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Short Communication

Electrochemical Degradation of Sago wastewater using Ti/PbO2 Electrode: optimisation using Response Surface Methodology

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The electrochemical treatment of sago wastewater was studied on lead dioxide coated titanium anode and stainless steel as cathode in the presence of NaCl electrolyte in a batch process. The treatment conditions were optimised using response surface methodology where pH was kept in range, current density and electrolyte concentration was kept as minimum for maximum % removal of COD. Analysis of variance (ANOVA) results revealed that the coefficient of determination value (R^2) of % COD removal was 0.9887. Optimum conditions at room temperature were obtained for the highest desirability of 0.920 at 18 mA/cm^2 current density, 6.5 pH, 80 min electrolysis time and 1g/l electrolyte concentration to achieve 58.85% COD removal and energy consumption as minimum. Hence, electrochemical method was more effective in degradation of pollutant at low operating cost and the results support the applicability of electrochemical treatment process to the sago wastewater as an alternative approach.

Keywords: synthetic sago wastewater, Ti/PbO$_2$ electrode, electrochemical treatment, COD removal, response surface methodology

1. INTRODUCTION

With the continuous development of agro based industries, sago industries are considered to be one of the largest sources of food processing wastewater, since it includes washing and extraction process. In the southern part of India, particularly in Tamil Nadu, there are about 800 small-scale units of sago industries discharging about 40,000 to 50,000 l of sago wastewater and 15 to 30 tonnes of sludge per unit per day [1, 2]. The sago industries cause severe environmental problems due to high consumption of fresh water and discharge large quantities of wastewater with high organic pollutants.

Sago wastewater does not have any toxic substances, but high organic matter which cause increase in COD level. Organic pollutants present in wastewater can be treated by i) physico chemical methods: it is good option regarding economical concern and volume reduction of the effluent [3], but they do not reduce the pollutants and sludge. ii) Biological methods: it is known for their process efficiency and economic feasibility [4], but it is impossible to achieve complete degradation of organic matter due to bio refractory nature of the substrates and requires additional treatment. Thus there is a necessity to meet increasingly rigorous discharge limit and treat the wastewater containing organic pollutants, by advanced treatment methods.

The electrochemical method is an interesting option to treat the wastewater with high removal rates. Proper selection of electrode is the key factor in the efficiency of EC treatment. Different types of electrodes have been investigated by various researchers for the treatment of various industrial wastewaters. Iron and aluminium electrodes were used in treating textile wastewater, since they are able to produce insitu coagulant to remove the dyes [5,6] dimensionally stable anodes (DSA), aluminium and mild steel were used for tannery wastewater [7,8], titanium coated with bored doped diamond (Ti/BDD) for domestic wastewater [9] but it is very expensive. Mild steel, iron, aluminium electrodes were used for dairy and deproteinated whey wastewater [10-15]. RuO_2/Ti and PbO_2/Ti were used for starch effluent [16]. Lead oxide coated on expanded titanium mesh (Ti/PbO_2) has been widely used in EC treatment due to its easy preparation, chemical stability and high overpotentials for oxygen evolution [17]. Ti/PbO_2, anode was used to improve the lifetime and electrocatalytic activity of the electrode. Thus Ti/PbO_2 was found to be corrosion resistant in the presence of starch and performance of the electrode is quite well in electrochemical mineralisation of organics [18].

In conventional electrochemical treatment, degradation of pollutants can be achieved by two mechanisms. i) direct oxidation: electron transfer directly to the anode ii) indirect oxidation: electro generated oxidising species such as hydroxyl radicals, hypochlorite, chlorine and absorbed $^{\cdot}$OH radicals are supposed to be generated from water electrolysis shown in reaction

$$M + H_2O \rightarrow M(\cdot OH) + H^+ + e^- \qquad (1)$$

Reaction (2) indicates that the “active” anodes $^{\cdot}$OH radicals may interact so strongly with their surface to form higher oxide MO [19, 20]

$$M(\cdot OH) \rightarrow MO + H^+ + e^- \qquad (2)$$

With active electrodes the redox couple MO/M pair is a mediator in the oxidation of organic compounds by reaction (3). In “non-active” anodes weak interaction exist between the hydroxyl radicals and electrode surface thus, the oxidation of organics is mediated by $^{\cdot}$OH radicals resulted in fully oxidised products by reaction (4)

$$MO + R \rightarrow M + RO \qquad (3)$$

$$M(\cdot OH) + R \rightarrow M + mCO_2 + nH_2O + H^+ + e^- \qquad (4)$$

In the above equations R is a fraction of organic matter containing no heteroatoms, which requires one oxygen atom to be completely transformed to CO_2. The EC activity and chemical reactivity of adsorbed $^{\cdot}$OH are strongly linked to the strength of M-$^{\cdot}$OH interaction. Henceforth the interactions become weaker and the anodic reaction was higher for the oxidation of organic pollutants.

In the conventional method of optimisation of one parameter is varied at a time while other remains constant. However, this method was difficult to understand complex interactions between the variables and responses [11]. Response surface methodology is a statistical tool for developing, improving and optimising complex processes and it can be used to evaluate the significance of affecting variables in the presence of complex interactions. The central composite design (CCD) was used for the RSM in the experimental design. The CCD is an effective design that is ideal for sequential experimentation and allows reasonable amount of information for testing lack of fit while not involving unusually large number of design points [5]. The main objective of this study focus to examine, analyse and interpret the effect of current density, electrolyte dosage, time and pH on COD removal in the EC treatment using Ti/PbO_2 anode.

2. MATERIALS AND METHODS

Preparation of synthetic sago wastewater (SSW) was reported elsewhere [3] and the physico chemical characteristics of the synthetic sago wastewater was analysed as per standards of American Public Health Association (APHA) [21] and are listed in the Table 1.

Table 1. Physicochemical characteristics of sago wastewater

Parameter	Value
pH	6.8
Chemical Oxygen Demand	2286 mg/l
Biological Oxygen Demand	840 mg/l
Total Dissolved Solids	1237 mg/l
Total Suspended Solids	537 mg/l
Volatile Solids	610 mg/l
Volatile Suspended Solids	1015 mg/l

2.1. Experimental Setup

The experiment was conducted in 2L glass beaker with lead oxide coated on expanded titanium mesh (Ti/PbO_2) as anode and stainless steel as cathode. The effective surface area of the electrodes was $24 cm^2$. The distance between the two electrodes was 2 cm and NaCl was used as supporting electrolyte during the study. Electrolysis was done using magnetic stirrer with constant speed of 100 rpm at room temperature of 30^0C. The electrodes were connected to a digital direct power supply of (0-8V) voltmeter and (0-5A) ammeter respectively.

2.2. Analytical methods

The general characteristics of SSW such as pH, COD, BOD, TSS, TDS, turbidity were determined according to the standard methods (APHA 2005). pH was measured and adjusted using NaOH or H_2SO_4 solution. Turbidity was measured using nephlometer (CL52D model). COD was determined by open reflux method. At proper time intervals the samples were drawn from the reactor and their COD values were studied. The percentage COD removal was determined using the following relationship.

$$\%\ COD\ removal\ (Y) = \frac{C_i - C_f}{C_i} \times 100 \qquad (5)$$

where C_i and C_f are initial and final COD concentration (mg/l) respectively. The energy consumption per volume of treated wastewater was estimated and expressed in kWh/m^3. The average cell voltage, during the electrolysis, is taken for calculating the energy consumption, as follows [22];

$$Energy\ consumption\ \left(\frac{kWh}{m^3}\right) = \frac{intensity\ (A) \times cellvoltage\ (V) \times time\,(hr)}{volume\ (L)} \qquad (6)$$

2.3. Experimental design

The popular second order design called CCD was used in the experimental design. The CCD based RSM with four factors at five level full factorial was applied using Design-expert 7.0. Four independent variables namely j (x_1): 7.5-37.5 mA/cm^2; m (x_2): 0-4 g/l; t (x_3): 20-100 min; pH (x_4): 4.5-10.5 was coded at five levels between -2 and +2 based on preliminary studies. Four factor designed experiments were augmented with six replicates at the design centre to evaluate the pure error and were carried in randomised order as required in many design procedures. In the experimental design, the response can be simply related to chosen factors by linear and quadratic models. The behaviour of the process is explained by the following quadratic equation:

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k}\sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon \qquad (7)$$

where Y is the process response or output (dependent variable), k is the number of the patterns, i and j are the index numbers for pattern, βo is the free or offset term called intercept term, βi is the first-order (linear) main effect, βii is the quadratic (squared) effect, βij is the interaction effect, and ε is the random error between predicted and measured values [12]. Analysis of variance (ANOVA) was used to obtain the interaction between the process variables and response. The quality of the fit of polynomial model was expressed by coefficient of determination R^2, adjusted R^2 and statistical significance was tested by the F-test. The desired goals were selected (+++++) for maximum COD removal at minimum electrolyte concentration.

3. RESULTS AND DISCUSSION

3.1. Model fitting and ANOVA

A total of 30 experiments were conducted as per the design matrix and the response such as % COD removal (Y) was measured and given in Table 2. Linear and second-order polynomial equations were fitted to the experimental data to obtain the regression equations. In order to decide the suitable model, sequential model sum of squares, model summary statistics were tested and the results are presented in Table 3. prob> F values for quadratic model was less than 0.0001, adjusted R^2 value and predicted R^2 value were found to be maximum of 0.9781, 0.9418 for % COD removal. Even though cubic model was found to be aliased, prob> F values were greater than 0.05. Therefore the quadratic model was chosen for further analysis of % COD removal and it can be described as following equation:

$$\begin{aligned}\%\,COD\ Removal\ (Y1) &= -229.26 + 9.18\,X_1 - 1.035\,X_2 + 1.541\,X_3 + 38.92\,X_4 - 0.109\,X_1X_2 \\ &+ 0.005\,X_1X_3 - 0.219\,X_1X_4 - 0.012\,X_2X_3 + 3.52\,X_2X_4 + 0.035\,X_3X_4 - 0.161\,X_1^2 \\ &- 6.28X_2^2 - 0.012\,X_3^2 - 3.199X_4^2 \end{aligned} \qquad (8)$$

Table 2. Experimental design matrix for electrochemical treatment

					% COD removal Y		
Run order	j	m	t	pH	Experimental value	Predicted value	Error
1	22.5	4	60	7.5	30.3	30.4	0.3
2	22.5	2	60	10.5	18.6	18.1	-2.8
3	30	3	80	9	38.2	37.9	-0.8
4	30	1	40	9	12.4	14.3	13.3
5	22.5	2	60	7.5	60.8	61.1	0.5
6	15	3	80	6	35.5	34.4	-3.2
7	7.5	2	60	7.5	20.1	17.8	-12.9
8	22.5	2	60	7.5	58.7	61.1	3.9
9	30	3	80	6	45.2	44.7	-1.1
10	22.5	2	60	7.5	61	61.1	0.2
11	15	3	40	6	20.7	21.9	5.5
12	30	3	40	6	31.2	28.8	-8.3
13	22.5	2	100	7.5	57.5	58.4	1.5
14	22.5	0	60	7.5	40.2	42.2	4.7
15	15	1	40	9	16.5	14	-17.9
16	30	3	40	9	19.2	17.8	-7.9
17	30	1	80	9	39.6	35.4	-11.9
18	22.5	2	20	7.5	23.6	24.8	4.8
19	37.5	2	60	7.5	28.1	30.8	-2.3
20	15	1	80	9	28.5	31.7	10.1
21	22.5	2	60	4.5	44.6	47.2	5.5
22	22.5	2	60	7.5	62.6	61.1	-2.5
23	15	3	40	9	19.5	20.8	6.3
24	15	3	80	9	36.7	37.5	2.1
25	22.5	2	60	7.5	63.2	61.1	-3.4
26	30	1	40	6	50.2	46.5	-8.0

27	30	1	80	6	63.8	63.4	-0.6
28	15	1	80	6	51.3	49.7	-3.2
29	15	1	40	6	35.2	36.2	2.8
30	22.5	2	60	7.5	60.5	61.1	1.0

ANOVA a statistical technique which subdivides the total variation in a set of data into component parts associated with specific sources of variation for the purpose of hypotheses testing of the variables [23]. ANOVA results for % COD removal are given in Table 4. In the table, F-value of the model was 93.68 for COD removal which shows statistical significance. "Adeq Precision" measures the signal to noise ratio and ratio greater than 4 is desirable. Therefore signal to noise ratio of 28.833 indicates an adequate signal for COD removal and also this model can be used to navigate the design space.

Table 3. Adequacy of the models tested for COD removal

Sequential Model Sum of Squares						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remark
Mean	45903.41	1	45903.41			
Linear	3389.92	4	847.48	4.61	0.0063	
2FI	585.04	6	97.51	0.46	0.8278	
Quadratic	3921.85	4	980.46	162.83	< 0.0001	Suggested
Cubic	56.67	8	7.08	1.47	0.3113	Aliased
Residual	33.65	7	4.81			
Total	53890.53	30	1796.35			
Model Summary Statistics						
Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	Remark
Linear	13.56	0.4244	0.3323	0.2807	5744.86	
2FI	14.53	0.4977	0.2333	0.1572	6731.23	
Quadratic	2.45	0.9883	0.9781	0.9418	464.64	Suggested
Cubic	2.19	0.9958	0.9825	0.6231	3010.50	Aliased

Table 4. ANNOVA of the second order polynomial equation for COD removal

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remarks
Model	7896.80	14	564.06	93.68	< 0.0001	significant
X_1	215.40	1	215.40	35.77	< 0.0001	significant
X_2	210.63	1	210.63	34.98	< 0.0001	significant

X_3	1695.12	1	1695.12	281.52	< 0.0001	significant
X_4	1268.76	1	1268.76	210.71	< 0.0001	significant
X_1x X_2	10.73	1	10.73	1.78	0.2019	
X_1x X_3	11.73	1	11.73	1.95	0.1831	
X_1x X_4	97.52	1	97.52	16.19	0.0011	significant
X_2x X_3	0.95	1	0.95	0.16	0.6967	
X_2x X_4	446.27	1	446.27	74.11	< 0.0001	significant
X_3x X_4	17.85	1	17.85	2.96	0.1057	
X_1^2	2258.38	1	2258.38	375.06	< 0.0001	significant
X_2^2	1083.97	1	1083.97	180.02	< 0.0001	significant
X_3^2	675.18	1	675.18	112.13	< 0.0001	significant
X_4^2	1421.49	1	1421.49	236.07	< 0.0001	significant
Residual	90.32	15	6.02			
Lack of Fit	77.45	10	7.74			
Pure Error	12.87	5	2.57			
Cor Total	7987.12	29				

3.2. Effect of electrolyte concentration

Electrolyte dosage is an important parameter on pollutant removal since its conductivity and actual wastewater usually contains certain amounts of salts. To visualise the effects of NaCl concentration at optimum condition, 3D and contour plots was shown in fig 1. It was observed that an increase of electrolyte concentration up to 2 g/l leading to the enhancement of the degradation of SSW. Further increase of NaCl concentration showed negative degradation and formation of salt film on the electrode surface, which would block the contact between electrode and wastewater. Hence, the probability of effective contact between the organic pollutants and $^{\cdot}$OH free radicals was decreased [17, 24]. At optimum condition of 1g/l the COD removal was about 58.85 % respectively.

3.3. Effect of current density

Current density is one of the important variable in electrochemical process hence it influences the anodic oxidation process. COD removal was maximum at optimum current density of 18 mA/cm^2 shown in fig 2. It could be observed that increasing current density above the optimum value decreases the COD removal at 80 min time interval. It is due to undesirable side reaction such as electrolysis of water and oxygen evolution from $^{\cdot}$OH free radicals[17] . However energy consumption leads to be higher for high current density and indicates that increase in current density led to less efficient process.

3.4. Effect of pH and electrolysis time

The COD removal efiiciency was higher in acidic medium than in alkaline.fig 3. Indicates that at optimum pH of 6.5 the COD removal was maximum of 58%. pH at acidic condition enhanced the free radical formation, therefore the organic matter was easily oxidised[25,26].

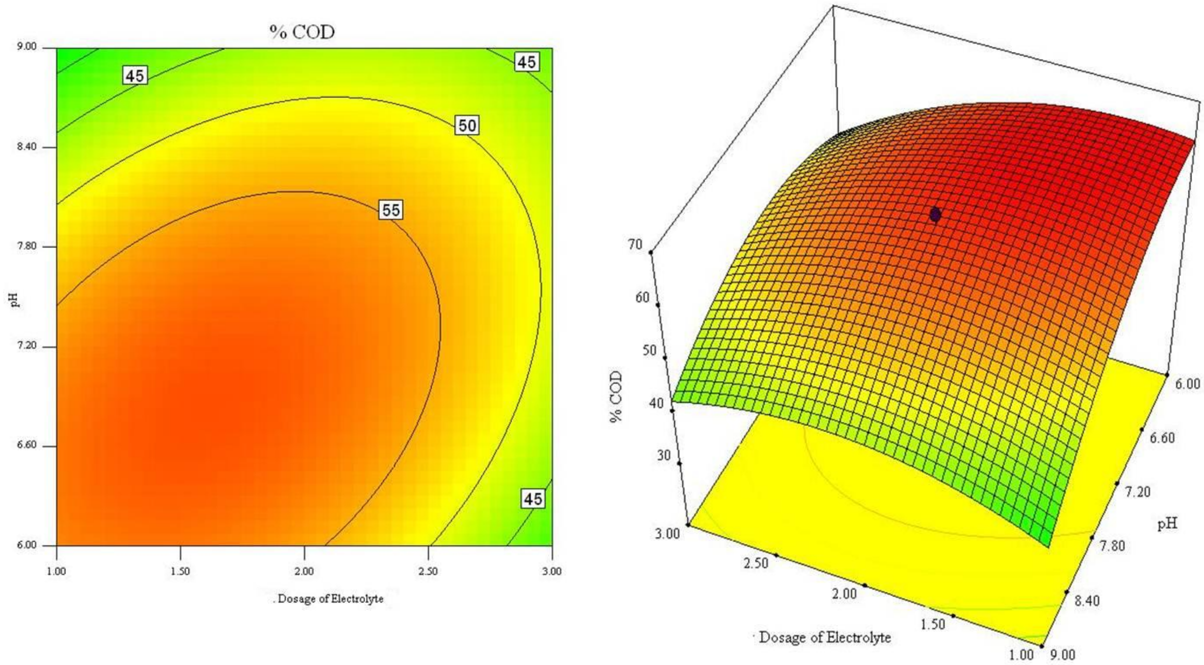

Figure 1. Effect of COD removal on electrolyte dosage

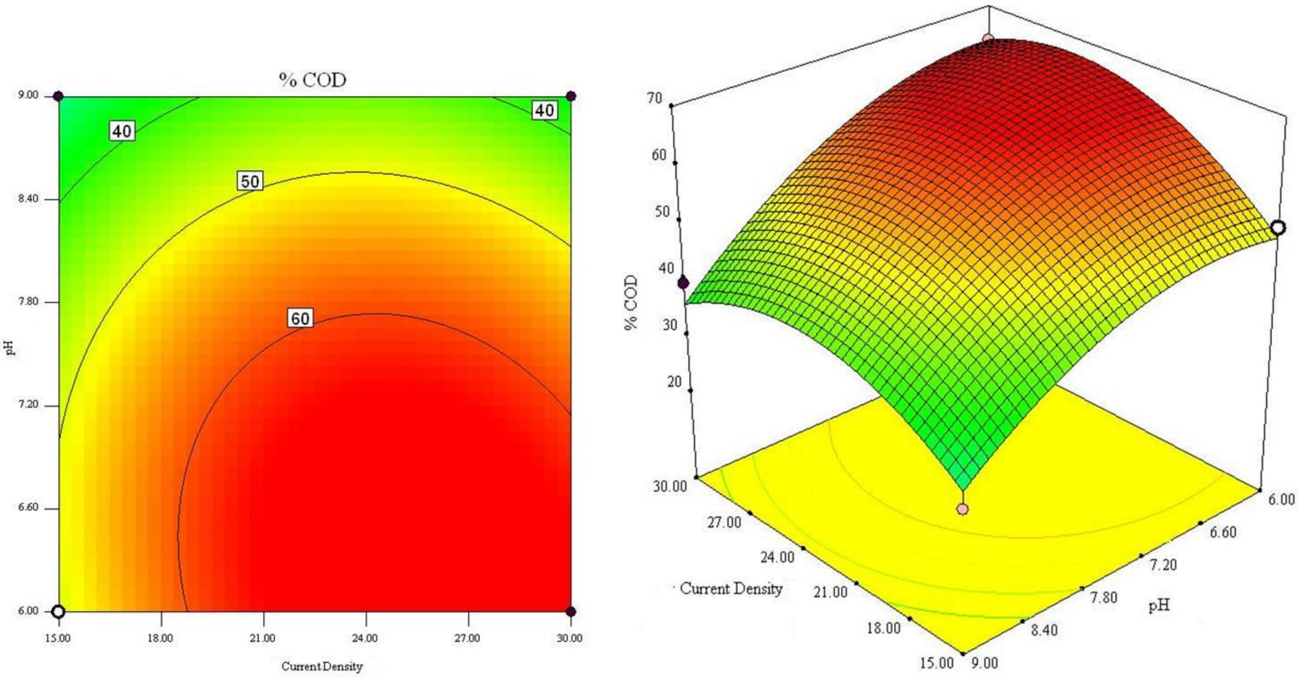

Figure 2. Effect of COD removal on current density

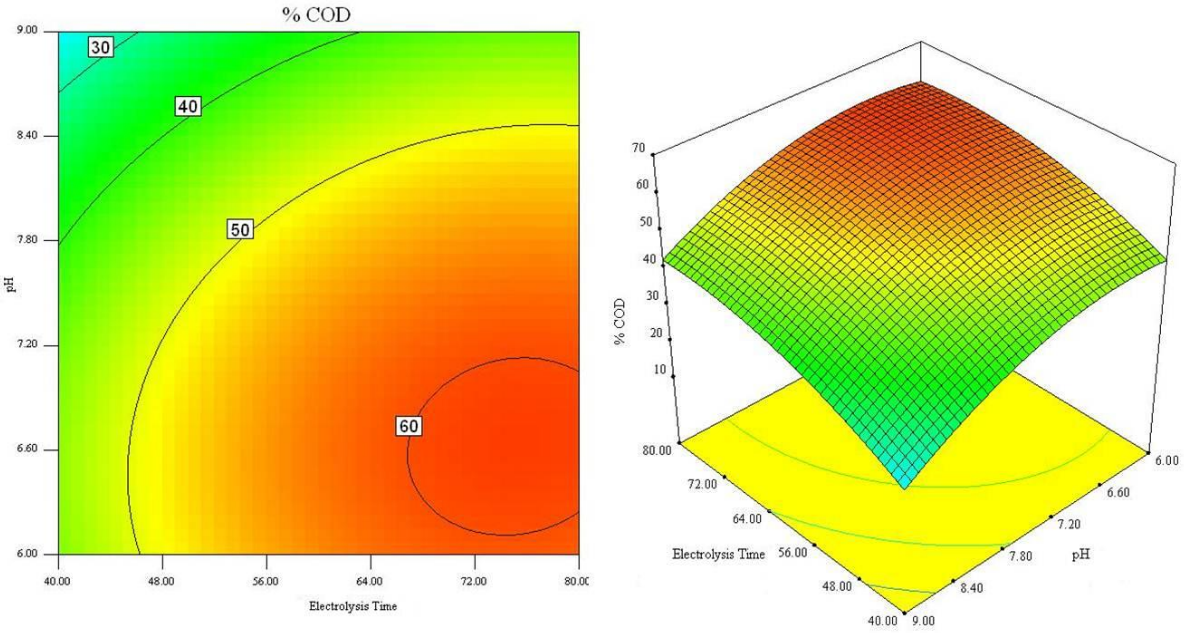

Figure 3. Effect of COD removal on pH and time

At alkaline pH the molecules loses the inonisable hydrogen atoms facilitating the oxidation by electrophilic OH radical. Henceforth increasing pH would decrease the oxygen evolution potential and increasing the rate of oxygen at the anode surface, resulting in slower diffusion of the organics at the anode [27]. Treatment time is related with energy consumption and wastewater treatment performance.It is well known that the removal efficiency did not improve much after 80 min electrolysis, but the prolonged time would increase the electrochemical treatment cost.

3.5. Optimum condition and energy consumption

Statistical analysis showed that the optimum value of j, m, pH and t were found to be 18mA/cm^2, 1g/l, 6.5 and 80 min and the maximum COD removal was found as 58.85% and turbidity removal was found as 95% for the optimum condition respectively. From eq (6) it is observed that the energy consumption for the optimum value was 16.2 kWh/m^3.

4. CONCLUSION

The electrochemical treatment of sago wastewater was investigated with Ti/PbO2 electrodes in the presence of NaCl electrolyte. The effects of operating parameters such as current density, pH and electrolysis time on COD removal were found batch-wise and the COD removal changed in the range of 12.4%–63.2% respectively. Due to electro catalytic nature of Ti/PbO2 anodes, removal of COD in the presence of NaCl electrolyte is a combined effect of direct as well as indirect anodic oxidation. The best operational conditions for COD removal of 58.85% were attained in 18mA/cm^2, 1g/l, 6.5 and 80 min respectively.The electrolysis time of 80 min is the main advantage of this method over conventional biological treatments. Thus the behaviour of the anodes was better evidenced in the electrolyses carried out and also the energy consumption was calculated. For the use of electrochemical treatment in industrial applications, treatment process was experimentally designed and optimized through response surface methodology, it may be a promising and cost driven approach to remove organic pollutants present in sago wastewater.

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