



Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Augmentation of biodegradability of pulp and paper industry wastewater by electrochemical pre-treatment and optimization by RSM

P.A. Soloman^a, C. Ahmed Basha^{b,*}, M. Velan^a, N. Balasubramanian^a, P. Marimuthu^c^a Department of Chemical Engineering, A.C. Tech Campus, Anna University-Chennai, Chennai 600025, India^b Central Electrochemical Research Institute, Karaikudi 630006, Tamilnadu, India^c Seshasayee Paper and Boards Limited, Erode 638007, Tamilnadu, India

ARTICLE INFO

Article history:

Received 5 December 2008

Received in revised form 5 May 2009

Accepted 6 July 2009

Keywords:

Electrochemical pre-treatment

Pulp and paper wastewater

Biodegradability

COD removal

Response surface methodology

ABSTRACT

Biological treatment of pulp and paper industry wastewater is made effective by giving a simple electrochemical pre-treatment. Biodegradability index is found to be improved from 0.11 to 0.46 by a short (6.9 min) treatment in mild conditions (current density: 112.9 A m⁻², pH 7.3). The optimal operating point for maximum biodegradability has been found out using response surface methodology (RSM). It is also noticed that there exists an optimal operating point for maximum biodegradability. The specific energy consumption and current efficiency figures at the optimal condition are also promising. Moreover there is considerable reduction in the pollutant load (COD removal: 55% and color removal: 87%). Performance of the process at this operating point has been validated by running biological treatment. Considerable reduction in the requirement of biological reactor volume can be expected by giving such a simple electrochemical pre-treatment.

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1. Introduction

The pulp and paper industry is one of the oldest and core industrial sector in India. It is a highly capital, energy, and water intensive industry. It is also a highly polluting process and requires substantial investments in pollution control equipments. India produces 6 million tonnes of paper per year though 311 mills by consuming around 900 million m³ of water and discharging 700 million m³ of wastewater. Out of these about 270 small paper mills (capacity ≤ 10 000 tonnes per annum (TPA), having a total installed capacity of 1.47 MTPA) do not have chemical recovery units [1]. India's current average fresh specific water consumption for large-scale wood based pulp and paper mill, of about 150 m³ per tonne of product is far above the global best specific water consumption of 28.66 m³ per tonne. This large gap is primarily attributed to the use of obsolete technology/equipments and poor water management practices. The large water requirements and consumption by the Indian pulp and paper industries has led to, water fast becoming a scarce commodity and lowering of the ground water table and thus increased pumping costs and more importantly water shortages in many regions.

The most significant sources of pollution among various process stages in pulp and paper industry are wood preparation, pulping,

pulp washing, bleaching and paper machine and coating operations. Common pollutants include suspended solids, oxygen demanding wastes, color, basicity, heavy metals, alkali and alkaline earth metals, phenols, chloro-organics, cyanide, sulphides and other soluble substances [2]. The resultant effects on the environment are slime growth, thermal impacts, scum formation, color problems and loss of aesthetic beauty. They also increase the amount of toxic substances in water, causing death to the zooplankton and fish, as well as profoundly affecting the terrestrial ecosystem [3].

Conventionally pulp and paper industries in India employ biological method of wastewater treatment. Even though the preliminary and primary step of the process improves the biodegradability index (BI), it seldom crosses 0.3. Thus the biological step is slow and demands larger reactor volume. Morais and Zamora [34] reported that samples with biodegradability index (defined as the ratio of BOD to COD) smaller than 0.3 are not appropriate for biological degradation. According to Chamarro et al. [35] for complete biodegradation, the effluent must present a biodegradability index of at least 0.4. Other treatment alternatives such as adsorption [4], wet oxidation [5], ozone treatment [6], fractional precipitation [7], ultra filtration [8], combined biological and membrane based treatment [9] etc. are still questionable on their technical and economic feasibility in large-scale operation.

Over the past two decades there has been increasing interest in the use of electrochemical techniques such as electro-coagulation, electro-flotation and electro-oxidation for the treatment of organic effluents. Technical feasibility of the treatment for various

* Corresponding author. Tel.: +91 4565 227550; fax: +91 4565 227713.

E-mail addresses: cab.50@yahoo.co.in, basha@cecric.res.in (C. Ahmed Basha).

industrial effluents such as electroplating wastewater [10]; potable water [11]; oil mill wastewater [12]; urban wastewater [13]; heavy metal laden wastewater [14]; nitrite effluent [15]; defluoridation [16]; arsenic removal [17]; textile dyes [18]; landfill leachate [19]; restaurant wastewater [20]; laundry wastewater [21]; surfactants [22]; agro industry wastewater [23], etc. have been established.

Electrochemical coagulation of pulp and paper effluent has been reported by five researchers [1,24–27]. All the researchers supported the technical feasibility of the process. From the literature and experiments it can be concluded that complete mineralization of large quantity of such a heavily loaded effluent will not be economically viable. Thus it has been thought of invoking for the possible distribution of treatment loads by integrating various techniques.

During the pulping process complete removal of the lignin available in wood/bagasse is not usually tried in the digester because of economic reasons. Such a trial will affect the productivity due to loss of wood fibers with the digestion chemicals. A higher load of lignin removal in the bleaching step increases the consumption of bleaching agents and resultant pollution. Thus, in practice, the proportion of lignin removal among the digestion and bleaching steps has been optimized. The bleaching effluent is so dilute in organic matter that the heat and chemical recovery is not economical. Therefore any level of process intensification is not going to avoid the presence of lignin and hemi-celluloses in the wastewater. It has to be treated and removed.

Tamilnadu Newsprint and Papers Limited (TNPL Ltd.), is one of the large-scale paper industry in south India located in Karur, Tamilnadu state. In the Kraft pulping process, lion share of the lignin and hemi-cellulose, removed from the wood and bagasse are separated in the washing section as black liquor. It is disposed by burning, recovering its heat value and chemical value in the recovery section of the plant. The major portion of the remaining lignin is coming out through the *Decker filtrate*, a rotary drum filtration arrangement. This stream, even though less in quantity ($4000\text{ m}^3\text{ day}^{-1}$) contributes much towards the lignin part and color of the total wastewater stream ($56,000\text{ m}^3\text{ day}^{-1}$).

TNPL Ltd. is treating highly loaded wastewater stream (mainly from bagasse wash, COD: 4500 mg L^{-1}) and moderately loaded stream (remaining combined stream, COD: 1500 mg L^{-1}) in different routes. The fuel value of the highly loaded stream is withdrawn in two up-flow anaerobic sludge blankets (UASBs) and mixed with primary clarified moderately loaded stream for aerobic treatment. The overall performance of the system treating $56,000\text{ m}^3$ every day is good. BOD of the treated effluent is 1, 2 or seldom 3 mg L^{-1} , but COD $150\text{--}250\text{ mg L}^{-1}$ with light brown in color. The result shows that any type of improvement (via. residence time or adding more units) on the biological treatment step on the existing process is not going to make any improvement in the final effluent composition. The high COD in this stream is because of the dissolved lignin part in the effluent.

It is attempted in the present investigation to study the enhancement of biodegradability of the *Decker filtrate* stream by electrochemical treatment. The electro-treated filtrate is further treated biologically in order to study the advantage of pre-treatment. The mechanism of electro-coagulation and the effect of individual parameters on the efficiency of electro-coagulation have been critically examined.

2. Mechanism of electro-coagulation

The coagulants and strong oxidizing agents generated in situ during the electro-coagulation process play roles in removing the organic part of the waste. The proportion or predominance of these

electro-coagulation and electro-oxidation mechanisms is decided by the electrolytic conditions. The coagulants remove the dissolved organic part by precipitation and suspended fines by adsorption. Electrolytic condition, especially pH, is influencing the predominance of these mechanisms. In general suspended fines, especially of cellulose, in the pulp and paper wastewater is the main reason for a low BI. It has been noticed from the Pourbaix diagram of iron hydroxides that at a pH of 7.3, the solubility is minimum, a condition in which adsorption may predominate causing more suspended fine removal. The current efficiencies based on amount of anode dissolved, in the order of 144% shows the involvement of non-electrochemical mechanisms of electrode dissolution such as chemical dissolution [28].

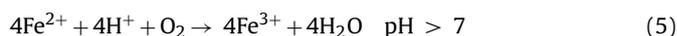
Electro-coagulation involves many chemical and physical phenomena, which can be summarized in three successive stages as the formation of coagulants in situ, by electrolytic oxidation of the sacrificial electrode, destabilization of the contaminants, particulate suspension (and breaking of emulsions) and aggregation of the destabilized phases to form flocs.

Electro-coagulation has been successfully employed in industrial effluents for removal of organic contaminants. In this process, a potential is applied to the metal anodes, typically fabricated from either iron or aluminum, which causes two separate reactions. Iron upon oxidation in an electrolytic system produces iron hydroxide, $\text{Fe}(\text{OH})_n$, where $n=2$ or 3. When a potential is applied from an external power source, the sacrificial anode undergoes oxidation. Mechanisms [29–31] that were proposed for the production of $\text{Fe}(\text{OH})_n$ are

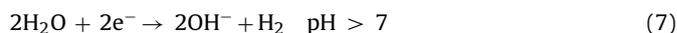
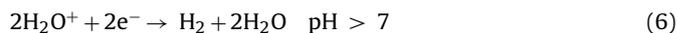
Anode



Bulk



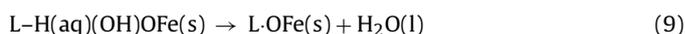
Cathode



In turn the ionic species of bulk may react to form $\text{Fe}(\text{OH})_2$ according to the reaction:



The electrolytic gases generated at the cathode helps to float the flocculated particles. The metal hydroxide flocs can take part in removing the organic matter present in the solution by precipitation and/or adsorption mechanism. Other iron hydroxides can also be formed. The monomeric forms of metal hydroxides can get polymerized giving various forms of ferric hydroxo complexes namely, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$, $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^{+}$, $\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$, $\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_2^{4+}$, $\text{Fe}(\text{OH})_4^-$, etc. The $\text{Fe}(\text{OH})_n$ formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation [32]. In surface complexation mode, the pollutant acts as a ligand (L) to chemically bind hydrous iron:



The prehydrolysis of Fe^{3+} cations also leads to the formation of reactive clusters for treatment. The performance of electrocoagulation is well described by the pseudo-first-order kinetics:

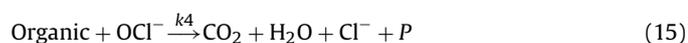
$$-\frac{dL}{dt} = kL \text{ or } -\frac{d[\text{COD}]}{dt} = k[\text{COD}] = k_L a [\text{COD}] \quad (10)$$

Or

$$[\text{COD}] = [\text{COD}]_0 \exp(-k_L a t) \quad (11)$$

' a ' is the specific electrode surface (cm^{-1}), defined as the ratio of active electrode surface to the electrolyte volume and k_L , the mass transfer coefficient (cm min^{-1}).

The contribution of separation by agglomeration of the particles by precipitation mechanism is predominant when pH is low, while adsorption plays a major role of separation mechanism in the case of operation at neutral to higher pH levels. The strong oxidizing agents produced in situ can take part in destructing the organic matter present in the waste by oxidizing them:



The hypochlorite ions can oxidize the long chain hydrocarbons to lower ones thereby improving the biodegradability to an extent, especially during the early stage of the treatment.

3. Materials and methods

All the chemicals used in the study were analytically pure. Wastewater investigated here is the *Decker filtrate* collected from TNPL Ltd., Karur, Tamilnadu, India. The wastewater was characterized for BOD, COD, pH, solids, dissolved salts and color by using the standard methods [33]. The characteristics of the wastewater are shown in Table 1.

3.1. Determination of BI

The biodegradability index is defined as the ratio of BOD to COD. The value ranges from zero to unity. Morais and Zamora [34] reported that samples with biodegradability index smaller than 0.3 are not appropriate for biological degradation. According to Chamarro et al. [35] for complete biodegradation, the effluent must present a biodegradability index of at least 0.4.

3.2. Response surface methodology (RSM)

In the present study, the response surface methodology (RSM) has been used to determine the relation between BI and operating parameters such as current density, time and pH. Table 2 gives the

Table 1
Characteristics of pulp and paper wastewater.

Characteristics	Value
pH	7.8 ± 0.6
Conductivity (mmhos cm^{-1})	5.6 ± 0.5
Cl^- (mg L^{-1})	80 ± 6
SO_4^{2-} (mg L^{-1})	490 ± 40
Color (platinum cobalt units, PCU)	1550 ± 110
COD (mg L^{-1})	925 ± 65
BOD (mg L^{-1})	102 ± 8
BOD/COD	0.11 ± 0.0165
Suspended solids (mg L^{-1})	235 ± 18
Dissolved solids (mg L^{-1})	310 ± 25
Total solids (mg L^{-1})	545 ± 42

Table 2
The level and range of variables chosen for electrochemical treatment.

Independent variable	Coded levels		
	-1	0	+1
Current density (A m^{-2})	50	100	150
Electrolysis time (min)	2	6	10
pH	5	7	9

parameters and the operating ranges covered. The current density, electrolysis time and pH are referred by uncoded variables as X_1 , X_2 , and X_3 respectively. The variables in uncoded form are converted to coded form: x_1 , x_2 and x_3 using the following equation [36]:

$$x = \frac{X - ((X_{\text{max}} + X_{\text{min}})/(2))}{(X_{\text{max}} - X_{\text{min}})/(2)} \quad (16)$$

The Box–Behnken experimental design of RSM has been chosen to find the relationship between the response functions and variables using the statistical software tool MINITAB 14 (PA, USA). The three level second-order design demand comparatively lesser number of experimental data for precise prediction. In the Box–Behnken method a total number of 15 experiments, including three centre points, are carried out to estimate the BI. The interaction between the variables and the analysis of variance (ANOVA) has been studied by using RSM. The quality of the fit of this model is expressed by the coefficient of determination R^2 . The fit is confirmed by means of the absolute average deviation (AAD) defined as

$$\text{AAD} = \left\{ \frac{\sum_{i=1}^p (|y_{i,\text{exp}} - y_{i,\text{pred}}|) / (y_{i,\text{exp}})}{p} \right\} \times 100 \quad (17)$$

where $y_{i,\text{exp}}$ and $y_{i,\text{pred}}$ refers the experimental and predicted responses and p refers the number of experimental runs.

3.3. Electrolysis system

Fig. 1 shows the schematic representation of the experimental apparatus. Experiments were conducted in batch process using undivided cell of 1500 mL capacity. Electrodes were positioned vertically and parallel to each other with an inner gap of 1 cm. Four pairs of electrodes, of active area ($10 \text{ cm} \times 4 \text{ cm}$) 40 cm^2 each, were used. The electrode plates were cleaned manually by abrasion with sand paper and by the treatment with 15% hydrochloric acid followed by washing with distilled water prior to every run. 3 g L^{-1} sodium chloride was added to the wastewater as supporting electrolyte. The wastewater was then adjusted to the required pH either by using sulphuric acid or sodium hydroxide. 1500 mL of the wastewater was filled in the reactor which dips 40 cm^2 of surface of the electrodes. The solution was constantly stirred at 200 rpm with a magnetic stirrer in order to maintain uniform concentration condition. dc supply was given to the electrodes in mono-polar mode according to the required current density and the experiments were carried out under constant current conditions. Samples were collected for estimation of COD, BOD and color. Weight of the anode metal dissolved, final pH and amount of sludge formed were also noticed.

Preliminary experiments were carried out on the enhancement of BI for the purpose of selecting the most influencing factors and their range. Different experimental runs, as given in Table 3, were started for every case as demanded by the Box–Behnken design. The best operating point giving maximum improvement in biodegradability of the effluent has been found out using RSM. The performance of the electrochemical treatment at this

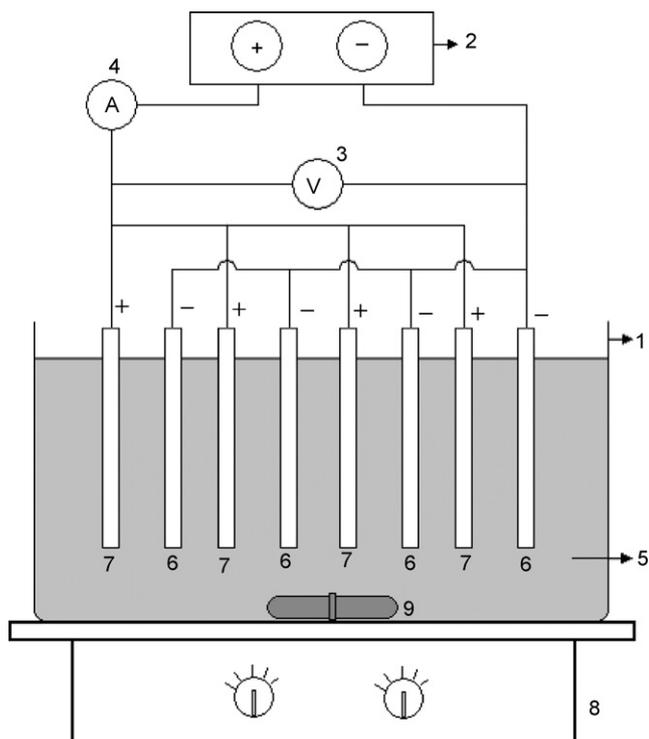


Fig. 1. Experimental set-up: (1) electro-coagulation cell, (2) dc regulated power supply, (3) digital voltmeter, (4) digital ammeter, (5) wastewater, (6) mild steel cathodes, (7) mild steel anodes, (8) magnetic stirring set-up and (9) magnetic stirring element.

operating point is further investigated by running experiments repeated for six times. The electro-treated effluent at the optimal condition was further treated in an aerated biological system in activated sludge. 500 ml of the effluent is added with nutrient solution: anhydrous potassium di-hydrogen phosphate (KH_2PO_4), anhydrous dipotassium hydrogen phosphate (K_2HPO_4), disodium hydrogen phosphate dihydrate ($\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$) and ammonium chloride (NH_4Cl): (i) magnesium sulphate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), (ii) anhydrous calcium chloride (CaCl_2) and (iii) anhydrous ferric chloride (FeCl_3). Preparation of the inoculum was carried out by collecting samples of activated sludge from the aeration tank of a nearby biological treatment facility. The inoculum was aerated at room temperature for 24 h before added to the effluent. The contents are aerated continuously and samples were withdrawn at regular intervals for the estimation of COD. The raw effluent ('Decker filtrate') is also biologically similarly treated in

order to quantify the improvement in biodegradability due to the pre-treatment.

4. Results and discussions

The Decker filtrate of a large-scale pulp and paper industry has been treated electrochemically using iron anode. The characteristics, as shown in Table 1, show that the wastewater is loaded with more amounts of slowly biodegradable substances such as lignin and cellulose. The experimental domain (current density: $50\text{--}150 \text{ A m}^{-2}$, time: 2–10 min, pH 5–9), as presented in Table 2, has been decided from the results of the preliminary runs. Moreover preliminary experiments were helpful in selecting the more effective anode. It was found that, in comparison with aluminium anode, mild steel anode giving better performance with respect to rate and completion of the reaction within the experimental domain. In all the cases stainless steel was used as the cathode. The effect of operating variables of current density, electrolysis time and pH on BI was investigated using RSM.

4.1. Response surface methodology

The responses such as cell voltage, amount of anode dissolved, COD removal, color removal, BI, weight of sludge formed and the final pH for the 15 experimental conditions as demanded by the Box–Behnken design is presented in Table 3. A second-order polynomial model, as given below, was fitted to the experimental data for BI:

$$y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \beta_3x_3 + \beta_{11}x_1^2 + \beta_{22}x_2^2 + \beta_{33}x_3^2 + \beta_{12}x_1x_2 + \beta_{13}x_1x_3 + \beta_{23}x_2x_3 \quad (18)$$

where y is the BI in coded units, β_0 is a constant, β_1 , β_2 and β_3 are the regression coefficients for linear effects, β_{11} , β_{22} and β_{33} are the quadratic coefficients and β_{12} , β_{13} and β_{23} are the interaction coefficients. The coefficients of the model are given in Table 4. By using the model for BI proposed by RSM it is possible to predict BI at any combination of the three parameters in consideration with in the experimental domain. The significance of regression coefficients were analysed using p - and t -test. The ' p ', ' t ' and significant level ($1 - p$) are given in Table 4. It can be observed from the table that all terms except the interaction terms are considerably influencing the response. The interaction terms of current density–pH and time–pH are the least influential terms in the model. Eq. (18) can also be represented in terms of uncoded variables as

$$Y = -1.2219 + 0.01155X_1 + 0.0856X_2 + 0.2006X_3 - 4.9 \times 10^{-5}X_1^2$$

Table 3
The design of experiment and experimental response for electrochemical treatment.

Sl. no.	X_1 (A m^{-2})	X_2 (min)	X_3	Voltage (V)	ΔW , anode (g)	COD rem. (%)	Color rem. (%)	BI	Wt. of sludge (g)	Final pH
1	50	2	7	1.4	0.044	15.6	48	0.13	0.68	7.2
2	150	2	7	3.8	0.220	26.8	72	0.29	1.8	7.2
3	50	10	7	1.4	0.338	35.8	70	0.22	2.4	7.6
4	150	10	7	3.9	1.279	57.0	96	0.32	6.2	7.4
5	50	6	5	1.4	0.156	31.2	62	0.18	1.78	6
6	150	6	5	3.8	0.735	45.3	82	0.34	4.1	6.4
7	50	6	9	1.4	0.147	32.6	70	0.2	1.9	8.4
8	150	6	9	3.8	0.808	48.2	86	0.37	4.6	7.9
9	100	2	5	2.4	0.103	21.3	55	0.23	1.6	5.8
10	100	10	5	2.4	0.838	51.5	86	0.34	4.6	6.8
11	100	2	9	2.4	0.103	23.1	54	0.28	1.1	8.4
12	100	10	9	2.4	0.882	54.1	91	0.38	1.32	8.1
13	100	6	7	2.4	0.485	52.3	52	0.45	3.6	7.5
14	100	6	7	2.4	0.529	53.8	53	0.46	3.7	7.5
15	100	6	7	2.4	0.470	53.1	52	0.44	3.5	7.5

Table 4
Estimated regression coefficients and corresponding 't' and 'p' values for BI.

Factor	Coefficient of the model in coded factors	't' value	'p' value	Significance level
β_0	0.45000	38.730	0.000	>99%
β_1	0.07375	10.365	0.000	>99%
β_2	0.04125	5.798	0.002	>99%
β_3	0.01750	2.460	0.057	>94%
β_{11}	-0.12250	-11.697	0.000	>99%
β_{22}	-0.08750	-8.355	0.000	>99%
β_{33}	-0.05500	-5.252	0.003	>99%
β_{12}	-0.01500	-1.491	0.196	>80%
β_{13}	0.00250	0.248	0.814	>18%
β_{23}	-0.00250	-0.248	0.814	>18%

Table 5
ANOVA results for the percentage COD removal.

Source	Degree of freedom	Sum of squares	Mean squares	F-value	p
Regression	9	0.144548	0.016061	39.66	0
Residual error	5	0.002025	0.000405		
Lack-of-fit	3	0.001825	0.000608	6.08	0.144
Pure error	2	0.0002	0.0001		
Total	14	0.146573			

$$\begin{aligned}
 & -0.00547X_2^2 - 0.01375X_3^2 - 7.5 \times 10^{-5}X_1X_2 + 2.5 \times 10^{-5}X_1X_3 \\
 & - 3.125 \times 10^{-4}X_2X_3
 \end{aligned}
 \tag{19}$$

where Y is BI in uncoded units. The analysis of variance (ANOVA), presented in Table 5 shows a higher F-value for regression and a lower (39.66) F-value for lack-of-fit (6.08) than the tabulated values of 4.77 and 8.81, respectively. This shows that the quadratic model can well navigate the design space.

4.2. Combined effect of variables

It is interesting to note that the trend of variation of BI with respect to the parameters in consideration is similar. In Figs. 2–4 as the parameter increases, BI increases to an extent and then decreases. The optimal condition giving maximum BI has been found out by the Monte-Carlo optimization technique (Solving the set of equations obtained by partially differentiating the RSM model and equate to zero) and reported as; current density: 112.9 A m⁻²,

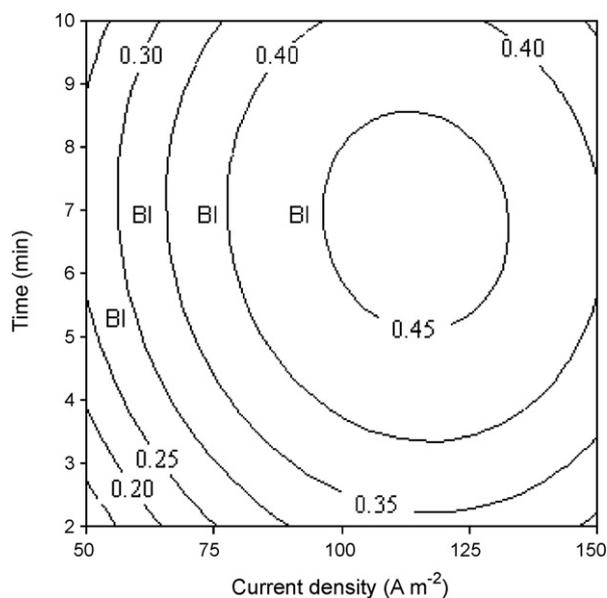


Fig. 2. Effect of current density and electrolysis time on BI at the pH of 7.3.

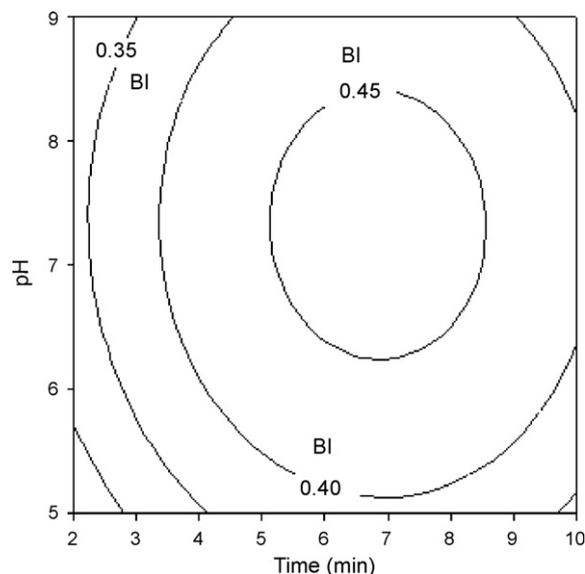


Fig. 3. Effect of electrolysis time and pH on BI at the current density of 112.9 A m⁻².

time: 6.9 min and pH 7.3; the corresponding BI being 0.4615. The third parameter in Figs. 2–4 is considered at its optimal value.

As can be read from Fig. 2, BI is directly related to both the electrolysis time and current density at the early stage of the treatment.

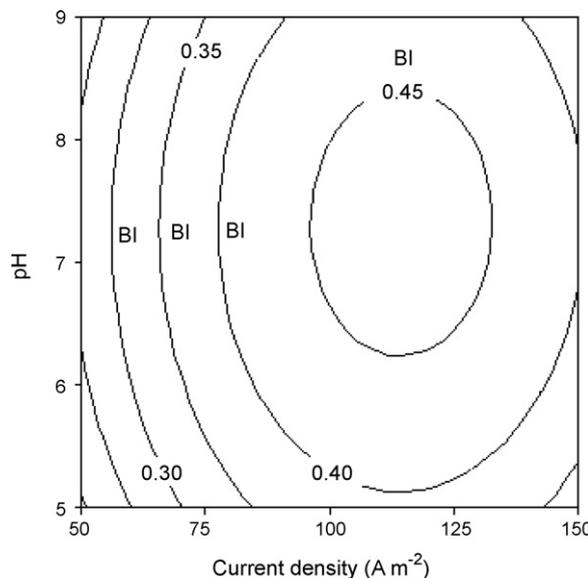


Fig. 4. Effect of current density and pH on BI in the electrolysis duration of 6.9 min.

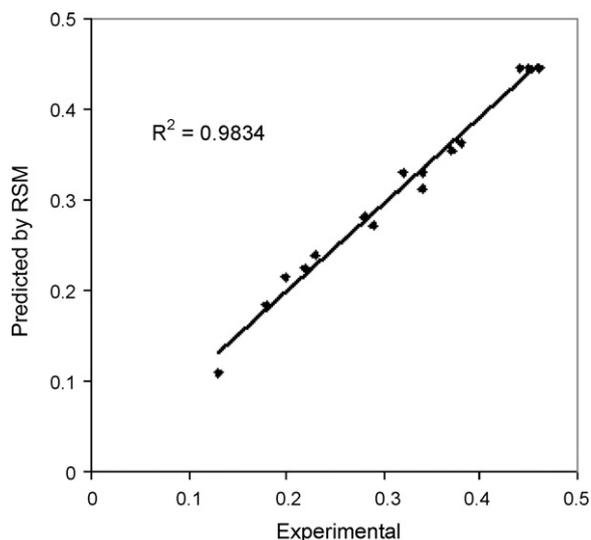


Fig. 5. Comparison of experimental BI vs. BI predicted by RSM.

There is a decrease in BI after treatment duration of 6.9 min and current density of 112.9 A m^{-2} . As explained in the mechanism of the process, there is a contribution of oxidation by the strong oxidizing agents generated in the process in degrading the organic matter. The long chain organic matter such as lignin may get converted into lower molecular weight components. This step will not considerably reduce COD but increases BOD, resulting in an increase in BI. Moreover, the other mechanism – coagulation – can first acts well on the suspended fines which are predominantly, cellulose fines, the other slowly degradable organic part of the waste. This early stage phenomenon can also significantly increase BI. After a definite period of operation, even though the oxidation and coagulation mechanisms remove organic matter, the proportion of easily degradable to slowly degradable part changes which results in a net decrease in BI. The effect of treatment duration on BI can also be noted from Fig. 3.

The effect of current density on BI can also be explained as because of the relative contribution of the oxidative–coagulate mechanisms. At a higher current density, it is expected to reach the optimal time for maximum BI early. After 112.9 A m^{-2} , in the present investigation, the oxidative–coagulate mechanisms started attacking more easily degradable part than the condition at lower current density values, which may result in a decrease in BI. The effect of current density on BI can also be noted from Fig. 4.

As explained before, the trend of BI with respect to the variation of pH also similar 7.3 being the best value of pH giving maximum BI. It has been noticed from the Pourbaix diagram of iron hydroxides that at a pH of 7.3, the solubility is minimum, a condition in which adsorption may predominate causing more suspended fine removal. This can be the reason for a higher value of BI at near neutral pH. During all the experiments including the preliminary runs, it was observed that the performance of mild steel electrode was superior at neutral than alkaline and acidic conditions, probably due to more hydroxide formation.

The model predictions are compared with the experimental observations and found satisfactory match, in Fig. 5. The AAD, R^2 and MSE were obtained as 4.4%, 0.9834 and 1.87×10^{-4} , respectively. These parameters show that the model accuracy is adequate enough to predict the performance of process. The combined effect of the parameters studied on COD removal is presented in Figs. 6 and 7. COD removal increases with increase in treatment duration and current density as shown Fig. 6. The rate of removal of COD is high in the early stage of operation. Later the COD removal rate diminishes.

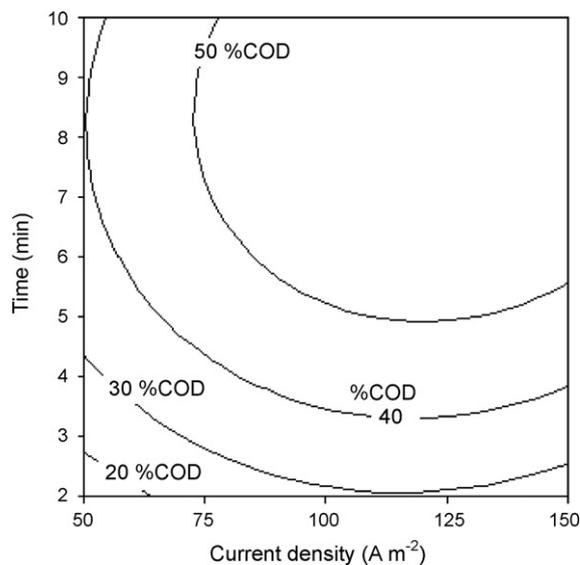


Fig. 6. Effect of current density and electrolysis time on COD removal efficiency (%), pH 7.3.

Fig. 7 shows that pH has got little effect on % COD removal. Moreover it shows that neutral pH is more favorable for COD removal.

The progress of COD destruction for operation at various current densities is presented in Fig. 8 which shows the better operating current density as 100 A m^{-2} . Considerable increase in COD destruction can be noticed when the operating current density increases from 50 to 100 A m^{-2} . The rate constant is found increased from 0.33 to 0.57 cm min^{-1} . A further increase in the same quantity in current density does give literally no increase in COD removal. This may because of the change over of the controlling mechanism of the process from current density controlled situation to other conditions as salt limited.

The condition of maximum BI is verified experimentally by repeating six times and examined in detail by estimating color removal (%), anode material dissolution, final pH, current efficiency (CE in %), specific energy consumption based on amount of COD digested (SEC_1 in $\text{kWh}(\text{kg COD})^{-1}$) and specific energy

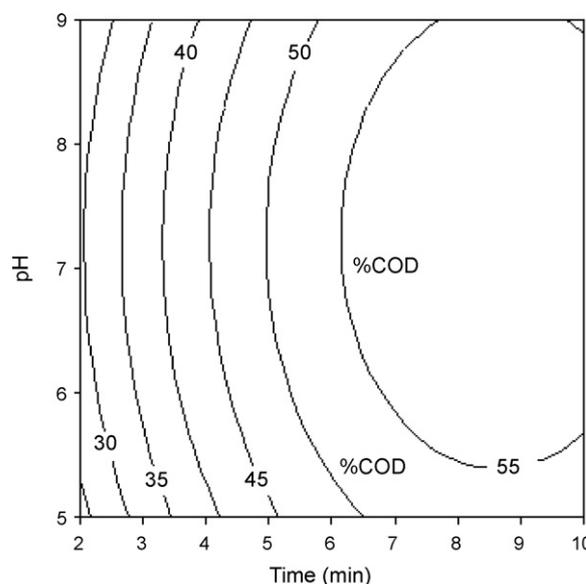


Fig. 7. Effect of electrolysis time and pH on COD removal efficiency (%), current density: 112.9 A m^{-2} .

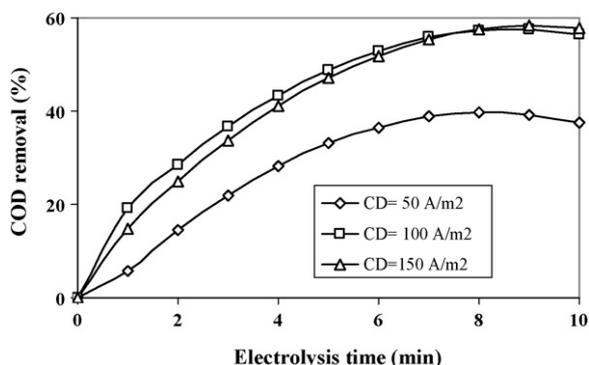


Fig. 8. Variation of COD removal efficiency (%) with electrolysis time at different current densities.

consumption based on amount of anode dissolved (SEC_2 in $kWh(kg Fe)^{-1}$), amount of sludge per COD digested ($g g^{-1}$) and amount of anode dissolved per COD digested ($g g^{-1}$) using the following equations:

$$CE = \frac{\Delta W_{actual}}{\Delta W_{theoretical}} \times 100 \quad (20)$$

$$\Delta W_{theoretical} = \frac{MIt}{zF} \times 3600 \quad (21)$$

$$SEC_1 = \frac{VIt}{\Delta C \times V_l \times 10^{-3} \times 3600} \quad (22)$$

$$SEC_2 = \frac{zFV}{M \times EE_2 \times 3600} \quad (23)$$

where ΔC is the difference in COD due to treatment in $mg L^{-1}$, V is the voltage (V), I is current (A), t is time (s), V_l is volume of the reactor (L), ΔW is the weight of anode metal consumed. M is the atomic weight of iron ($56 g mol^{-1}$), z is the valence ($z_{Fe} = 2$) and F the Faraday's constant ($96485.3 C equiv^{-1}$). The results are presented in Table 6.

Current efficiency more than 100% is a clear indication of other mechanism than electrochemical in dissolving the anode probably chemical dissolution. Obviously the coagulants generated so, also will take part in the pollutant removal work, thereby improves the specific energy consumption based on COD removal (SEC_1). The amount of sludge formed will also influenced by the part of anode chemically dissolved. The amount of sludge formed is considerably lower than that during the chemical coagulation process. The energy figures of the process are remarkably better than other electrochemical works reported mainly because of the shorter period of operation, lower current density and better conductivity of the effluent.

Many researchers (for example Mahesh et al. [1]) have reported the expression for current efficiency (%) of electro-coagulation pro-

cess as

$$CE = \frac{\Delta C \times V_l \times 10^{-3} \times F}{8 \times I \times t} \times 100 \quad (24)$$

This expression is correct only when the COD is removed by oxidative mechanism alone. But in electro-coagulation the oxidation mechanism plays a small part of the role in removing COD. Lion share of the organic matter is removed by coagulation mechanism. This is the reason for better energy figures of electro-coagulation process in comparison with electro-oxidation, disadvantage being the sludge formation.

To ensure that the microorganisms will grow, they must be allowed to remain in the system long enough to reproduce. This period depends on their growth rate, which is related directly to the rate at which they metabolize or utilize the waste. If the environmental conditions are controlled properly, the growth rate of the microorganisms can ensure effective waste stabilization. In the system the rate of growth of bacterial cells can be defined by the following relationship:

$$r_g = \frac{dX}{dt} = \mu X \quad (25)$$

where r_g is the rate of bacterial growth, μ the specific growth rate and X is the concentration of microorganisms. Experimentally it has been found that the effect of a limiting substrate or nutrient can often be defined adequately using the following expression proposed by Monod:

$$\mu = \mu_m \frac{S}{k_s + S} \quad (26)$$

where μ_m is the maximum specific growth rate, S the concentration of growth-limiting substrate in solution and k_s is the half-velocity constant, substrate concentration at one-half the maximum growth rate. Because the quantity of the new cell produced has been observed to be reproducible for given substrate, the following relationship has been developed the rate of substrate utilization and the rate of growth:

$$\frac{dX}{dt} = -Y \frac{dS}{dt} \quad (27)$$

Y is the maximum yield coefficient (defined as the ratio of the mass of cell formed to the mass of substrate consumed). $r_{su} = dS/dt$ is the substrate utilization rate. Combining Eq. (25–27) the expression for the rate of substrate utilization can be written as follows:

$$\frac{dS}{dt} = -\mu_m \frac{XS}{Y(k_s + S)} \quad (28)$$

In equation (28), the term $\mu_m X/Y$ is often replaced by the term C , defined as the maximum rate of substrate utilization, the resulting expression is

$$\frac{dS}{dt} = -\frac{CS}{k_s + S} \quad (29)$$

In bacteria systems used for wastewater treatment, the distribution of cell age is such that not all the cells in the system are in the log-growth phase. Consequently, the expression for the rate of growth must be corrected to account for the energy required for cell maintenance. However, if most of the cells in the bacterial system are in lag-growth phase, the solution of equation (29) is

$$k_s \ln \left(\frac{S}{S_0} \right) + (S - S_0) = -Ct \quad (30)$$

where S_0 is the initial substrate concentration. We can rewrite Eq. (30) as

$$\frac{\ln(S/S_0)}{(S - S_0)} = -\frac{C}{k_s} \frac{t}{(S - S_0)} - \frac{1}{k_s} \quad (31)$$

Table 6 Detailed result of six experimental runs at optimal condition for maximum BI.

Term	Value			
	Maximum	Minimum	Average	Std. dev.
Color removal (%)	89	82	86.67	2.73
COD removal (%)	56.2	54	55.13	0.911
CE (%)	150.1	136.9	144.38	4.53
SEC_1 ($kWh(kg COD)^{-1}$)	1.21	1.17	1.19	0.019
SEC_2 ($kWh(kg Fe)^{-1}$)	1.75	1.59	1.66	0.053
Weight of sludge formed ($g(g COD)^{-1}$)	5.22	4.77	5.03	0.178
Weight of anode dissolved ($g(g COD)^{-1}$)	0.75	0.67	0.72	0.027

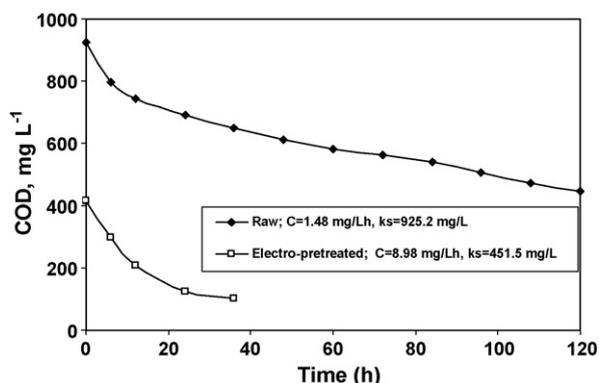


Fig. 9. Rate of fall of COD for raw effluent and electro-pre-treated effluent.

The plot of $\ln(S/S_0)/(S - S_0)$ vs. $t/(S - S_0)$ will be linear if the above kinetics (Monod) follows. From the intercept half-velocity constant can be computed and the maximum utilization rate of substrate is obtained by dividing slope by intercept.

The rate of COD removal in an aerated biological system in activated sludge for electro-pre-treated effluent (treated at the optimal condition), and raw effluent is presented in Fig. 9. It can be read from the figure that biodegradability of the *Decker filtrate* has been improved considerably due to the electro-pre-treatment. Considerable reduction in the requirement of biological reactor volume can be expected by giving such a simple electrochemical pre-treatment. For the present case to understand the effect of electro-pre-treatment on k_s , the half-velocity constant and C , the maximum substrate utilization rate for biological degradation on aeration in batch reactor are computed using Eq. (31) by least square method and shown in Fig. 8. The rate of fall of COD was remarkably higher ($k_s = 451.5 \text{ mg L}^{-1}$, $C = 8.98 \text{ mg L}^{-1} \text{ h}^{-1}$) in comparison with the case of a similar biological treatment given to a raw effluent ($k_s = 925.2 \text{ mg L}^{-1}$, $C = 1.48 \text{ mg L}^{-1} \text{ h}^{-1}$). Considerable reduction in the requirement of reactor volume or residence time of the existing aerated biological treatment system of the total wastewater stream can be expected by giving such a simple electrochemical pre-treatment to one of the low-volume stream.

5. Conclusion

The wastewater stream, *Decker filtrate* is only around one-fourteenth in quantity in comparison with the total wastewater stream ($56,000 \text{ m}^3 \text{ day}^{-1}$) of TNPL, India, but contributes much towards its slowly biodegradable organic part and color. A simple electrochemical treatment is applied to enhance the biodegradability of *Decker filtrate* using iron electrodes. The optimal operating point (current density: 112.9 A m^{-2} , time: 6.9 min, pH 7.3) giving maximum enhancement of biodegradability (biodegradability index is improved from 0.11 to 0.46) has been found using RSM. The removal of pollution load (COD: 55% and color: 87%); and the specific energy consumption ($1.19 \text{ kWh (kg COD)}^{-1}$), current efficiency (144.38%), weight of sludge formed ($5.03 \text{ gm (gm COD)}^{-1}$) and weight of anode dissolved ($0.72 \text{ gm (gm COD)}^{-1}$) figures at this optimal operating point are promising. Performance of the process at this operating point has been studied in detail and validated by running post-biological treatment. The rate of fall of COD was remarkably higher ($k_s = 451.5 \text{ mg L}^{-1}$, $C = 8.98 \text{ mg L}^{-1} \text{ h}^{-1}$) in comparison with the case of a similar biological treatment given to a raw effluent ($k_s = 925.2 \text{ mg L}^{-1}$, $C = 1.48 \text{ mg L}^{-1} \text{ h}^{-1}$). Considerable reduction in the requirement of reactor volume or residence time

of the existing aerated biological treatment system of the total wastewater stream can be expected by giving such a simple electrochemical pre-treatment to one of the low-volume stream. The electrochemical steps are optimally loaded to perform the targeted purpose of removing organic part and color and improving biodegradability, in order to make the process economically more attractive.

The current efficiency and specific energy consumption figures show that the process is well accepted with respect to economic feasibility.

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