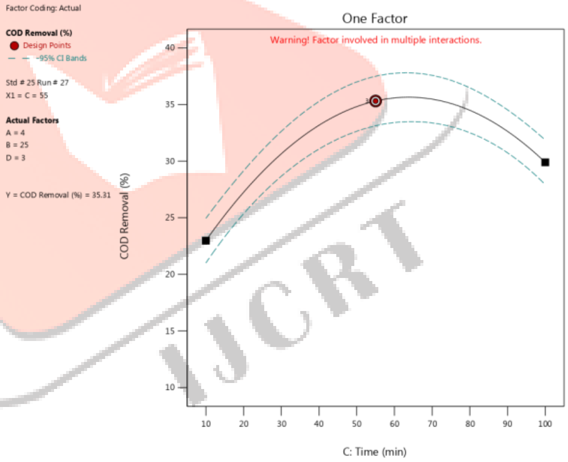


Fig. 11 Influence of Reaction Time for COD reduction

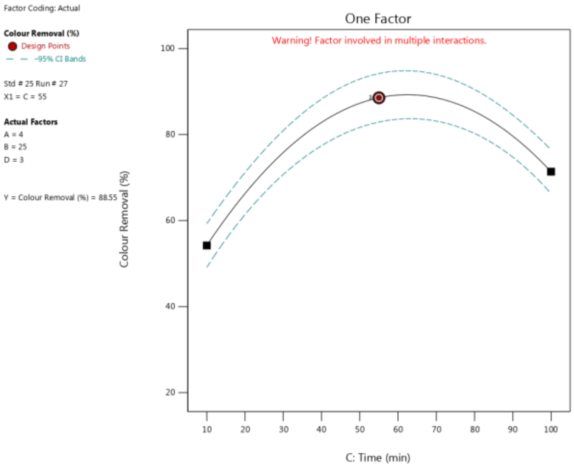


Fig. 12 Influence of Reaction Time for Colour reduction

Effects of Voltage on COD and Colour reduction

The effects of voltage on COD and colour reduction were investigated. To minimize the power consumption during electro-Fenton process, the voltage for treating the spentwash must be kept as low as possible. Fig. 13 and 14 shows voltage from 1V to 3V the COD and colour reduction increased from 11.28% to 35.31% and 20.36% to 88.55% respectively. For voltage beyond 3V, the removal efficiency of COD and colour was reduced from 35.31% to 14.36% and 88.55% to 27.41% respectively. According to the results, voltage 3V was had the maximum COD and colour removal efficiency of 35.31% and 88.55% respectively.

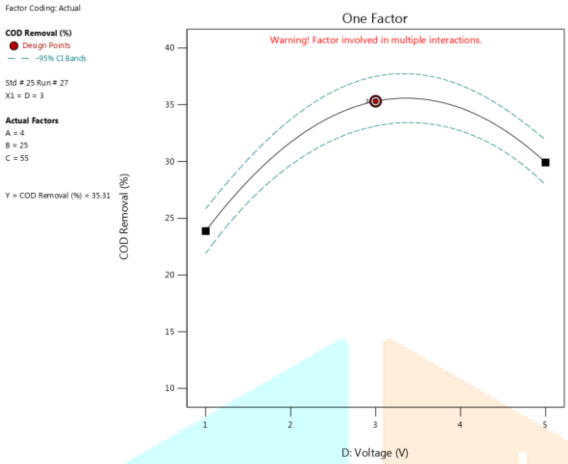


Fig. 13 Influence of Voltage for COD reduction

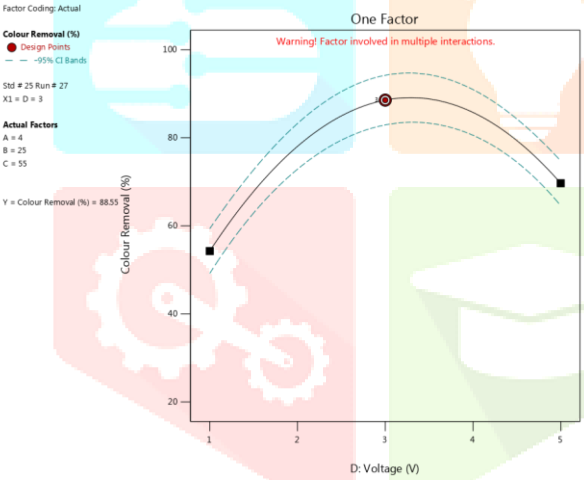
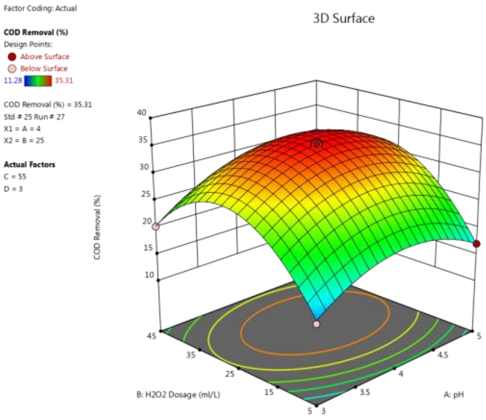


Fig. 14 Influence of Voltage for Colour reduction



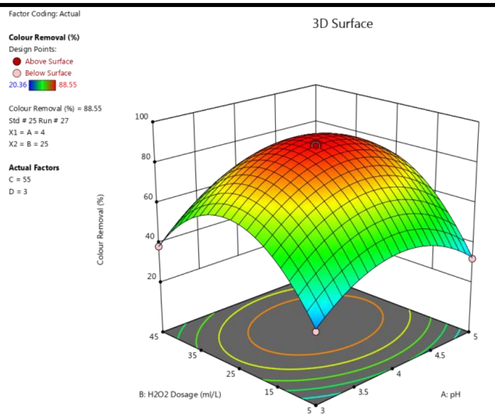
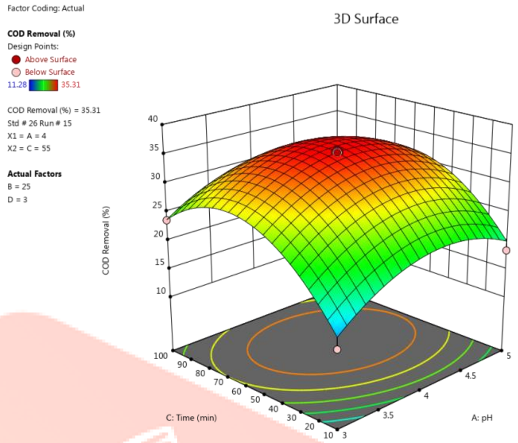


Fig. 15 3D plot of pH and H_2O_2 Dosage interaction for COD and Colour reduction



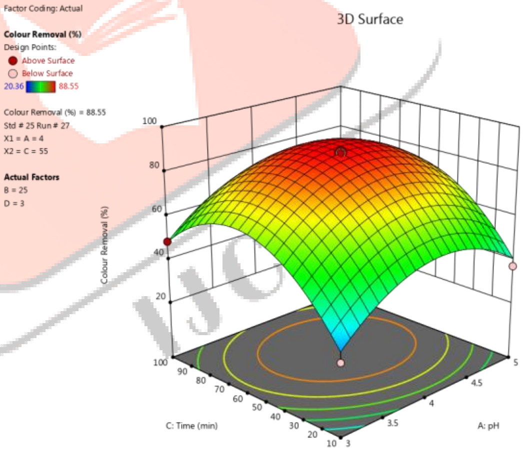
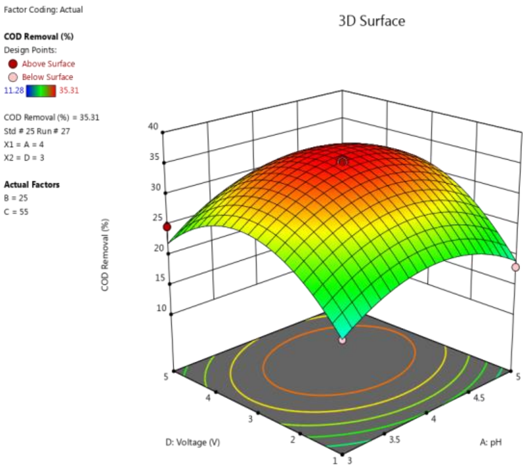


Fig.16 3D plot of pH and Reaction Time interaction for COD and Colour reduction



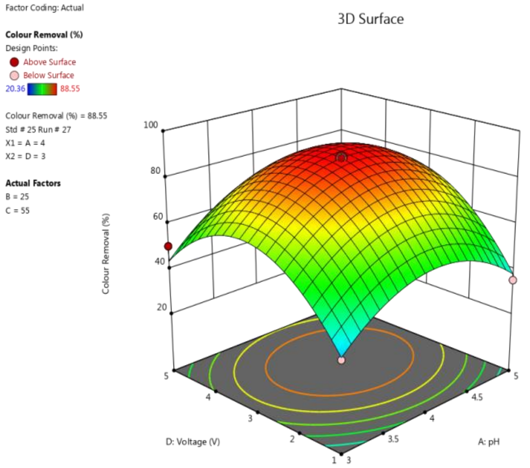


Fig. 17 3D plot of pH and Voltage interaction for COD and Colour reduction

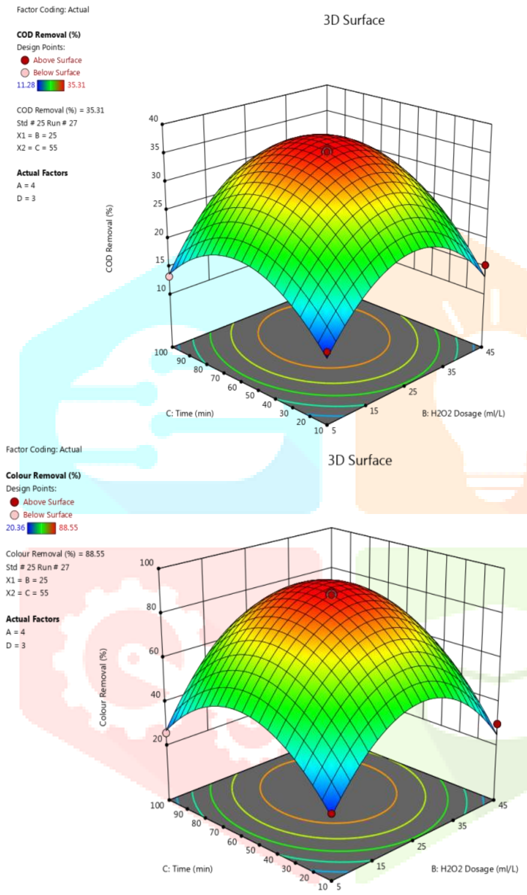
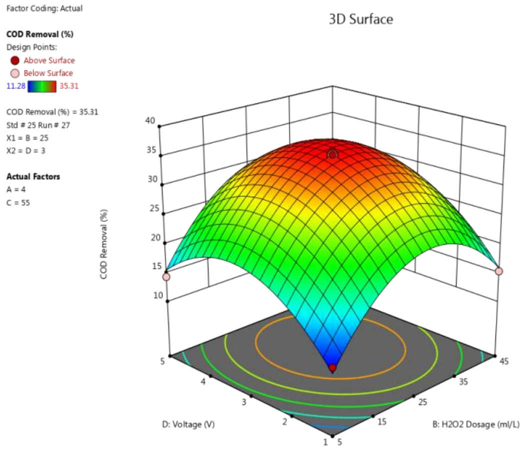


Fig.18 3D plot of H_2O_2 Dosage and Reaction Time interaction for COD and Colour reduction



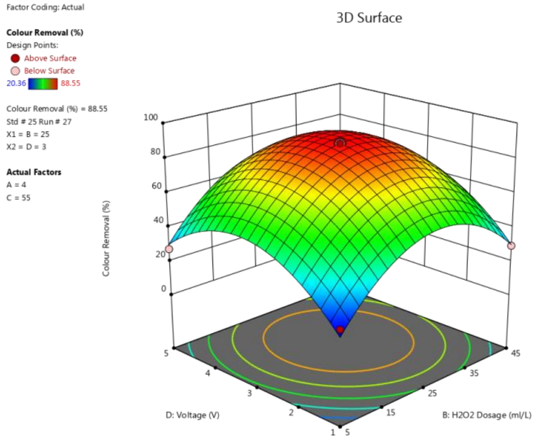


Fig. 19 3D plot of H_2O_2 Dosage and Voltage interaction for COD and Colour reduction

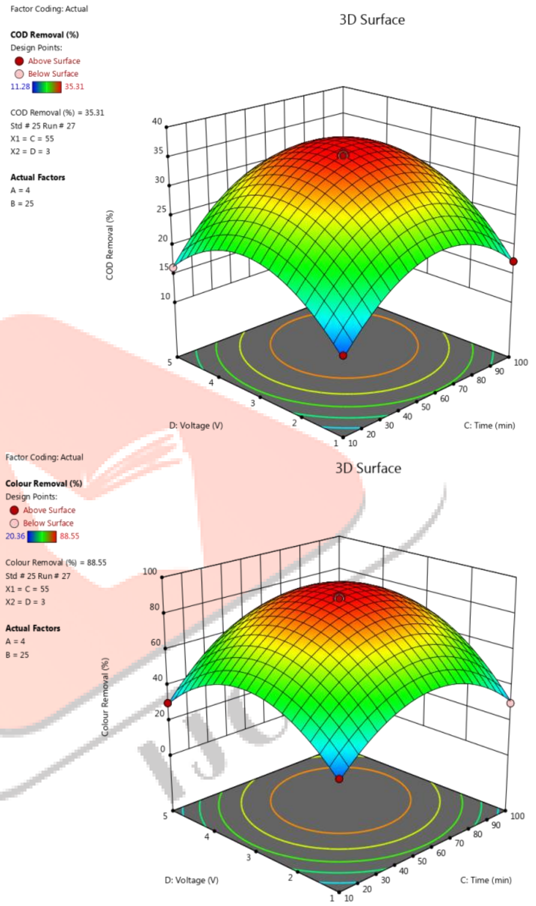


Fig. 20 3D plot of Reaction time and Voltage interaction for COD and Colour reduction

The 3D plots of the interactions between two parameters are shown in Figs. 15 to 20, and these graphs demonstrate that, pH and H_2O_2 dosage interaction was showed that pH from 3 to 4 and H_2O_2 dosage from 5ml/L to 25ml/L, the COD and colour reduction increased but for pH and H_2O_2 dosage values beyond 4 and 25ml/L respectively, the COD and colour removal efficiency was reduced due to process favorable in acidic conditions and excess H_2O_2 dosage inhibit the reaction. The pH and reaction time interaction was showed that pH from 3 to 4 and reaction time from 10min to 55min, the COD and colour reduction increased but for pH and reaction time values beyond 4 and 55min respectively, the removal efficiency of COD and colour was reduced due to process favorable in acidic conditions and excess reaction time limit the reaction. The pH and voltage interaction was showed that voltage from 1V to 3V and pH from 3 to 4, the COD and colour reduction increased but for pH and voltage values beyond 4 and 3V respectively, the COD and colour removal efficiency was reduced due to process favorable in acidic conditions and high voltage produce foam which limit the reaction. The H_2O_2 dosage and reaction time interaction was showed that H_2O_2 dosage from 5ml/L to 25ml/L and reaction time from 10min to 55min, the COD and colour reduction increased but for H_2O_2 dosage and reaction time values beyond 25ml/L and 55min respectively, the removal efficiency of COD and colour was reduced due to excess H_2O_2 dosage and excess reaction time inhibit the reaction. The H_2O_2 dosage and voltage interaction was showed that H_2O_2 dosage from 5ml/L to 25ml/L and voltage from 1V to 3V, the COD and colour reduction increased but for H_2O_2 dosage and voltage values beyond 25ml/L and 3V respectively, the COD and colour removal efficiency was reduced due to excess H_2O_2 dosage and high voltage produce foam which limit the reaction. The reaction time and voltage interaction was showed that reaction time from 10 min to 55 min and voltage from 1V to 3V, the COD and colour reduction increased but for reaction time and voltage values beyond 3V and 55 min respectively, the removal efficiency of COD and colour was reduced due to excess reaction time and high voltage produce foam which limit the reaction.

Fit Summary Analysis for COD and Colour Response

Design Expert v.11 was used to do a model fit study for responses from electro-chemical process. Four process models were developed for COD and colour removal: linear, 2 Factor interaction (FI), Quadratic, and Cubic. The suggested quadratic model for COD and colour responses (Tables 9 and 10) were chosen for further investigation due to its Predicted R^2 values, which is close to Adjusted R^2.

Table 9 Model fit analysis for COD response

Source	**Sequential p-values**	**Adjusted R^2 values**	**Predicted R^2 values**	
Linear	0.0810	0.1770	0.1472	
2FI	0.9947	-0.0887	-0.1267	
Quadratic	**< 0.0001**	**0.9416**	**0.8448**	**Suggested**
Cubic	0.5238	0.9430	-0.2633	Aliased

Table 10 Model fit analysis for colour response

Source	**Sequential p-value**	**Adjusted R^2**	**Predicted R^2**	
Linear	0.1793	0.1010	0.0870	
2FI	0.9932	-0.1851	-0.1374	
Quadratic	**< 0.0001**	**0.9515**	**0.8709**	**Suggested**
Cubic	0.3214	0.9668	0.2635	Aliased

ANOVA for COD and colour response

Table 11 ANOVA for Quadratic model, COD response

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	1309.40	14	93.53	30.96	< 0.0001	significant
A-pH	29.48	1	29.48	9.76	0.0088	
B-H_2O_2 Dosage	125.78	1	125.78	41.63	< 0.0001	
C-Time	143.59	1	143.59	47.53	< 0.0001	
D-Voltage	109.75	1	109.75	36.33	< 0.0001	
AB	1.11	1	1.11	0.3684	0.5552	
AC	2.53	1	2.53	0.8369	0.3783	
AD	3.84	1	3.84	1.27	0.2815	
BC	20.75	1	20.75	6.87	0.0224	
BD	0.6806	1	0.6806	0.2253	0.6436	
CD	6.60	1	6.60	2.19	0.1650	
A^2	153.51	1	153.51	50.82	< 0.0001	
B^2	618.63	1	618.63	204.78	< 0.0001	
C^2	419.85	1	419.85	138.98	< 0.0001	
D^2	378.11	1	378.11	125.16	< 0.0001	
Residual	36.25	12	3.02			
Lack of Fit	36.25	10	3.63			
Pure Error	0.0000	2	0.0000			
Cor Total	1345.65	26				

Table 12 ANOVA for Quadratic model, colour response

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	10514.15	14	751.01	37.40	< 0.0001	significant
A-pH	275.90	1	275.90	13.74	0.0030	
B-H2O2 Dosage	702.12	1	702.12	34.96	< 0.0001	
C-Time	883.57	1	883.57	44.00	< 0.0001	
D-Voltage	712.10	1	712.10	35.46	< 0.0001	
AB	42.51	1	42.51	2.12	0.1713	
AC	0.4422	1	0.4422	0.0220	0.8845	
AD	26.99	1	26.99	1.34	0.2689	
BC	136.77	1	136.77	6.81	0.0228	
BD	1.96	1	1.96	0.0976	0.7601	
CD	129.16	1	129.16	6.43	0.0261	
A^2	1849.26	1	1849.26	92.09	< 0.0001	
B^2	5187.38	1	5187.38	258.32	< 0.0001	
C^2	3538.28	1	3538.28	176.20	< 0.0001	
D^2	3767.51	1	3767.51	187.61	< 0.0001	
Residual	240.98	12	20.08			
Lack of Fit	240.98	10	24.10			
Pure Error	0.0000	2	0.0000			
Cor Total	10755.12	26				

Factor coding is **coded**.
Sum of squares is **Type III – Partial**

The Tables 11 and 12 gives the "**Model F-value"** of 30.96 and 37.40 for COD and colour responses respectively. It suggests that the model is statistically significant. The probability that noise caused this high F-value to happen is comparatively low (0.01%).

The Tables 11 and 12 shows the model terms are significant when the P-value is less than 0.0500. For COD the model terms A, B, C, D, BC, A^2, B^2, C^2, and D^2 were significant and for colour the model terms A, B, C, D, BC, CD, A^2, B^2, C^2, D^2 were significant in this case; however AC, AB, BD, AD are not significant for both COD and colour responses

Fit Statistics for COD and Colour Response

Table 13 Fit statistics for COD response

Std. Dev.	1.74		**R^2**	0.9731
Mean	20.45		**Adjusted R^2**	0.9416
C.V. %	8.50		**Predicted R^2**	0.8448
			Adeq Precision	19.3279

Table 14 Fit statistics for colour response

Std. Dev.	4.48		**R²**	0.9776
Mean	43.15		**Adjusted R²**	0.9515
C.V. %	10.38		**Predicted R²**	0.8709
			Adeq Precision	21.6813

The Tables 13 and 14 for both the COD and colour response, the difference between the Predicted R^2 of 0.8448 & 0.8709 and the Adjusted R^2 of 0.9416 & 0.9515 respectively is less than 0.2. The ratio of signal to noise is measured by Adeq Precision. A ratio of at least 4 is recommended. Your signal is strong enough based on your ratio of 19.328 and 21.681 respectively, for both COD and colour responses. To navigate the design space, this model can be utilized.

Phytotoxicity Evaluation

The results of germination tests conducted on two seeds after Electro-Fenton process. The raw spentwash showed a characteristic that inhibited the germination of all species due to high COD and dissolved solids. Following the application of EF, the GI values of radish and fenugreek were increased to 78.61% and 49.53% respectively. The results obtained showed a reduction in phytotoxicity of the treated effluents.

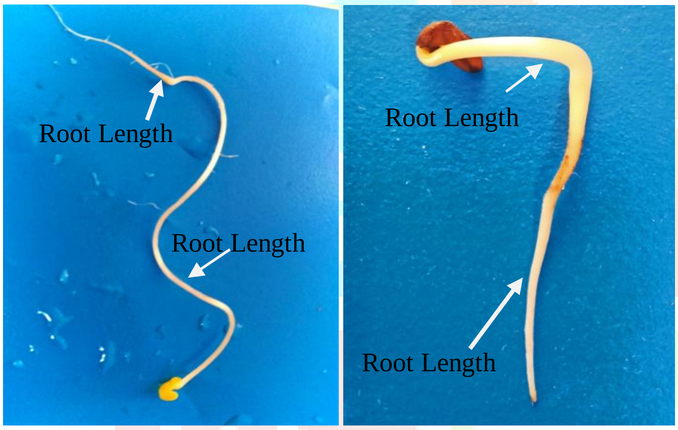


Fig 21 Root length and shoot length of germinated seeds

Table 15 Root length values for Control and EF processes

Sl.No	**Root Length of Control (cm)**		**Root Length of EF (cm)**	
	Radish Seeds	Fenugreek Seeds	Radish Seeds	Fenugreek Seeds
1	1.6	6	5	2.4
2	5	3.2	2.2	1.9
3	2.5	3	2.5	1.2
4	1.5	2.2	4	1.4
5	5	2.5	3.6	0.6
6	7	5	2.4	1.5
7	3	8.1	5.1	4
8	4.2	2	4.5	1.5
9	3.5	1.5	3.8	1
10	1	4.1	3.6	1.7
11	3.5	4	3.2	1.5
12	2	2.5	1.9	1.8
13	6	1	1.7	1.4
14	7	3.5	2	1.6
15	3	2.6	2.5	0.7
16	1.5	0.8	1.2	1.2
17	3.5	0.5	4	0.9
18	2.2	1	0.5	0.2
19	2.8	-	0.5	-
20	2.7	-	-	-

CONCLUSION

The treatment of distillery spentwash in this study involved the utilization of electrochemical (EF) method. The reduction efficiency of electro-Fenton (EF) for COD and colour removal were examined independently in the test. DOE was performed with Design Expert (Trial Version) software, and RSM (Box-Behnken) was used to optimize the influencing parameters, including pH, oxidant dosage, reaction duration, and voltage. For electro-Fenton method, RSM offered 27 experimental runs. The procedure works best when the pH of 4, the H_2O_2 dosage of 25 ml/L, the voltage of 3V, and the reaction time of 55 minutes. Under these conditions, the efficiency of COD and colour removal increases to 35.31% and 88.55%, respectively. The results obtained showed a reduction in phytotoxicity of the treated effluents. Following the application of EF, the GI values of radish and fenugreek were increased to 78.61% and 49.53% respectively.

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