A Comparative Study on the Competitiveness of Photo-Assisted Chemical Oxidation (PACO) with Electrocoagulation (EC) for the Effective Decolorization of Reactive Blue Dye

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ABSTRACT: *Accumulation of large quantity of non-biodegradable textile dyes into the environment made much attention to finding a suitable solution for the degradation of textile dyes. In this present study, decolorization efficiency of two different treatment technologies such as Photo-Assisted Chemical Oxidation (PACO – UV/H_2O_2) and Electrocoagulation (EC) on Reactive Blue 194 dye solution (RB194) at different operational conditions were analyzed and the competitiveness of the treatment technologies in terms of energy consumption and operational costs were discussed. Even though both the processes follow different mechanistic approach for the degradation of dye solution, both the processes achieved more than 99% of decolorization efficiency. In terms of material/chemical consumption for the decolorization of dye solution PACO (US$ 0.016) competes with the EC (US$ 0.5937). But in terms of electrical energy consumption as well as the overall operating cost EC process compete (US$ 0.0481 & US$ 0.6418) with the PACO process (US$ 1.0267 & US$ 1.04337).*

KEYWORDS: *EC; PACO; UV/H_2O_2; RB194; Energy consumption; Decolorization.*

INTRODUCTION

A Large volume of water and chemicals were consumed for the wet processing of fabrics in textile Industries Effluent from this industry causes tremendous threats by giving changes to water quality parameters of water bodies.

Due to the consumption of large quantity of azo dyes in the dyeing processes increased considerable amount of strong color with low biodegradability in the textile effluent [1]. Many of the conventional treatment processes such as biological treatment, adsorption, chemical coagulation and flocculation were not successful in the degradation process due to the high complex structure of present dyes [2]. In the recent years, advanced oxidation process [3], electrocoagulation [4], reverse osmosis [5] and nano-filtration [6] showed remarkable record on the treatment efficiency of the textile wastewater. Among this electrocoagulation showed an attention due to its wide usage on treating the variety of wastewater such as paper mills [7], phosphate [8], boron [9], arsenic [10] and tannery industries [11]. On the other hand, advanced oxidation processes have gained much attention due to their production of OH° radicals which are capable of destroying components that are hard to be oxidized [12-14]. So in this context, comparison of competence of EC process with PACO on treatability of non-biodegradable azo dyes (Reactive Blue – 194, RB194) was carried out.

EXPERIMENTAL SECTION
A brief description of Treatment technologies
Selection of dye

Based on the characteristic study on the real time textile effluents [15], among the different classes of dye, due to the higher complexity of degradation of textile dyes, azo dyes are preferred for this study. The electronic transition between the molecular orbitals determines the intensity of the color of the dye. Understanding the basic structure and its complexity of the dye is much important before going into the experimentation. In general, at least one nitrogen-nitrogen (N=N) double bond present in azo dyes, but many different structures are also possible. Two, three or more azo groups may be present in some of the dye molecules are called as mono azo, diazo or poly azo dyes. These azo groups are connected with the side groups (such as benzene, naphthalene or aromatic compounds) that are necessary for bring the color and intensity to the dye molecules. Table 1 showed the chemical structure and characteristics of selected dye for the study (sulphonated diazo dyes - RB194 dye) was given in Table 1.

Where:

S	C	B	R	L
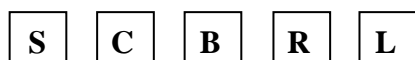
S = Water solubilizing group, **C** = Chromogen, **B** = Bringing group (can be part of chromogen), **R** = Reactive group, **L** = Fiber reactive or leaving group
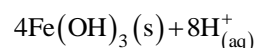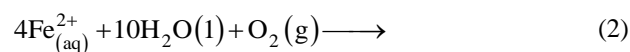
Electrocoagulation (EC)

EC is a simple electrochemical technique which showed significant advantages such as compact, high velocity of treatment, short time, easy handling and no additional chemical usage [16]. Sacrificial anode generates a metal ion that follows different mechanism to produce hydroxide or poly hydroxide in the bulk of the solution, which strongly absorbs dispersed compound molecules and results in coagulation [17]. Hydrogen is produced in cathodes can help mass particles float and come out of water [18,19]. *Daneshvar et al.*, proposed two mechanisms for the production of the metal hydroxide during EC process [20].
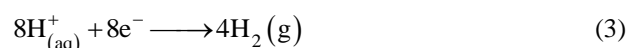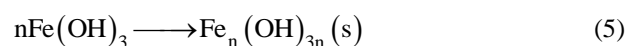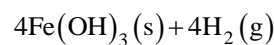
Mechanism 1:

At the anode

$$4Fe(s) \longrightarrow 4Fe^{2+}_{(aq)} + 8e^- \tag{1}$$

At the bulk of the solution

$$4Fe^{2+}_{(aq)} + 10H_2O(1) + O_2(g) \longrightarrow \tag{2}$$
$$4Fe(OH)_3(s) + 8H^+_{(aq)}$$

At the cathode

$$8H^+_{(aq)} + 8e^- \longrightarrow 4H_2(g) \tag{3}$$

Overall reaction

$$4Fe(s) + 10H_2O(1) + O_2(g) \longrightarrow \tag{4}$$
$$4Fe(OH)_3(s) + 4H_2(g)$$

$$nFe(OH)_3 \longrightarrow Fe_n(OH)_{3n}(s) \tag{5}$$

Mechanism 2:

At the anode

$$Fe(s) \longrightarrow 4Fe^{2+}_{(aq)} + 2e^- \tag{6}$$

At the bulk of the solution

$$4Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Fe(OH)_2(s) \tag{7}$$
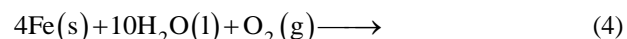
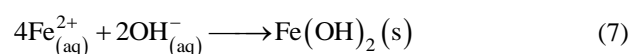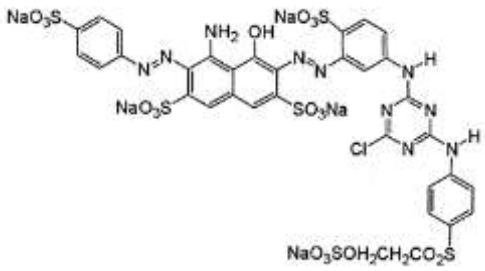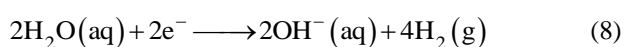***Table 1: Chemical structure and characteristics of Reactive Blue 194 (RB194).***

Chemical Structure	Chemical Formula	CAS Registry Number	Chemical Class	λ_{max}	Molecular weight
	$C_{33}H_{22}ClN_{10}Na_5O_{19}S_6$	93050-78-3	Sulphonated diazo	590	1205.38

At the cathode

$$2H_2O(aq) + 2e^- \longrightarrow 2OH^-(aq) + 4H_2(g) \tag{8}$$

Overall reaction

$$Fe(s) + 2H_2O(l) \longrightarrow Fe(OH)_2(s) + H_2(g) \tag{9}$$
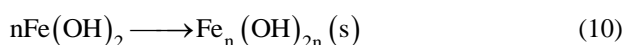
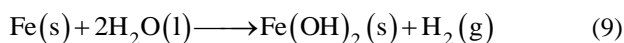$$nFe(OH)_2 \longrightarrow Fe_n(OH)_{2n}(s) \tag{10}$$

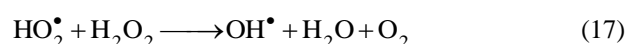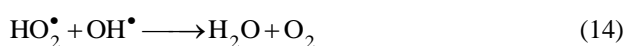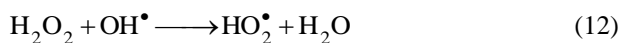### *Photo-Assisted Chemical Oxidation (PACO)*

One of the advanced oxidation processes, the combination of UV with hydrogen peroxide is successfully applied for the effective treatment of various types of water pollutants. It involves the generation of very powerful oxidizing species (hydroxyl radicals), which decompose / mineralize rapidly electron rich organic compounds / organic contaminates without producing any secondary pollutants.

A common scheme for the production of hydroxyl radicals are summarized as [21–23]
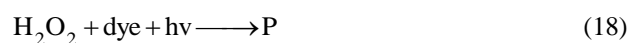
Initiation

$$H_2O_2 + h\nu \longrightarrow 2HO^\bullet \tag{11}$$

Hydroxyl radical propagation and termination

$$H_2O_2 + OH^\bullet \longrightarrow HO_2^\bullet + H_2O \tag{12}$$

$$2OH^\bullet \longrightarrow H_2O_2 \tag{13}$$

$$HO_2^\bullet + OH^\bullet \longrightarrow H_2O + O_2 \tag{14}$$

$$OH^\bullet + dye \longrightarrow P \tag{15}$$

$$HO_2^\bullet + dye \longrightarrow P \tag{16}$$

$$HO_2^\bullet + H_2O_2 \longrightarrow OH^\bullet + H_2O + O_2 \tag{17}$$

Overall reaction

$$H_2O_2 + dye + h\nu \longrightarrow P \tag{18}$$

Hydroxyl groups that can capable of oxidizing the components are listed in Table 2 [24]. The overall aim of this study is to identify the level of treatment efficiency and competence of EC process and advanced oxidation process on textile industrial dye wastewater. For the evaluation of the effectiveness of two treatment processes, experiments were carried out by changing the parameters such as initial concentration of the dye, pH, electrode potential for EC process and the parameters such as initial concentration of dye, pH, and initial concentration of oxidant for the advanced oxidation process.

Experimental Procedure
Electrocoagulation (EC)

The experimental setup for EC is schematically shown in Fig. 1. The unit consists of a 0.5 l electrochemical reactor with SS anode and cathode (SS304 grade). The electrodes dimensions were 50mm×50mm×2mm and the distance between electrodes was 1 cm. In order to avoid passivation on the SS electrodes, the electrodes were rubbed with emery sheet then the surface was cleaned with dilute hydrochloric acid and sodium hydroxide solution. 300 mL of the dye solution was taken in the electrochemical reactor. Initial pH of the dye solution was adjusted with 0.1 M HCl and 0.1 M NaOH solutions. The necessary applied voltage was supplied by constant DC power supply. The samples were analyzed to identify the efficiency of the treatability via the decrease in absorbance at 590 nm, the maximum wavelength of

Table 2: Oxidizable compounds by hydroxyl radicals [24].

| Targeted Group	Targeted Compounds
Acids	Formic, gluconic, lactic, malic, propionic, tartaric
Alcohols	Benzyl, tert-butyl, ethanol, ethylene glycol, glycerol, isopropanol, methanol, propenediol
Aldehydes	Acetaldehyde, benzaldehyde, formaldehyde, glyoxal, isobutryaldehyde, trichloroacetaldehyde
Aromatics	Benzene, chlorobenzene, chlorophenol, creosote, dichlorophenol, hydroquinone, p-nitrophenol, phenol, toluene, trichlorophenol, xylene, trinitrotoluene
Amines	Aniline, cyclic amines, diethylamine, dimethylformamide, EDTA, propanediamine, n-propylamine
Esters	Tetrahydrofuran
Ketones	Dihydroxyacetone, methyl ethyl ketone
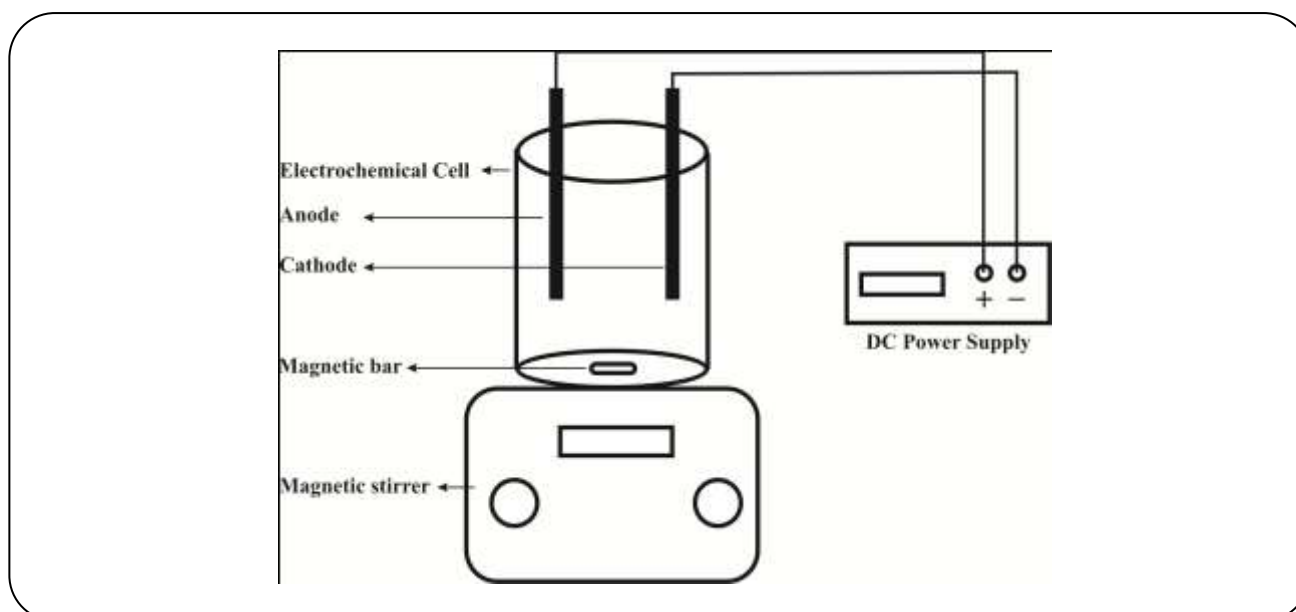
Fig. 1: Experimental Setup for Electrocoagulation.

RB194, at different time intervals using HACH spectrophotometer. Energy, consumption of electrodes and operating cost were calculated for each sample as a function of time [25].

$$\text{Operating cost} = aC_{energy} + bC_{electrode} + D \qquad (19)$$

Where (*a*) the energy cost (*b*) cost of SS electrode *D* is the cost of the chemicals used.

$$\text{Energy could be calculated as } C_{energy}\left(kWh/m^3\right) = \qquad (20)$$

$$U_c XIXt/V$$

Where *U* is the cell voltage (Volts), *I* is the current (Ampere), *t* is the time of EC (hour) and *V* is the volume of dye solution (m^3)

According to Faraday's law consumption of electrode could be calculated as

$$C_{electrode}\left(kg/m^3\right) = IXtXM/nFV \qquad (21)$$

Where *M* is the molecular mass of iron (55.84 g/mol), *z* is the number of electrons transferred (z =2) and *F* is Faraday's constant (96,487 C/mol).

The color removal efficiency could be calculated in the experiments as:

$$CR(\%) = 100X\frac{\left(C_0 - C\right)}{C_0} \qquad (22)$$

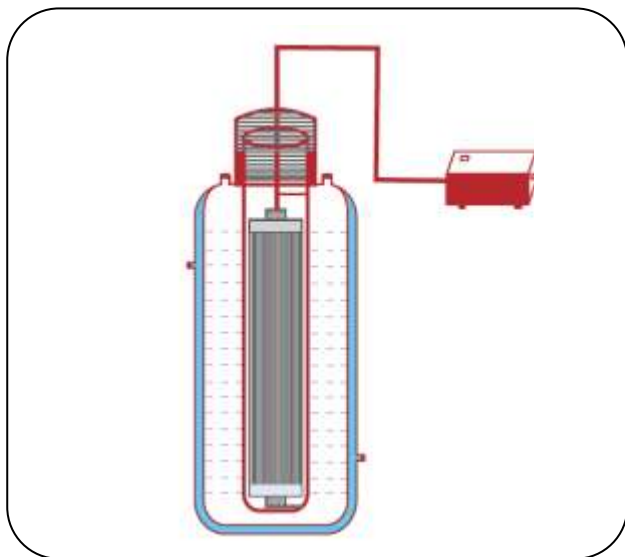Where *C$_0$* and *C* are concentrations of dye before and after treatment process in mg/L, respectively.

Fig. 2: Experimental Setup for Photo-assisted chemical oxidation.

Photo-assisted chemical oxidation process (PACO - UV/H₂O₂)

PACO process (UV/H$_2$O$_2$) were carried out in immersion type photo reactor made of quartz tube surrounded by water cooling jacket supplied by HEBER Scientific (Model: HEBER : HPSLIV16254), Chennai. Low-pressure mercury lamp with the emission of 254 nm is used as a source of UV radiation (Fig. 2). Experiments were carried out with the necessary quantity of the RB194 dye and H$_2$O$_2$ into the photo reactor. The solution was stirred in magnetic stirrer and the temperature was maintained at 25°C by circulation of water in the cooling jacket. The pH of the solution was measured by pH meter and adjusted by using dilute hydrochloric acid or sodium hydroxide. The samples were taken at definite time intervals to identify the loss of aromaticity and color removal efficiency of the dye during the photo degradation.

Electrical energy required to reduce the concentration of the pollutant in 1 m^3 of dye water could be calculated as [26, 27],

$$EEO\left(kWh/m^3\right) = \frac{PXt}{V} \tag{23}$$

Where *P* is the rated power of the lamp in kWh, *t* is the treatment time in minutes and *V* is the volume of dye solution in liter respectively.

$$Operating\ coast = a\,EE0 + D \tag{24}$$

Where *a* is the cost of energy; *D* is the cost of the chemicals used.

RESULTS AND DISCUSSION

Both the treatment process has different operational parameters and follows the different methodology of degradation of the dye. So initially both the processes were analyzed with different operational parameters, compared with the electrical energy consumption and cost of the treatment process under the optimized conditions.

Optimization of EC process
Effect of initial concentration of the dye

Initial concentrations of the dye ranged from 100–1000 mg/L were treated by EC (applied voltage of 3V, electrode distance of 3cm, pH 3 and supporting electrolyte 1 g/L). Fig. 3.a & 3.b showed that the color removal efficiency at the different level of initial concentration of dye solution with time. The color removal efficiency decreased (98.64% to 75.51%) with an increase in dye concentration from 100 to 1000 mg/L. An explanation is that, according to Faraday's law, a constant amount of Fe^{2+} (0.1736 kg/m^3) passed into the solution at the same current density and hence the same amount of flocs would be formed in the solutions. As a result, the flocs produced at high dye concentration were insufficient to adsorb all of the dye molecules of the solution. The flocs remain in the aqueous phase as a gelatinous suspension, which can remove pollutants from wastewater either by electrostatic attraction or by complexation followed by coagulation.

Effect of pH

To evaluate the effect of the pH on dye removal efficiency, the experiments were conducted by adjusting 10 level of the initial pH of the RB194 solution from 3 to 12. Fig 4.b. shows the observed variation of initial pH and final pH during experiments. It is evident from the Fig.4.b that, the pH of the medium increased during the reactive phase and then stabilizes at a pH range of 8.0–9.0 depending on the initial pH (initial pH of 4 increased to final pH of 8.27, initial pH of 5 increased to final pH of 8.82, and initial pH of 7 increased to final pH of 8.95). After the initial pH 9.0, there is no such an increase in final pH was observed during the experimentation (initial pH of 9.0 to final pH of 9.28 and initial pH of 10 to final pH of 10.16). The increase in pH during the reaction phase can be explained by the evolution of hydrogen and production of OH$^-$ ions (Eqs. (3) and (8)) at the
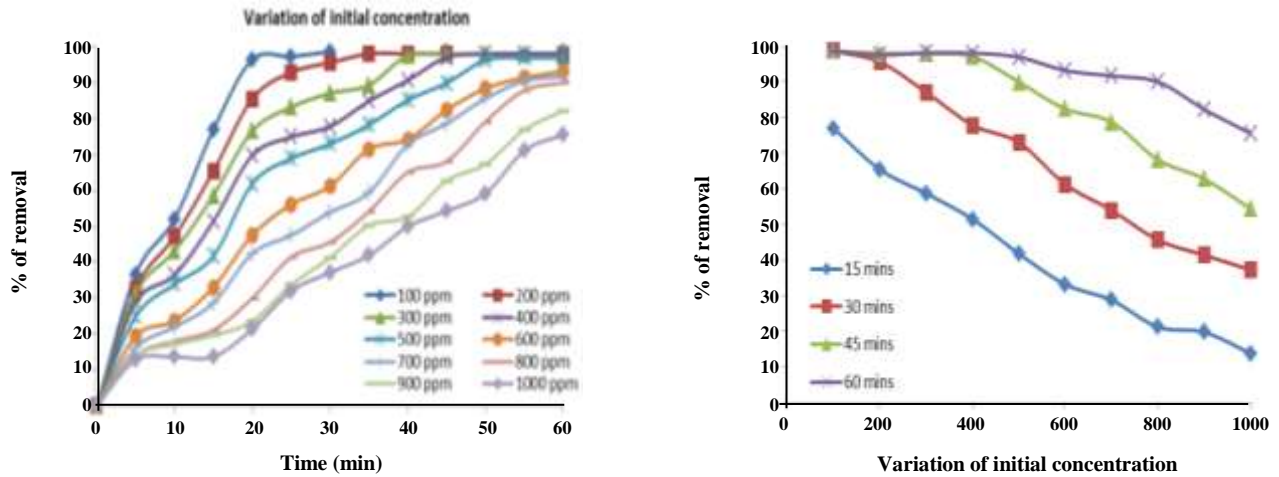
***Fig. 3a and 3b Effect of initial concentration of the dye solution with respect to time on decolourization by EC process
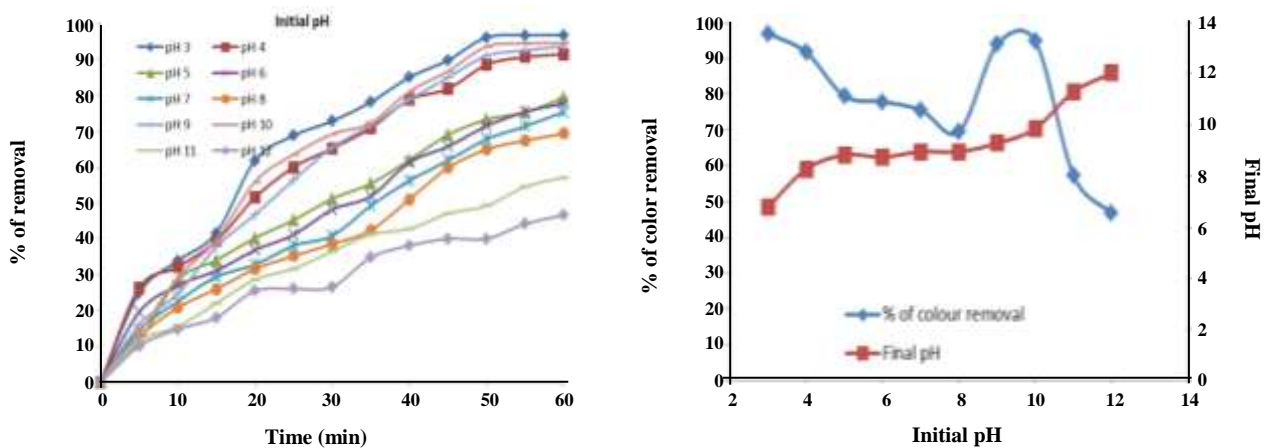(pH 9, [NaCl] 3 g/L and applied voltage 3 V).***

***Fig. 4: a) Effect of initial pH of the dye solution with respect to time by EC process (initial concentration of the dye solution
500 ppm, [NaCl]=3 g/L and applied voltage 3 V). b) Effect of initial of pH of the dye solution on the final solution pH and   color
removal efficiency by EC process.***

cathode surface. The stability of pH afterward may be due to the formation of Fe(OH)$_3$ flocs and the other metal hydroxides [28].
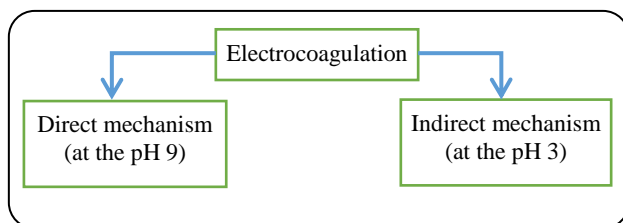
The dye removal efficiency at different initial pH for the initial dye concentration of 500 ppm as a function of time is shown in Fig.4a. The maximum removal efficiency of 96.91% and 94.69% was observed at the initial pH 3 and 10. But the removal efficiency was decreased when the initial pH of the RB194 dye solution was increased from 4 to 8 and from 11 to 12. In the basic medium, the maximum color removal efficiency of 93.82% at the initial pH 9 and 94.69% at the initial pH 10 could be due to the formation of the majority of iron complexes (coagulants). There is a competition between the indirect (chlorine) and direct mechanism (electrocoagulation) arises in between the pH range 3-4 and 9-10. Beyond the initial

Table 3: Comparison of variation of applied voltage with kinetic constant and electrode consumption by EC process.

Applied Voltage (V)	Current (A)	Treatment Time (min)	% of colour removal	R^2	k (min^{-1})	Electrode consumption (kg/m^3)
2	0.02	60	51.68	0.8988	0.0123	0.0694
3	0.05	60	96.91	0.9397	0.0553	0.1736
4	0.07	50	96.95	0.9798	0.0608	0.2026
5	0.11	30	99.25	0.9191	0.1439	0.1909
6	0.14	30	99.63	0.9286	0.1769	0.2430

pH 10, color removal efficiency decreased because of the presence of more dominant species $Fe(OH)_4^-$, which unable to form flocs at very high alkaline pH [29]. In the acidic medium, the maximum color removal efficiency of 96.91% at the initial pH 3 and 91.6% at the initial pH 4 could be due to the presence of chlorine in the solution in the form of hypochlorous acid (which is having higher oxidation potential 1.49 V) [30].

Effect of applied voltage

The most important reaction rate controlling parameter in EC processes are applied voltage and time of electrolysis, which decides the production rate and total production of coagulants. The dye removal efficiency increased from 51.68% to 99.63% with an increase in applied voltage from 2V to 6V respectively. But, more than 95% of dye removal was observed for all the applied voltage above 3V. So the variation in the applied voltage has a lesser effect on the final color removal efficiency, but the rate of dye removal efficiency increased (0.0123 to 0.1769 min^{-1}) with an increase in applied voltage (2V to 6V). From the Table 3, this can be explained by the fact that increase in applied voltage (2V to 6V) increased the rate of consumption of electrode (0.0694 to 0.2430 kg/m^3) and hence the floc formation increases which in turn increased the dye removal efficiency. It was further supported by the analysis of byproducts formed during EC process.

A surface characterization of EC byproduct was determined using SEM. SEM image of dried sludge was taken after carrying out the experiment which was shown in Fig. 5 indicated the crystalline structure of the sludge. From the Fig. 5 it can be visualized that the aggregated dye molecules remained on the crystalline surface of iron hydroxides which are formed due to anodic oxidation of the sacrificial SS electrodes. Energy Dispersive Analysis of X-ray diffraction (EDAX) spectral
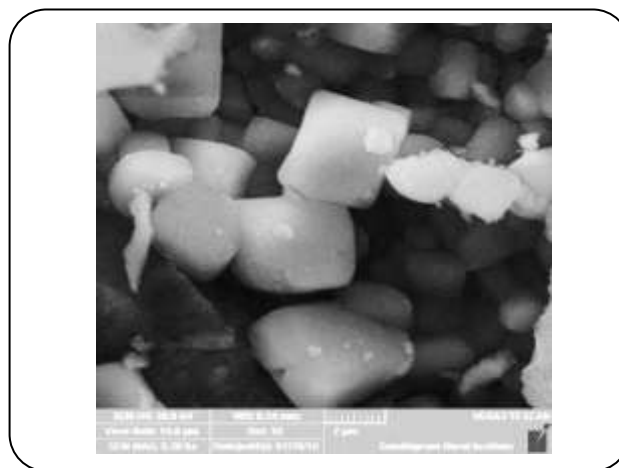
Fig. 5: SEM image of the sludge.

the analysis was also taken to estimate the elemental composition of sludge was presented in Fig. 6. The peaks of C, O, Fe, N, Cr and Na were shown in the spectrum indicating its presence in the sample. EDAX graph conveys that the byproduct of EC consists of carbon, Nitrogen, and oxygen from destroyed dye molecule, sodium peak appeared due to added sodium chloride salt and iron and chromium from the dissolution of SS electrode.

At very low applied voltage (2V), it was observed that 51.68% dye removal efficiency was achieved after 60 min of operation. This was due to the total amount of flocs formed was not enough to remove all the dye molecules in the solution. The electrode consumption of 0.1736 kg/m^3 of the electrode were more than enough to degrade 96.91% of the dye solution in 60 minutes of time. Even though the required decolorization percentage of more than 97.% of dye removal was achieved, the further increment in the applied voltage reduces the time required to achieve the same decolorization percentage.
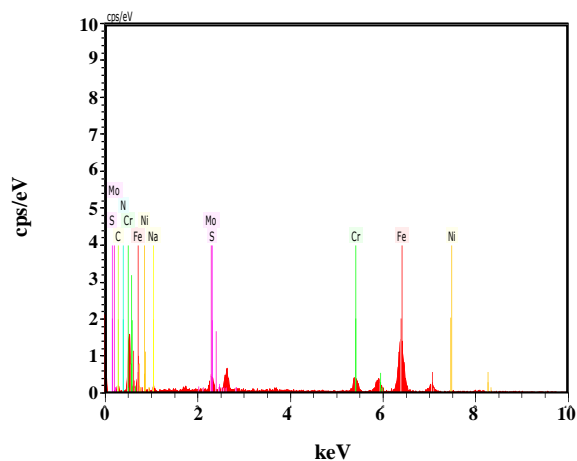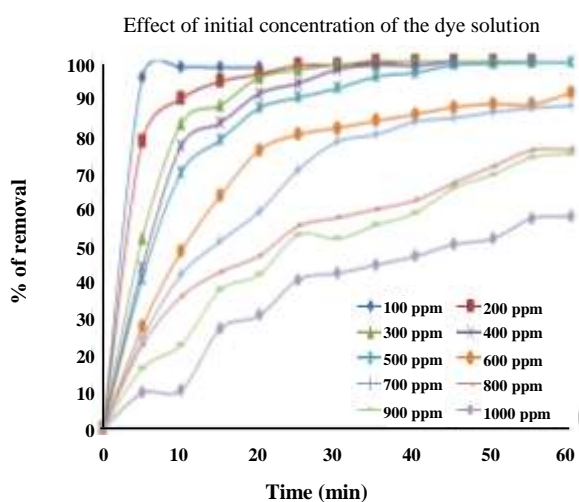
Fig. 6: EDAX spectrum of sludge.

Fig.: 7: Effect of initial concentration of the dye solution with respect to time on decolourization by PACO process (pH 9 and initial oxidant concentration 20 mmol)

Optimization of PACO process

Effect of initial concentration of the dye

The effect of initial concentration of dye on decolorization efficiency was monitored at different concentration level from 100 mg/l to 1000 mg/lit and presented in Fig. 7. The decolorization efficiency was decreased (98.18% to 57.71%) with the increase of the concentration level of the dye solution (100 mg/L to 1000 mg/L) [31]. The decolorization of the dye solution was mainly due to the formation of the more and more number of OH˚ radical (Eq. (11)). The molar absorption coefficient of the dye solution at 254 nm is very high so that an increase in the dye concentration induces

the internal optical density and the solution becomes highly impermeable to UV radiation. This may lead to the decrease in production of hydroxyl radicals and hence the removal efficiency was decreased.

Effect of pH

The influence of pH on the decolorization of the dye solution was investigated at different initial pH values from 3.0 to 12.0 (Fig.8.a & b). It is evident from the Fig. 8b that increase in the initial pH (until the pH value of 10) decreased the pH of the medium during the reactive phase to acidic (Final pH). The drop in the solution pH during the reaction phase is mainly due to the formation organic acid as well as inorganic acid during UV irradiation of the dye solution [32, 33]. Upon increasing the initial pH of the dye solution (from 10 to 12), no remarkable changes in the final pH was observed during the reactive phase due to the formation of weak organic acid as a reaction product.

Close examination of the color removal efficiency versus pH (Fig. 8.a) clearly indicated that the removal efficiency was decreased (96.26 to 83.80%) on increasing the initial pH of solution from 3 to 5 and afterwards the removal efficiency gradually increases (83.80 to 99.64%) when the pH of the solution increases up to 9. Upon increasing, initial pH of the solution decreased the color removal efficiency to 69.00% at the pH 12. The better results were in pH's 9 and 10; the worst was at pH 12. The deactivation of OH˚ is more predominant at the pH of the solution from 11 and 12. The reaction of OH˚ with HO_2^- is approximately 100 times faster than its reaction with H_2O_2. Therefore, the instantaneous concentration of OH˚ was lower than expected and hence the decolorization efficiency decreases.

Effect of initial concentration of oxidant

The reaction of dye solution in the absence of H_2O_2 (UV alone) and in the presence of H_2O_2 was very slow and resulted in less than 10% degradation in 60 minutes which was in agreement with the literature [34].

$$Dye + h\nu \longrightarrow Product \qquad (25)$$

In contrast, significant dye removal efficiency was observed when they were applied simultaneously. Combination of UV and H_2O_2 was, therefore, necessary for the production of OH˚ radicals to initiate the
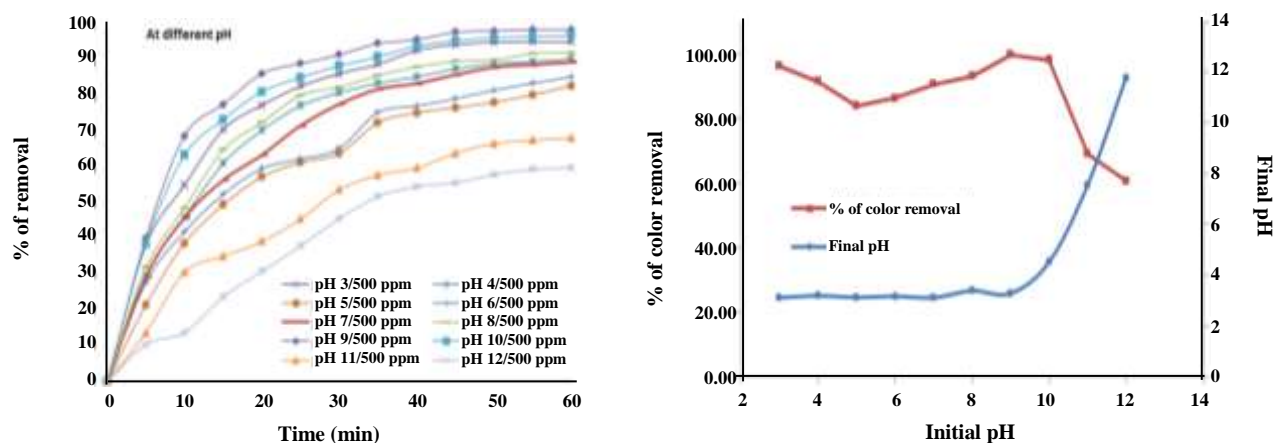
Fig. 8: a) Effect of initial pH of the dye solution with respect to time by PACO process (initial concentration of the dye solution 500 ppm and initial oxidant concentration 20 mmol). B) Effect of initial of pH of the dye solution on the final solution pH and color removal efficiency by PACO process.
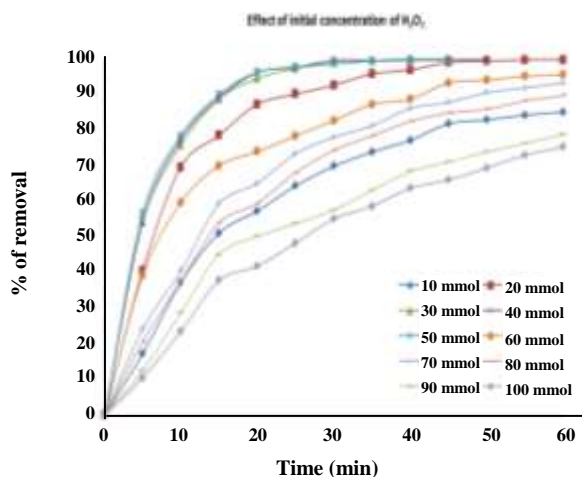

Fig. 9: Effect of initial oxidant concentration of the dye solution with respect to time by PACO process (initial of the dye solution 500 ppm and pH 9).

decolorization of dye. In order to observe the effect of oxidant concentration on the rate of decolorization of dye in PACO process, experiments were carried out by varying the initial concentration of oxidant from 10 to 100 mM. The results were illustrated in Fig. 9 that the decolorization efficiency was enhanced by the addition of oxidant due to the generation of more quantity of OH° radicals. This OH° radical have enough energy to effectively degrade the large quantity of the dye molecules. The possible degradation pathway with its major by-products was shown in Fig. 10.

The results from the Fig. 9 showed that the increase in the initial concentration of oxidant from 10 mM to 50 mM increased the color removal efficiency from 85.02 to 99.80%. Further increase in the dose of initial oxidant concentration from 60 mM to 100 mM, increased the resistance to the destruction of dye molecules by hydroxyl radicals and hence the color removal efficiency of the dye solution was decreased from 95.45% to 75.21%. The fact that hydroxyl radicals formed was consumed by the excess of oxidant to form hydroperoxyl radicals which have lower oxidation capability than the OH° radicals (Eq. (12)).

Comparison of competitiveness
Efficiency comparison

Comparison of efficiencies of EC and PACO processes on decolorization of RB194 dye solution was presented in Tables 4 & 5. Even though both the processes follow different mechanism for the decolorization of the dye solution, we compare the competitiveness between the processes under the similar conditions for the decolorization of the dye solution.

Both the processes performed well in lower concentrations of the dye solutions and at the initial pH of 3, 9 and 10. Almost 99.63% and 99.80% of color removal was achieved in EC and PACO process. Increasing the applied voltage in EC process as well as increasing quantity of oxidants in PACO process increases the performance of the process as indicated in Table 4 & 5.
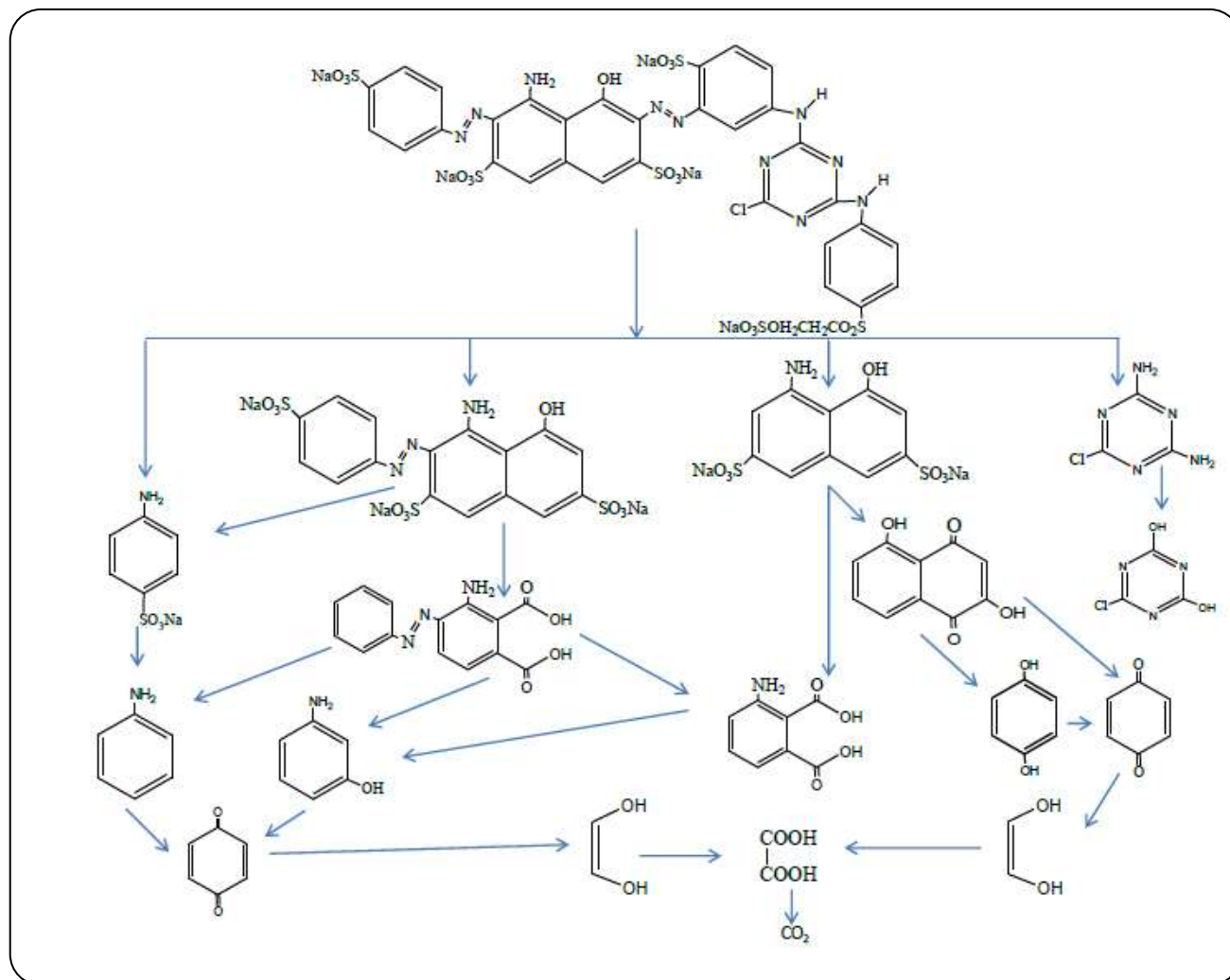
Fig. 10 Possible degradation path way with its major byproducts by PACO process

Energy consumption favors the EC process because energy consumption for the dye removal was very high (10.667 kWh/m^3) in PACO process than the EC process (0.700 kwh/m^3). But analysis of byproduct formed during the process favors the PACO process. Since in PACO process, no solid by-products of dye were formed during the decolorization. This process seemed to be a promising environmental engineering technique.

Cost estimation

In this preliminary investigation in order to calculate the economy of the processes, energy and material costs involved was taken into account as major cost items. The operating cost was calculated based on the Eq. (19) and 24 (Table 6). PACO process showed lower chemical consumption than the electrode consumption in EC

process. But energy consumption of PACO process was much higher than the EC process. EC process showed lesser overall cost than the PACO process as US$ 0.6418 (Fig. 11).

CONCLUSIONS

Close examination of the two processes PACO and EC showed the best removal efficiency of reactive blue 194 dye in the optimal reaction conditions. The complete decolorization (99.64%) of the diazo dye was done at the initial concentration of 500 ppm, initial oxidant concentration of 20 mM and at the pH 9 by photochemical oxidation by PACO process. The increase in oxidant dosage increases the decolorization rate by enhancing the generation of OH°, but beyond the critical limit, it showed the negative impact on the reaction rate.

Table 4: Comparison of efficiency of the EC process.

Variable Parameters	Quantity of variable parameters	Time (mins)	Percentage of dye removed (%)	Amount of dye removed kg/m³	Amount of Energy required kW.h/m³	Efficiency	
						in terms of kW.h/m³	in terms of kg/m³
Initial Concentration of dye (mg/L)	100	30	98.64	98.640	0.250	0.0025	394.56
	200	35	97.54	195.080	0.292	0.0015	668.08
	300	50	98.15	294.444	0.417	0.0014	706.10
	400	55	98.07	392.264	0.458	0.0012	856.47
	500	55	96.91	484.527	0.458	0.0009	1057.92
	600	60	93.18	559.091	0.600	0.0011	931.82
	700	60	91.66	641.595	0.600	0.0009	1069.33
	800	60	89.97	719.778	0.700	0.0010	1028.25
	900	60	82.24	740.175	0.700	0.0009	1057.39
	1000	60	75.51	755.102	0.700	0.0009	***
Applied voltage (V)	2	60	51.68	258.401	0.133	0.0005	***
	3	55	96.91	484.527	0.458	0.0009	1057.919
	4	45	96.95	484.762	0.700	0.0014	692.517
	5	30	99.25	496.230	0.917	0.0018	541.145
	6	30	99.63	498.165	1.400	0.0028	355.832
Initial pH	3	55	96.91	484.527	0.458	0.0009	1057.919
	4	60	91.60	458.008	0.500	0.0011	916.016
	5	60	79.41	397.059	0.500	0.0013	***
	6	60	77.85	389.272	0.500	0.0013	***
	7	60	75.54	377.712	0.500	0.0013	***
	8	60	69.47	347.332	0.500	0.0014	***
	9	60	93.82	469.077	0.500	0.0011	938.154
	10	60	94.69	473.456	0.500	0.0011	946.911
	11	60	57.22	286.124	0.700	0.0024	***
	12	60	46.70	233.516	1.600	0.0069	***

*** indicate less than 80% of decolourization and hence not included in the comparison.
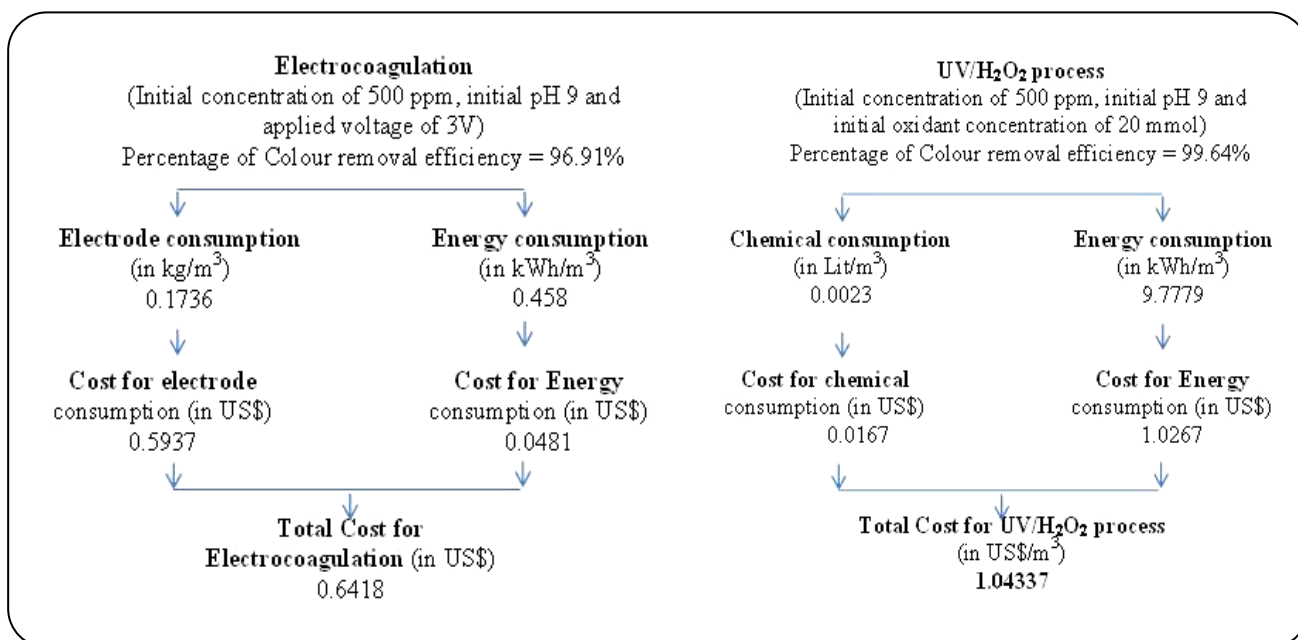
Table 5: Comparison of efficiency of the PACO process.

Variable Parameters	Quantity of variable parameters	Time (mins)	Percentage of dye removed (%)	Amount of dye removed kg/m³	Amount of Energy required kW.h/m³	Efficiency in terms of kW.h/m³	in terms of kg/m³
Initial Concentration of dye (mg/L)	100	10	98.18	98.180	1.7778	0.0181	55.226
	200	30	98.81	197.610	5.3334	0.0270	37.051
	300	35	98.92	296.791	6.2222	0.0210	47.699
	400	40	98.70	394.805	7.1112	0.0180	55.519
	500	55	99.64	498.221	9.7779	0.0196	50.954
	600	60	91.31	547.872	10.667	0.0195	51.362
	700	60	87.77	614.388	10.667	0.0174	57.598
	800	60	75.86	606.866	10.667	0.0176	***
	900	60	74.72	672.446	10.667	0.0159	***
	1000	60	57.71	577.071	10.667	0.0185	***
Initial Concentration of H₂O₂ (mg/L)	10	60	85.02	425.110	10.667	0.0251	39.854
	20	60	99.64	498.221	9.7779	0.0196	50.954
	30	45	99.54	497.685	8.000	0.0161	62.211
	40	45	99.65	498.236	8.000	0.0161	62.280
	50	45	99.80	499.006	8.000	0.0160	62.376
	60	60	95.45	477.226	10.667	0.0224	44.740
	70	60	93.22	466.102	10.667	0.0229	43.697
	80	60	89.60	447.983	10.667	0.0238	41.999
	90	60	78.66	393.285	10.667	0.0271	***
	100	60	75.21	376.050	10.667	0.0284	***
Initial pH	3	55	96.26	481.317	9.7779	0.0203	49.225
	4	60	91.41	457.055	10.667	0.0233	42.849
	5	60	83.80	418.977	10.667	0.0255	39.279
	6	60	86.25	431.238	10.667	0.0247	40.429
	7	60	90.43	452.128	10.667	0.0236	42.387
	8	60	93.06	465.291	10.667	0.0229	43.621
	9	55	99.64	498.221	9.7779	0.0196	50.954
	10	60	98.07	490.366	10.667	0.0218	45.972
	11	60	69.00	344.978	10.667	0.0309	***
	12	60	60.58	302.885	10.667	0.0352	***

*** indicate less than 80% of decolourization and hence not included in the comparison.*

Table 6: Cost of Material and Energy.

Item	Cost in US$
Material and chemical cost	
Electrocoagulation process	
1. Cost of SS electrode (per kg)	3.42
UV/H_2O_2 process	
1. Cost of the 30% H_2O_2 (per lit)	7.26
Energy cost	
1. Power cost (per kWh)	0.105

Fig. 11: Comparison of cost estimation.

Similarly, EC process was also performed equally with PACO process. It also exhibits two different mechanisms at acidic and basic medium. The increase in applied voltage increases the efficiency of the process, but higher voltage increases the more electrode dissolution. The material cost of the PACO process of the dye solution competes with the EC process. But it fails to keep the energy efficiency in the competition with the EC process. The cost of the treatment of EC process (US$ 0.6418/m^3 of the dye solution) was very less compared to the PACO process.

Acknowledgement

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