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Research Article

Electrochemical Treatment of Silk Industry Effluent and Comparison of the Electrodes to Improve the Bod/Cod Ratio of the Effluent

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Abstract

The present study is to treat the effluent from the silk industry using an advanced method i.e., Batch electrochemical coagulation (BECC) for the removal of COD and color using both iron and aluminium electrode in a lab scale and presenting a comparative study of these electrodes. It has been found that the removal can be achieved using both Iron and Aluminium electrodes. And in this study,the voltage is varied from 4 – 14V for both the electrodes and treatability study is done for around 120 minutes and also optimizing the voltage such that high efficiency of removal is achieved in lower voltage using the electrodes. As it has been found that Al is efficient in 10 and 12V - 90% of COD removal and similarly Fe is found to be efficient in 6 and 8V-82% of COD removal and color removal was around 70-90% using both electrodes. Recommending this advanced treatment method to the industry since the BOD/COD ratio of the effluent varies from 0.1 -0.2 which needs a physico-chemical treatment to improve the BOD/COD ratio of the effluent for the further treatment.

Keywords: *BECC, silk industry, BOD, Fe and Al electrodes, Color, BOD/COD.*

1. Introduction

The textile industry is one of the leading sectors in the Indian economy as it contributes nearly 14 percent to the total industrial production (business.mapsofindia.com). The silk industry comes under the section of textile industry. The untreated effluent can cause serious effect on the environment, when it is discharged in land it causes soil contamination due to high bod, high cod values which affects the growth of plants after a certain limit and even when the effluent is discharged into the streams and rivers it causes depletion of DO which in turn affect the aquatic organism and the environment. The quality of such effluent can be analyzed by their physico-chemical and biological analysis. Textile industries are one of the most polluting industries in terms of the volume and complexity of its effluent discharge. The dyeing and finishing operations in textile industry contribute a major share to wastewater generation. Dye bath effluents, in particular are not only aesthetic pollutants by nature of their color, but may interfere with light penetration in the receiving bodies of water, thereby disturbing biological process. Furthermore, dye effluent contains chemicals which are toxic and carcinogenic. Moreover, textile wastewater are known to vary with pH, high temperature, high biological oxygen demand, high chemical oxygen demand and high concentration of suspended solids. Textile mill effluents are characterized by high levels of color caused by residual dyes.

The waste liquors generated from silk industries typically consists of the following:

- Wastewater generated from the soaking section which contains certain amount of oil and is alkaline in nature.
- Wastewater generating from the degumming unit will contain sericin of the silk and other organic materials.
- Wastewater generated from the dyeing section which is highly colored and acidic by nature.(Mahesh *et al*,2012)

The degree of treatment provided to the wastewater will largely be based on the effluent standards prescribed by the regulatory agencies when the treated effluent is to be discharged into a watercourse or land. If the effluent is to be reused, the quality of the effluent required to support such reuse will indicate the degree of treatment necessary. The complete treatment of wastewater is brought by a sequential combination of various physical unit operations, and chemical and biological unit processes in the silk industry.The risk factor in the silk industry is associated with the dye process such as soaking, degumming and dyeing process where the chemicals are used. These chemicals can cause damage, if not properly treated before discharging into environment.

2. Methods and methodology

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The Effluent Treatment Plant as shown in above figure, it consists of several treatment unit mainly biological treatment and adsorption unit. Basis on analysis and comparison of discharge standards of the effluents with the silk industry effluent it has been found that COD, BOD are not within the limits and also complete color removal is not achieved due to the presence of dye.

Based on the literature review, the electrochemical treatment is found efficient in COD removal and color which are mainly considered in the study. Industrial wastewater is in possession of impurities including colloidal particles and dissolved organic substances. The finely dispersed colloids or suspended solids are usually repelled by their outer layer of negative electrical charges and maintain the colloidal nature until treated by flocculants/coagulants for their removal. The process of flocculation andCoagulation can be defined as "the ionic bridging between the finely divided particles to make flocs followed by their grouping into larger aggregates to be settled under gravity". The terms; flocculation and coagulation can separately be restricted to the preparation offlocs and grouping of flocs into aggregates respectively. The mechanism involved is theneutralization of the charges on the suspended solids or compression of the double layer of charges on the suspended solids. Overdose of coagulants may reverse the charge at theouter layer of the colloidal particles to re-stabilize them in a reverse mode. The wastewatertreatment and down streaming of industrial fluids can be performed by using a number offlocculating/coagulating agents based on chemical salts and organic polymers.For the color removal and COD removal, the ECC treatment is more efficient.

Generally, three main processes occur serially during electrocoagulation:

(a) Electrolytic reactions at electrode surfaces,
(b) Formation of coagulants in aqueous phase,
(c) Adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation or floatation

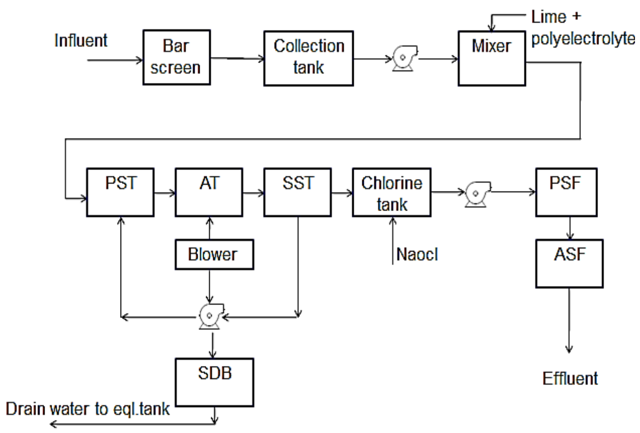

Fig 2.1 The schema of Effluent treatment plant in the Silk industry, Mysore.

Table.2.1 Comparison of iron and aluminium electrode reaction at the anode and at the cathode and forming the metal hydroxides which acts as flocs in the coagulation process. Source : (Khanittha Charoenlarp & Wichan Choyphan)

Aluminum electrode	**Iron electrode**
At anode:	At anode:
$Al \rightarrow Al^{3+} + 3e$	$4Fe_{(s)} \rightarrow 4Fe^{+}_{2(aq)} + 8e-$
$2Al + 6H_2O + 2OH^{-} \rightarrow 2Al(OH)^{4-} + 3H_2$	$4Fe_{2(aq)} + 10H_2O_{(l)} + O_{2(g)} 4Fe(OH)_{3(s)} + 8H^{+}_{(aq)} \rightarrow$
At cathode:	**At cathode:**
$3H_2O + 3e \rightarrow 3/2H_2 + 3OH^{-}$	$8H^{+}_{(aq)} + 8e^{-} 4H2_{(g)}$
Overall reaction :	**Overall reaction:**
$2Al(s) + 6H_2O_{(l)} \rightarrow 2Al(OH)_{3(s)} + 3H_{2(g)}$	$4Fe_{(s)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)}$

The experimental set up is shown below consists of a DC power supply, magnetic stirrer and I lr beaker with electrodes.

Fig 2.2 Experimental set up of electrochemical coagulation treatment in a lab scale

Meanwhile, if anode potential is sufficiently high, secondary reactions may occur also, suchdirect oxidation of organic compounds and of Cl^{-}ions present in wastewater.

$2Cl^{-} \rightarrow Cl_2 + 2e^{-}$

Dissociation of water by EC generates hydroxide ions which are known as one of the most reactive aqueous radical species and this radical has the ability to oxidize organic compounds. The generated hydroxides or polyhydroxides have strong attractions towards dispersed particles as well as counter ions to cause coagulation. The gases evolved at the electrodes are also helpful to remove the suspended solids in upward direction. A number of electrochemical reactions are involved within the electrocoagulation reactor. Reduction of metal anodes is responsible to produce hydroxide complexes causing flocculation of suspended solids into stable agglomerates. Production of oxygen and hydrogen as a result of electrolytic dissociation of water molecules cause emulsified oil droplets to be freed from water molecules making a separate layer on the surface. The same mechanism is involved in case of dyes, inks and other type of emulsions. In the presence of chlorine, metal ions can make chlorides which are also helpful in flocculation/coagulation of the wastewater. The production of oxygen in the electrocoagulation chamber can oxidize or bleach the chemicals like dyes. An Electrocoagulation reactor consists of anode and cathode like a battery cell, metal plates of specific dimensions are used as electrodes and supplied with adequate direct current using power supply. The dimension of the electrode used are 5cm*5cm*1mm for both aluminium and iron electrodes and the samples obtained for every 10 minutes are characterized for different parameter such as COD, absorbance, pH, nitrate, sulphate and phosphate etc., the below figure shows the treated sample with the sludge after the complete treatment. From this figure we can see that color removal is achieved by characterizing the sample we can even come to know the COD removal efficiency.

(a) before (b) after

Fig 2.3 before and after electrochemical coagulation treatment (a) and (b) respectively

Chemical oxygen demand(COD) is an important parameter in water pollution control analysis. It is closely related to the organic contamination level of a waste water sample. Analysis of COD is done by closed reflux titrimetric method. A sample is refluxed in strongly acid solution with a known excess $K_2Cr_2O_7$. After digestion, the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous ammonium sulphate to determine the amount of $K_2Cr_2O_7$ consumed and the oxidisable matter is calculated in terms of oxygen equivalent. The digester should be pre-heated to 150^0C and the standard reflux time is two hours.

Absorbance is measured using UV spectrophotometer. An atom absorbs light over very narrow range of wavelengths or gives the lines which are characteristics of atoms or molecules in gases. In liquid the molecules are very close to each other. Thus, they influence each other's energy levels randomly. The resulting absorption spectrum consists of broad bands-hundreds f angstroms units wide.

Analysis of pH is done using pH meter, which is an electronic instrument measuring the acidity or alkalinity of a liquid. Firstly, the glass electrode connected to an electric meter that measures and displays pH reading is calibrated and then the electrode is placed in the sample. The pH is displayed.

Biological oxygen demand is defined as the amount of oxygen required by the bacteria while stabilizes decomposable organic matter under aerobic condition. BOD is a test used to assess the level of biodegradable organic matter present in wastewater. The experimental procedure depends upon the fact that oxygen oxidizes Mn^{2+} to a higher state of valency under alkaline conditions and Manganese in the higher state of valency is capable of oxidizing Iodine to Iodide released is equivalent to the dissolved oxygen originally present. The iodine is measured with standard sodium thiosulphate and the results are interpreted in terms of dissolved oxygen.

3. Result and discussion

The electrochemical treatment is found effective since it can effectively reduce COD and color removal. As in the lab scale studies, the different voltages has been tried varying from 4-14V for 120 minutes. As a result, it has been found that COD removal gradually increases with the time with different voltages. When the voltage is increased the COD removal efficiency removal can be achieved in high rate with the increase in voltage and the color also removed gradually till the end of treatment. Because of these reasons, it has been found that electrochemical can effectively treat the dye effluent for both color removal and COD removal. The pH of the effluent also increases gradually from 5 – 8 around and the effluent standards is also achieved since the value must be within 6.5-8.5. In textile industry they also face problem regarding BOD/COD ratio, it comprises of acidic dye effluent which keeps the ratio less than 0.35 so subjecting it to biological treatment is not found effective in industry since the effluent does not meet the discharge standards. So the electrochemical treatment prescribed with a post treatment can effectively get the effluent within the limits. As the optimum voltages found for both Al and Fe electrode is to be 10-12V and 6-8V respectively.

Fig 1 shows that BOD/COD value increases gradually for Iron electrodes with the time since the COD degrades as the time passes the effluent will have improvement in the BOD/COD ratio. It can be observed with the graph that when the voltage increase the COD degradation also increases which in turn increases the BOD/COD ratio of the effluent.

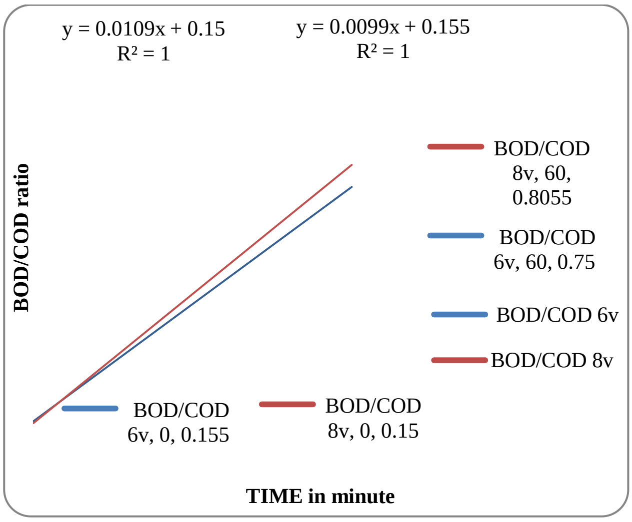

Fig .3.1 the variation of BOD/COD along with thetime for Iron electrodes

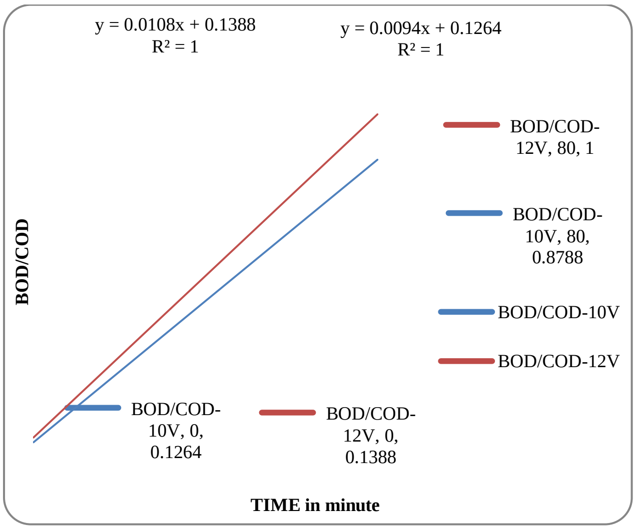

Fig 3.2 the variation of BOD/COD along with the time for Aluminium electrodes

Similarly from figure 2 it can be observed using aluminium electrodes that BOD/COD value increases gradually along with the time and even the degradation of COD is more when compared to the iron electrodes, that is only due to the reason here the optimum voltage which has been taken is around 10V so it degrades more than the optimum voltage of Iron electrodes. And it is a fact that BOD/COD is increase with the increase in voltage that can be observed with both the electrodes.

From the analysis, COD removal efficiency also plotted against time in graph for the comparative study of both Al and Fe electrodes and also to know about the efficiency of removal. The graph below shows that increase in percentage COD removal along with time and increase in voltage. For Fe electrode of 8V – 88.75% and 6V – 86% of COD removal efficiency is achieved.

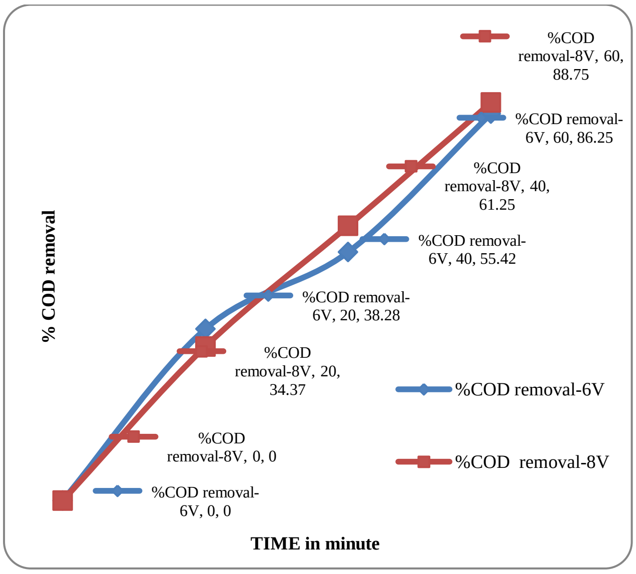

Fig 3.3 the variation of %COD removal along with the time for Fe electrodes

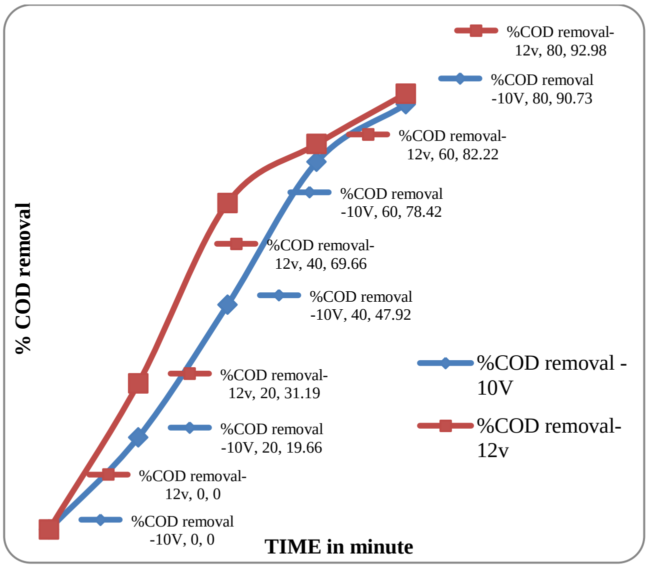

Fig 3.4 the variation of %COD removal along with the time for Al electrodes

Similarly for Al electrodes the % COD removal is plotted against time and it can be known that COD degradation and removal efficiency is high at higher voltage. For Al 12V-93% and 10V-90.73% of COD removal is achieved. pH of textile effluent is acidic at the beginning and during gradual treatment the pH of the effluent also increases which is well within the discharge limit 8.5 using both Al and Fe electrode which can be observed from the graph.

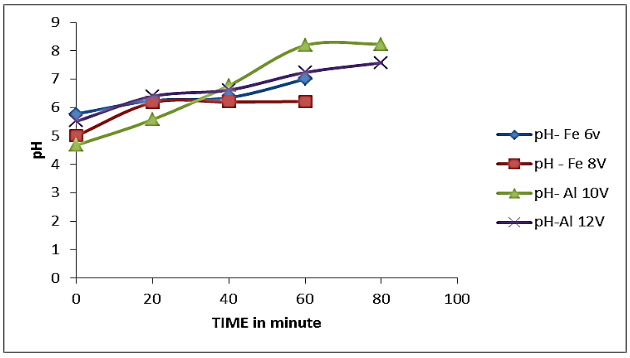

Fig 3.5 the variation of pH along with time for both Al and Fe electrodes

Table3.1 The comparison of percentage color removal efficiency of both Al and Fe electrodes with respect to optimum voltage and respective time required.

Time required(min)	Electrode with volts	% color removal efficiency
60	Fe-6V	74.23
60	Fe-8V	72.86
80	Al-10V	82.32
80	Al-12V	85.23

From the above table it can observe that using iron electrodes percentage color removal efficiency can be achieved. After slight increasing of the % color removal again the removal % starts to decrease its due to the iron electrodes since it has the capability impart color in the effluent. Similarly using Al high % color removal efficiency is achieved.

4. Conclusion

Based on the results obtained from the experiment it can be seen that for Iron and Aluminium electrodes different COD and Color removal efficiency was achieved.

Iron electrodes:

(i) Color removal efficiency - Fe 6V -74.23% and Fe 8V – 72.86%

(ii) COD removal - Fe 6V – 86% and Fe 8V – 88.75%

(iii) Anode dissolution Fe 6V- 0.84 g/l and Fe 8V – 1.02 g/l

Aluminium electrodes:

(i) Color removal efficiency Al 10V – 82.32% and Al 12V – 85.23%

(ii) COD removal Al 10V – 90.73% and 12V – 93%

(iii) Anode dissolution Al 10V -0.4 g/l and Al 12V – 0.64 g/l.

After the ECC treatment the BOD/COD ratio also been increased considerably and need a post treatment like filtration and adsorption are required. And other parameters such as nitrate, phosphate and sulphate are considerably reduced by the ECC treatment and were within the discharge standards. The sludge produced from ECC will have good calorific value since it is a physico-chemical treatment and it can be used as an fuel in incineration or as an additive in cement manufacturing. These results strongly indicate that ECC can be adopted for the treatment of raw textile wastewater for complete decolorization and COD removal.

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