

Removal of Lignin from Wastewater through Electro-Coagulation

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Received December 08, 2013; Revised May 14, 2013; Accepted May 15, 2013

Abstract The present work deals with the removal of lignin (expressed as COD removal) from synthetic wastewater through electro coagulation in a batch reactor using Aluminum as a sacrificial electrode. Effect of various parameters such as current density, pH, NaCl concentration and treatment time on the removal of COD from synthetic wastewater has been investigated to determine the most suitable process conditions for maximum removal of COD (lignin). A central composite design (CCD) has been used to design the experimental conditions for developing mathematical models to correlate the removal efficiency with the process variables. The most suitable conditions for the removal of lignin from synthetic solution were found to be as current density: 100A/m², pH: 7.6, NaCl concentration: 0.75mg/l and treatment time: 75min. The proposed model gives prediction on COD (lignin) removal with the error limit of around +9 to -7%.

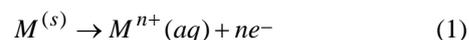
Keywords: electro coagulation, lignin, wastewater, COD, paper and pulp industry

1. Introduction

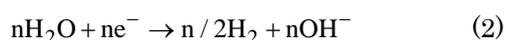
Pulp and paper industry is a water intensive chemical process industry and generates significant quantities of wastewater (20 to 250m³ per ton of pulp produced) containing high concentration of lignin and its derivatives [1]. Some other components such as fatty acid, tannins, resin acid, sulphur compounds, phenol and its derivatives etc. are also present in pulp and paper industry wastewater [2]. The wastewater is generated in five steps in a paper industry such as debarking, pulping, bleaching and alkali extraction, washing and paper production. Amongst the above pollutants, lignin and its derivatives particularly chlorolignin produced during bleaching stage, hold the major share for the development of colour in wastewater. Lignin in solution shows very low BOD: COD ratio (biodegradability index); 600mg/l lignin can contribute around 0-20mg/l of BOD and 750-780mg/l COD value to the wastewater [3]. Due to the low biodegradability index (<0.02) of lignin compounds [3], biochemical methods are not so efficient for the removal of lignin from wastewater as well as for the treatment of pulp and paper industry wastewater. Further, other conventional techniques such as adsorption, chemical oxidation and chemical coagulation require chemicals and produce secondary pollutants. Thus, efforts are on for the development of effective treatment technique for the treatment of pulp and paper industry wastewater around the world. In recent years, electro coagulation (EC) technique has got strong research interest because it produces coagulants in situ by dissolving electrodes in the cell, which helps the removal of the pollutants producing negligible secondary pollutants.

In electro coagulation process, the coagulant is generated in-situ by electro-oxidation of anodes [4]. The generated metal ions due to electro-oxidation of anodes hydrolyze to some extent in water and form soluble monomeric and polymeric hydroxo-metal complexes as shown through Equation.1-4.

Oxidation of anode:



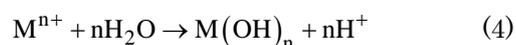
Water reduction at cathode:



At alkaline conditions:



At acidic conditions:



These hydroxo-metal complexes act as coagulant and the whole process occurs through the following steps [4]:

1. Anode dissolution
2. Formation of OH⁻ ions and H₂ at the cathode
3. Electrolytic reactions at electrode surfaces
4. Adsorption of colloidal pollutants on coagulant
5. Removal by sedimentation or flotation

Electro-coagulation cannot remove materials that do not form precipitate such as sodium and potassium. If a contaminant cannot form flocks or cannot flocculate, the process will not work out. Therefore the contaminants such as benzene, toluene or similar organic compounds cannot be removed. However, lignin, the macro molecule composed of three monomers namely *p*-coumaryl alcohol,

coniferyl alcohol, and sinapyl alcohol or its derivatives can be removed by electro coagulation.

Some papers are available in literature on the treatment of pulp and paper industry wastewater using electro coagulation process [5,6,7,8,9]. In most of these papers colour, COD and BOD removal has been considered, however, these papers do not give insight on the removal of COD originated due to lignin compounds. Further, hardly any literature is available, which describes the removal of lignin compounds from wastewater [2].

In the present work the removal of lignin from synthetic waste water by using electro coagulation with aluminum as a sacrificial electrode in a batch reactor has been described in terms of removal of COD. In the present case the BOD value of the synthetic solution was $\sim 26\text{mg/l}$ (below the permissible limit) thus, it was not considered as a parameter for study. Effect of various parameters such as current density, pH, NaCl concentration and treatment time on the removal of COD from synthetic wastewater has been investigated to determine the most suitable process conditions for maximum removal of COD (lignin). A central composite design (CCD) has been used to design the experiment conditions for developing mathematical models to correlate the removal efficiency with the process variables and also to study the interactive influences of parameters on the removal efficiency of pollutants.

2. Materials and Methods

The aluminum used as electrode was sourced from local market in Roorkee, India. The lignin was obtained from Sigma Aldrich, USA and all other chemicals used in the present study were of A. R. grade and purchased from Himedia, Mumbai, India.

Table 1. Characteristics of synthetic solution

Parameters	Values
Lignin(mg/l)	1852
COD (mg/l)	2500
BOD (mg/l)	26
pH	9.28

The synthetic solution was prepared by mixing 1852g of lignin in one litre double distilled water followed by stirring at 5000RPM for 10 minutes. The characteristic of the synthetic solution is shown in Table 1.

2.1. Pretreatment and Characterization of Electrode

The electrode plates were cleaned manually by abrasion with sandpaper followed by further cleaning with 15% HCl for cleaning and washing with distilled water prior to its use. The electrodes were dried for half an hour in an oven and weighted.

2.2. Batch Electro-Coagulation Studies for Synthetic Sample

Each 1.5 l of lignin solution was taken in the batch reactor and desired amount of NaCl was added. Then pH of the solution was adjusted using 0.1M HCl and 0.1M NaOH solution. The experimental conditions (current density, pH, NaCl concentration and treatment time) were decided on the basis of a design of experiment as shown in Table 2.

Table 2. Four factor five level central composite design for preparing synthetic sample

Experiment Number	A	B	C	D
1	70	7	0.75	45
2	130	7	0.75	45
3	70	11	0.75	45
4	130	11	0.75	45
5	70	7	2.25	45
6	130	7	2.25	45
7	70	11	2.25	45
8	130	11	2.25	45
9	70	7	0.75	75
10	130	7	0.75	75
11	70	11	0.75	75
12	130	11	0.75	75
13	70	7	2.25	75
14	130	7	2.25	75
15	70	11	2.25	75
16	130	11	2.25	75
17	40	9	1.5	60
18	160	9	1.5	60
19	100	5	1.5	60
20	100	13	1.5	60
21	100	9	0	60
22	100	9	3	60
23	100	9	1.5	30
24	100	9	1.5	90
25	100	9	1.5	60

A:current density (A/m^2), B: pH, C: NaCl concentration (mg/l), D:time(min)

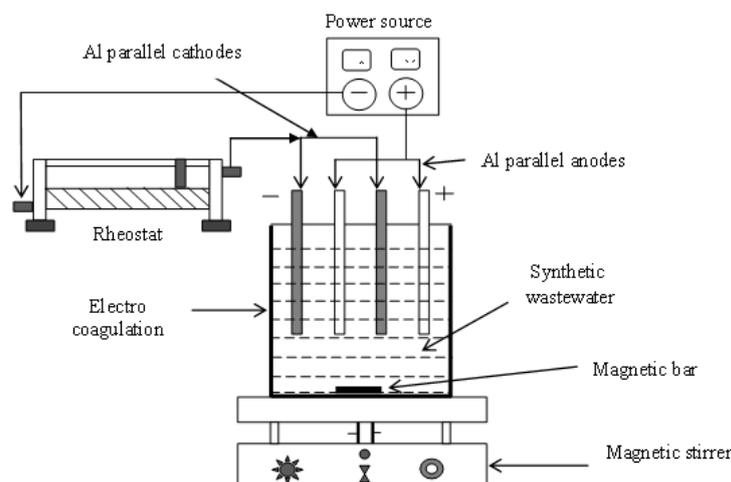


Figure 1. Schematic diagram of the experimental setup

The schematic diagram of the experimental setup is shown in Figure 1. Four aluminum plates, 64cm² each, were positioned in reactor at distance 1cm from each other. The magnetic stirrer and DC power supply were kept at desired value. The constant current condition was obtained by adjusting the knob of rheostat. After completion of experiment, the sample was centrifuged for 30min at 10000RPM and COD was measured according to closed reflux, colorimetric method [9]. COD value was determined by COD analyzer (SN 09/17443 LOVIBOND Spectrophotometer) after adding desired chemicals and digestion period of 2h in COD Reactor (ET 125SC LOVIBOND).

Lignin content was measured using Folin phenol reagent by UV- spectrophotometer (UV-1800, shimadzu, Japan). BOD₅ was measured using BOD analyzer (AL606, Germany) as per standard method [10] using municipal wastewater activated sludge collected from Jagjitpur, Haridwar, as a seed. The experimental data were used to regress mathematical expressions correlating removal efficiency of lignin with the process parameters and to find out a suitable expression through ANOVA using MINITAB software. Error on lignin removal was computed as per Equation.5.

$$\text{Percentage error (\%)} = \frac{(EV - MV)}{EV} \times 100 \quad (5)$$

Here, EV and MV are the experimental and modeled value.

3. Result and Discussion

Effect of various parameters such as current density, pH, NaCl concentration and treatment time on the removal of lignin/COD from synthetic wastewater, model development and interaction effects of process parameters and the validation of the model is described below.

3.1. Effects of Process Parameters

A combined effect of current density and initial pH on COD removal is shown in Fig.2. In the present study the COD is generated only due to the lignin in the synthetic solution. Thus, the removal of lignin is proportional to the COD removal, which results same value of % removal for lignin and COD. From Fig. 2 it is evident that COD removal increases with increase in current density and decreases with increase in pH value. According to Faraday law, the the amount of anode materials that dissolve in solution increase with current density and time as per the following expression.

$$m = Mjt \div ZF$$

Where m = amount of ion produced per unit surface area by current density j passed for a duration time t

Z = number of electron involved in the oxidation/reduction reaction, for aluminium(Al), $Z=3$.

M = atomic weight of material, for Al, $M = 26.98\text{g/mol}$ and F is Faraday constant= 96486C/mol .

Thus, at higher current density, higher dissolution of electrode with higher rate of formation of aluminium hydroxides results in higher pollutant removal efficiency via co- precipitation and sweep coagulation. However,

higher current density also increases solution pH, which reduces the removal efficiency. Under the experimental conditions the most suitable value of j was found as 100A/m^2 .

The effects of pH on the COD (lignin) removal can be explained on the basis of aqueous phase chemistry of lignin and the hydroxo-metal complexes produced by the oxidation of anodic material. The results reveal that at pH ~ 7.6 , the removal efficiency is maximum.

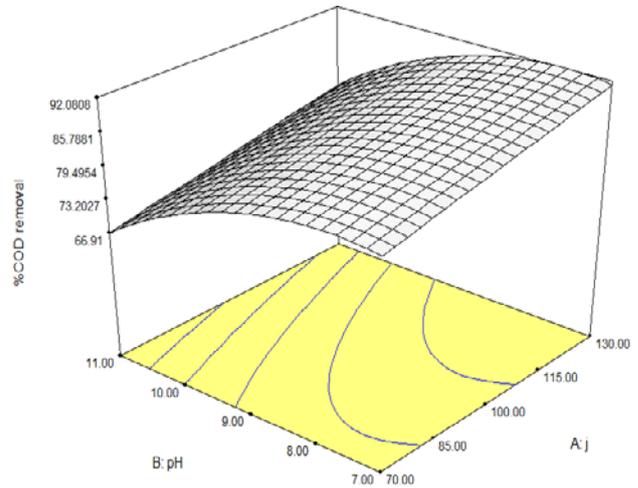


Figure 2. Effect of initial pH and current density on COD removal

3.2. Effect of NaCl Concentration and PH

The effect of NaCl concentration and pH on the COD(lignin) removal is shown in Figure 3. From Figure 3 it seems that the removal of COD decreases with the increase in NaCl concentration as well as increase in pH. The addition of sodium chloride increases the conductivity of the wastewater and thus energy consumption becomes low with addition of electrolyte. Sodium chloride was selected because of low toxicity, reasonable cost and the fact that NaCl prevents the organic matter to attach on the surface of anode, which can create inhibition. However, a higher dosage of it induces overconsumption of electrodes, which increases the aluminum content in sludge; consequently removal efficiency of COD (lignin) is reduced. The most suitable value of NaCl concentration is found to be 0.75mg/l .

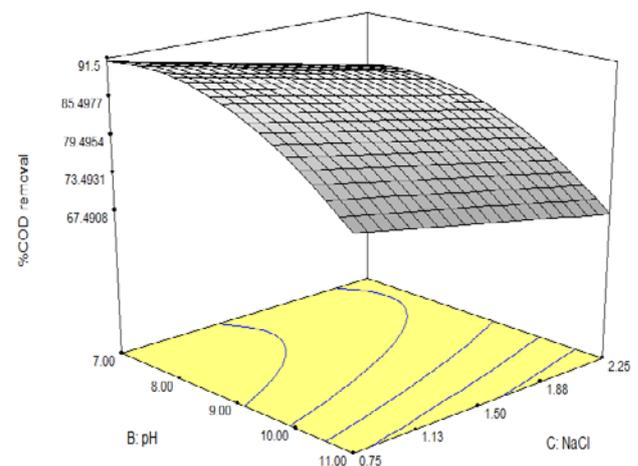


Figure 3. Effect of initial pH and NaCl concentration on COD removal

3.3. Effect of Treatment Time and NaCl Concentration

The effect of treatment time and NaCl concentration on the removal efficiency of COD (lignin) is shown in Figure 4.

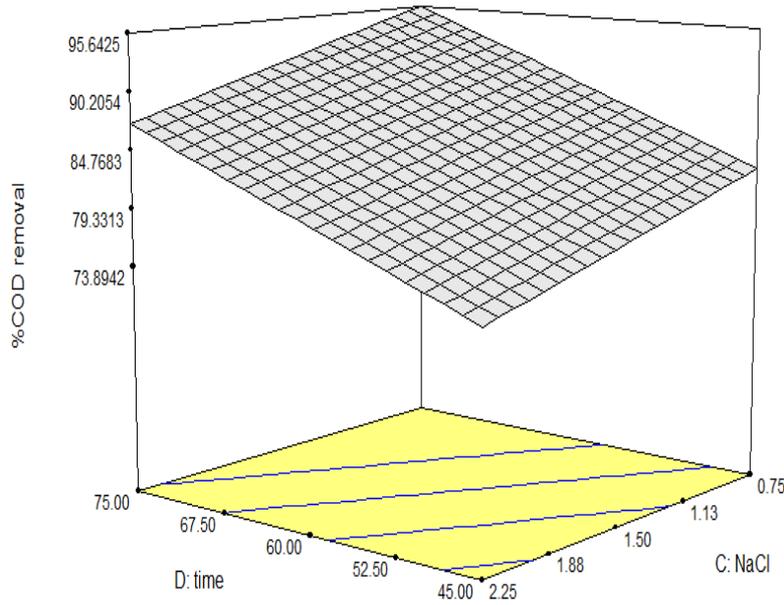


Figure 4. Effect of time and NaCl concentration on COD removal

From Figure 4 it is clear that with increase in treatment time the COD (lignin) removal increases. The increase in removal with time can be explained on the basis of Faraday’s law which shows that the amount of Al ion and their flocks generated are proportional to time. It has been observed that a treatment time of 75min is sufficient to remove ~ 95% of the COD (lignin) from the solution under the experimental conditions.

where, A= Current density (A/m²), B = pH, C = NaCl concentration (mg/l), D = time (min)

From the above equation it seems that NaCl concentration highly influences the COD (lignin) removal and the interaction of pH and NaCl concentration is also highest amongst the above process parameters. This is in accordance with the effect of pH and NaCl concentration as discussed above.

3.4. Model Development

The proposed model equation to correlate COD (lignin) removal with input process parameters in coded factors is shown in Equation.6.

$$\begin{aligned}
 \text{COD(lignin) removal} = & 61.1 + 0.183A - 2.46B + 11.0C \\
 & + 0.834D + 0.0207AB - 2.76BC \\
 & - 0.032CD - 0.00604DA + 0.000176ABCD
 \end{aligned}
 \tag{6}$$

(R² = 0.85, F vaule 18.99, P vaule < 0.05)

From the main effect of the process parameters (developed from MINITAB software) on the % removal of COD (P) from waste water as shown in Figure.5, it is evident that the % removal of COD (lignin) decreases with increase in the pH(B) and NaCl concentration (C), whereas it increases with increase in current density(A) and time (D). The above model is able to predict the % removal of COD (lignin) with the error limit of +9 to -7%.

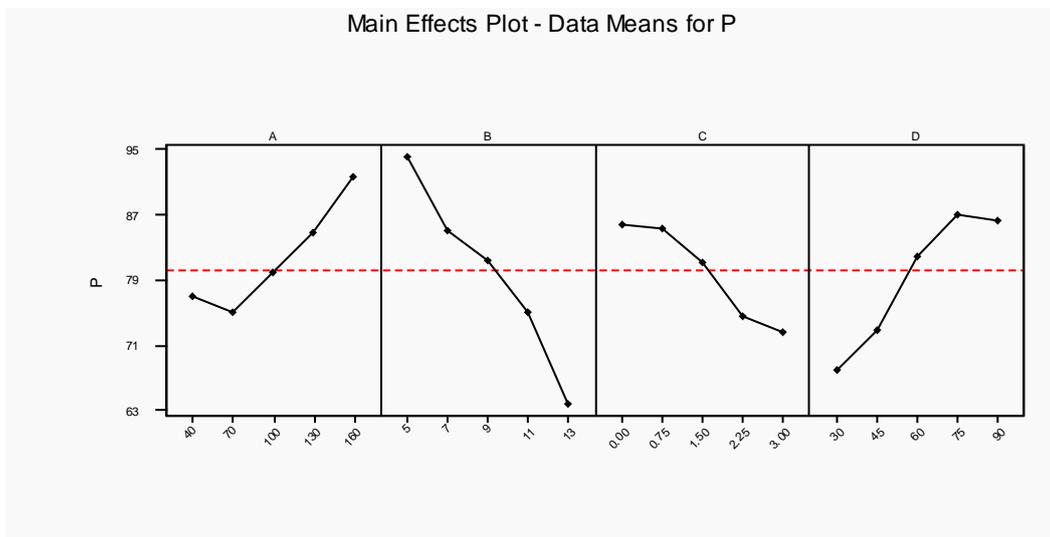


Figure 5. Main effects of process variables on the % removal of COD (obtained from MINITAB software)

4. Conclusions

Removal of COD (lignin) increases with increase in current density and treatment time and decreases with increase in pH and NaCl concentration. Under the most suitable conditions i.e, current density: 100A/m², pH: 7.6, NaCl concentration: 0.75mg/l and treatment time: 75min, around 95% removal of COD (lignin) is achieved from the synthetic solution. The empirical model gives prediction on the % removal of COD (lignin) with + 9 to - 7% error limit. The present process can reduce COD value from ~2500mg/l to ~ 125mg/l after treatment, which is below the maximum permissible limit of COD in discharge water.

Statement of Competing Interests

The authors have no competing interests.

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