Experimental Investigation and statistical Regression analysis for the reduction of COD from paper and pulp industry waste water using Advanced Oxidation Process

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Abstract
This study investigates the reduction of COD level in the paper and pulp industry waste water using the advanced oxidation process. The experimental values were compared with the predicted values obtained with the statistical regression analysis. The Fenton process which is an advanced oxidation process, is used here for the reduction of COD. In this process, the Fenton's reagent (Iron and Hydrogen peroxide) is capable of producing hydroxy radicals and the produced hydroxyl radicals have the ability to oxidise the organic compounds and to reduce the COD level in the waste water. The process depends on the different experimental parameters such as pH, concentration of hydrogen peroxide (H_2O_2), concentration of iron (Fe) and the contact time. All the experimental parameters were optimized by conducting a batch study in the lab scale.

From the optimization studies, it is found that the maximum reduction of COD is obtained at pH 3, 140 mL of $FeSO_4$, 60 mL of H_2O_2 and contact time of 75 minutes. At pH 3, the reduction efficiency is 95%, 89% for 140 mL of $FeSO_4$, 91% for 60 mL of H_2O_2 and 96% at 75 minutes. Further, statistical regression analysis was also done to confirm the reliability of the experimental results. From the regression analysis and the standard residual plot, it is found that the values are within the 5% level of significance and it follows alternative hypothesis.

Keywords: Paper and pulp industry waste water, COD reduction, Fenton's Process, Regression.

Introduction

The increase in population has a great demand for industrial development. The industrial development in turn exploits the availability of natural resources such as land and water. The exploitation of natural resources will result in water and land pollution. Among the different industries, the pulp and paper industry is highly water consuming industry[7].Under Indian scenario, 100–250 m^3 of freshwater is required to produce one ton of paper. Out of the total quantity of water used in the production process, 75-85 percentage of water will be turning out as waste water[12]. The pulp and paper industry finds it difficult to comply with environmental regulations which are very strict. The effluent generated depends on the nature and effectiveness of the process in the different stages of pulp and paper production.

The discharge of the effluent generated from the pulp and paper industry in the land and aquatic ecosystem creates an environmental impact on land and damages the aquatic life. The generated effluent may contain different compounds. It may also include non-biodegradable organic materials, adsorbable organic halogens (AOX), phenolic compounds etc. depending upon the applied pulping process, additive chemicals and the amount of water consumed[2,5]. Alkyl phenols, resin acids are known to cause toxicity in the aquatic ecosystem even at the very low concentrations. Lots of research are being conducted to develop suitable technologies to treat the wastewater effluent obtained in paper and pulp industry. The latest suitable technologies developed for the effluent treatment may reduce the operational and discharge cost substantially.

Wastewater treatment process is generally divided into primary, secondary and tertiary treatment. Primary treatment in the paper and pulp industry includes clarifiers wherein the majority of the suspended solids are removed and the BOD is generally removed about 25-40%. Secondary treatment also known as biological treatment is usually employed to remove high substrate concentration and to remove BOD about 85-90%[15]. Secondary treatment units may be activated sludge process, rotating biological contactor or moving bed biofilm reactor. Moreover, moving bed biofilm reactors are usually used in the treatment of wastewater generated from paper and pulp industry. The effluent from the secondary treatment is still not found to meet the discharge standards, Tertiary treatment is adopted for further treatment[9].

From the literature review, it is identified that the advanced oxidation processes belong to efficient tertiary treatment and are effective in degrading both the biodegradable and non-biodegradableorganic contaminants. Hydroxyl radicals (•OH) are produced in the advanced oxidation processes as oxidizing agents which are capable to mineralize the complex chemicals in the wastewater effluent. Hydroxyl radicals are able to mineralize the complex chemicals efficiently when compared with the other oxidants because of the oxidation potential of 2.8 eV. The oxidation potential of hydroxyl radical is higher than chlorine and ozone and it also possesses the following properties: (a) they are powerful oxidants (b) highly reactive (c) short-lived (d) easily produced and (e) nonselective[17]. Fenton process which is an advanced oxidation process, is capable of producing hydroxyl radicals (•OH) with the help of Fenton's reagent

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(Fe^{2+}/H_2O_2). The reactions in the Fenton process are illustrated in the following equations:

$Fe^{2+} + H_2O_2 \longrightarrow \bullet OH + OH^- + Fe^{3+}$
$RH + \bullet OH \longrightarrow R^* + H_2O$
$R^* + Fe^{3+} \longrightarrow R^+ + Fe2^+$
$\bullet OH + Fe2+ \longrightarrow Fe^{3+} + OH$

Material and Methods

The paper and pulp industry wastewater was collected from a local paper mill which is situated near Sankarankovil, Kovilpatti. After collection, the effluent sample was stored at 4°C until use. The chemicals and reagents that were used for the determination of COD are sulphuric acid, silver sulphate, mercury sulphate, potassium dichromate, ferrous ammonium sulphate and Ferroin Indicator. The chemicals that were used for the experimental methods, of analytical grade. The distilled water used was millipure water and double distilled[21]. The initial characteristics of the paper and pulp industry effluent were determined and are tabulated in table 1.

Experimental Setup: This experimental study was carried out in order to obtain maximum removal of COD using Fenton's process. The removal efficiency of COD using Fenton's process depends on the different experimental parameters such as pH, H_2O_2, $FeSO_4$ dosage and contact time and so these experimental parameters need to be optimized for the maximum removal efficiency of COD. Initially, the COD of paper and pulp industry effluent was determined and then the Fenton oxidation processes was carried out as batch study. The effluent with an initial COD of 23200 mg/L was fed in to the beaker and the pH was varied between 1 and 8 using acid or alkaline solution and it depend on the characteristics of the effluent[19].

The pH is varied almost between 1 and 8 as the Fenton process is effective and performs better in the acidic conditions. Further, the Fenton's reagent (H_2O_2 and $FeSO_4$) was added and the uniform stirring is given with the help of a magnetic stirrer. The contact time is set as 60 minutes for the reaction to take place. The optimum pH at which the maximum COD removal was obtained, is noted. And then, the process was repeated to determine the optimum $FeSO_4$, keeping the optimized pH value, H_2O_2 and contact time constant. Similarly, the optimized values for H_2O_2 contact time was determined by varying them and keeping the other parameters constant.

Results and Discussion

Effect of pH: pH is a detrimental parameter in the Fenton's process. Fenton's process is known to perform better in the acidic conditions. In order to check and optimize the pH in acidic condition, a batch reactor study was conducted in the lab scale. pH was varied between 1 and 8 linearly and the COD removal efficiency corresponding to the particular pH was noted. A statistical linear regression analysis was performed to validate the experimental results. The experimental results and the predicted results from the regression analysis is plotted in the figure 1 and the residuals which is the difference between the experimental and predicted results, is plotted in the figure 2. From the figure 1, it is found that the COD removal efficiency is high in the acidic condition especially between pH 1 and 3.

Based on the literature, it is confirmed that the acidic pH is very suitable for $OH^{\cdot}$ production[13,14]. The combined effect of hydrogen peroxide and Fe^{2+} ion will result in the conversion of Fe^{2+} and Fe^{3+} to $Fe(OH)_n$-type structures and it leads to COD degradation. Furthermore, the decrease in H^+ concentration will not support for the H_2O_2 reduction reaction at high pH[3,22]. The COD removal efficiency is 95% at pH 3 from experiment and the predicted removal efficiency is 93.33% at pH 1. All the data are within the 5% level of significance and follow alternative hypothesis as per ANOVA and standard residual result.

Table 1
Characteristics of Paper and pulp Industry Effluent

S.N.	Parameters	Value Obtained
1	pH	7.13 (no unit)
2	Chlorides	4500 mg/L
3	Total Solids	9600 mg/L
4	Total Suspended Solids	8400 mg/L
5	ChemicalOxygen demand(COD)	9200 mg/L

Table 2
Output obtained for different experimental parameters based on Linear Regression

Parameters	Multiple R	R Square	Standard Error	P-Value	Standard Residuals
pH	0.909866967	0.827857898	7.741482775	0.001709077	< 3
Ferrous Sulphate	0.979772708	0.959954558	3.173551413	0.000609577	< 3
Hydrogen Peroxide	0.339365586	0.115169001	15.40516302	0.510493819	< 3
Contact time	0.05529132	0.00305713	13.65083287	0.896539871	< 3

Table 3
Experimental and Predicted values for different experimental parameters based on Linear Regression

Parameter	Observations	Experimental values	Predicted values	Residuals	Std Residual
pH	1	82	93.33	-11.33	-1.58
	2	88	86.92	1.08	0.15
	3	95	80.50	14.50	2.02
	4	74	74.08	-0.08	-0.01
	5	70	67.67	2.33	0.33
	6	59	61.25	-2.25	-0.31
	7	53	54.83	-1.83	-0.26
	8	46	48.42	-2.42	-0.34
FeSO4	1	52	54.43	-2.43	-0.86
	2	65	61.86	3.14	1.11
	3	69	69.29	-0.29	-0.10
	4	75	76.71	-1.71	-0.60
	5	88	84.14	3.86	1.36
	6	89	91.57	-2.57	-0.91
H2O2	1	58	70.19	-12.19	-0.88
	2	63	72.85	-0.85	-0.06
	3	72	75.50	10.50	0.76
	4	86	78.16	9.84	0.71
	5	88	80.82	13.18	0.96
	6	94	83.48	-20.48	-1.49
Contact Time	1	60	76.75	-16.75	-1.33
	2	63	77.04	-5.04	-0.40
	3	72	77.32	9.68	0.77
	4	74	77.61	10.39	0.82
	5	82	77.89	18.11	1.43
	6	87	78.18	3.82	0.30
	7	88	78.46	-4.46	-0.35
	8	96	78.75	-15.75	-1.25

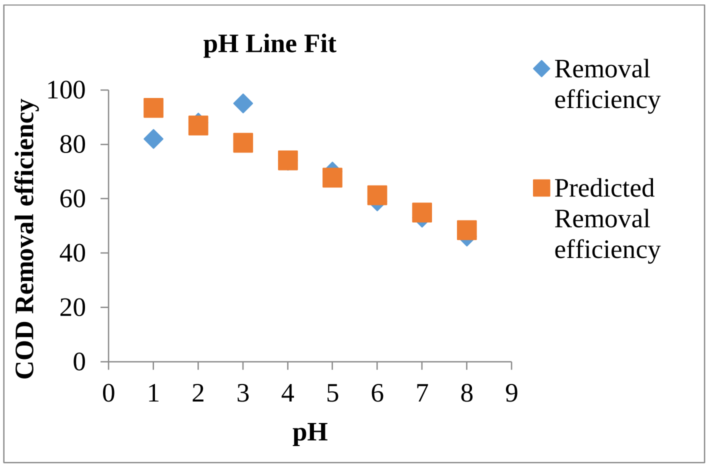

Figure 1: COD Removal Efficiency for different pH

Effect of $FeSO_4$: The efficiency of the treatment process depends on the quantity of Fenton's reagent (Fe and Hydrogen peroxide). Hence it is important to optimize the Fe content for the treatment process. The optimization was done by varying the concentration of $FeSO_4$ linearly between 20 and 140 in a batch reactor and the corresponding removal efficiency is plotted in the fig. 3. The reaction time was given as one hour and the pH was maintained at 3 which is obtained from the optimization of pH. At the end of the reaction time, the COD removal efficiency was determined using closed reflux method. The removal efficiency increased gradually and it reached a maximum of 89% at 140 mL of $FeSO_4$ and it was 91% as per the predicted result shown in figure 3.

The values are found to fit well and the R-square is 0.95. The P-value and the standard residual obtained from the ANOVA confirm that the data are within the level of significance and follow alternative hypothesis[6,16]. The alternative hypothesis confirms that there is a linear relationship between $FeSO_4$ and COD removal efficiency.

Effect of Hydrogen Peroxide: The dosage of hydrogen peroxide needs to be optimized in a way similar to the optimization of $FeSO_4$. The dosage of hydrogen peroxide was varied linearly from 10 to 70 maintaining pH at 3 and the quantity of $FeSO_4$ as 140 mL. The entire reaction is allowed for 60 minutes in the magnetic stirrer. The variation of removal efficiency for different doses of hydrogen peroxide is shown in fig. 5. The COD removal efficiency for each dosage of hydrogen peroxide is noted and it is confirmed with the statistical regression analysis. The maximum COD removal efficiency is achieved at 50 mL with 94% and the predicted removal efficiency from the regression analysis was 83.47 % at 60 mL.

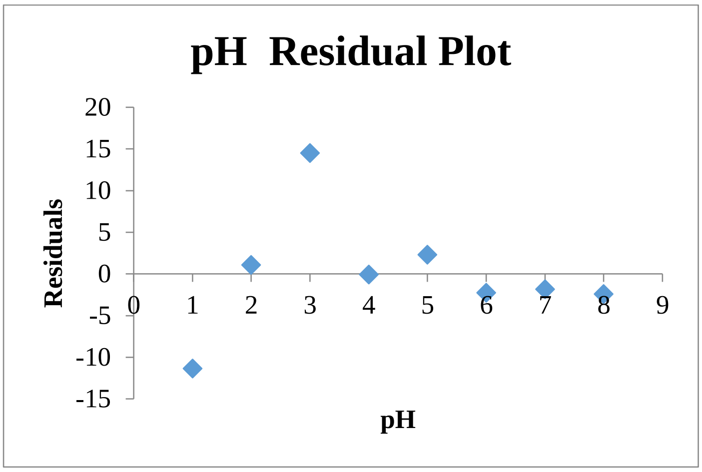

Figure 2: Residual plot for different pH

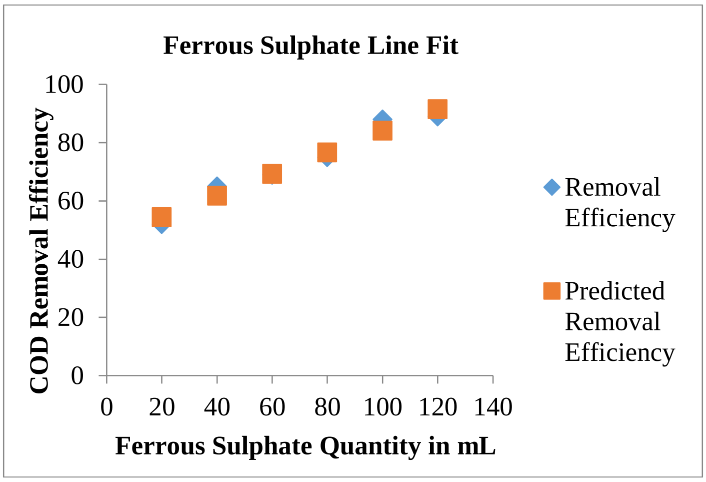

Figure 3: COD Removal Efficiency for different $FeSO_4$ concentration

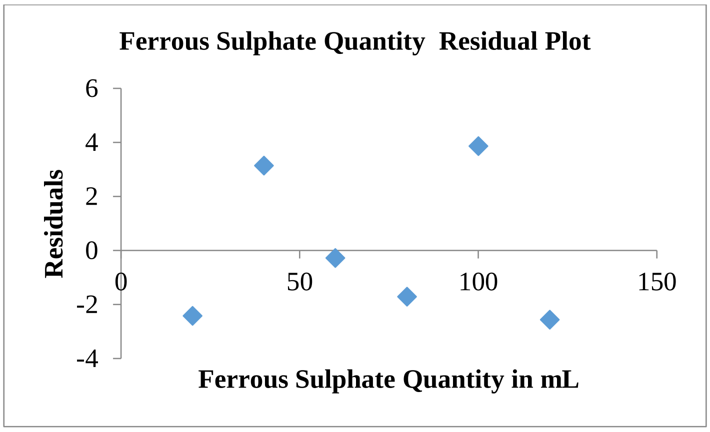

Figure 4: Residual plot for different $FeSO_4$ concentration

The reduction in the efficiency after 50 mL of H_2O_2 is due to the fact that the OH• radicals react quickly with H_2O_2 to form OOH• and the OOH• radicals are less reactive than OH• radicals which will lower the degradation of COD[20]. As H_2O_2 scavenges OH• and having too much doses of H_2O_2 can lower COD removal efficiencies due to the scavenging effect. On the contrary, if H_2O_2 doses are low, OH• production will be less, thus lowering treatment efficiency. A good balance must be maintained between high and low H_2O_2 levels to obtain a maximum efficiency in COD reduction[21,22]. The P-value and the standard residuals obtained as a result of ANOVA imply that the data does not follow null hypothesis and it is confirmed with the 5% level of significance.

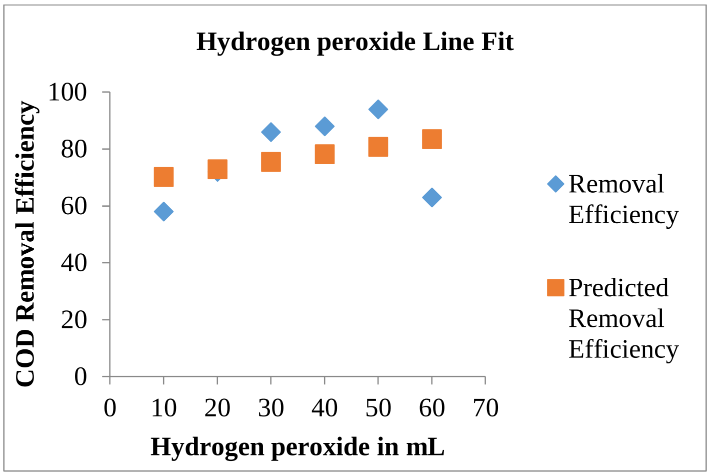

Figure 5: COD Removal Efficiency for different Hydrogen peroxide concentration

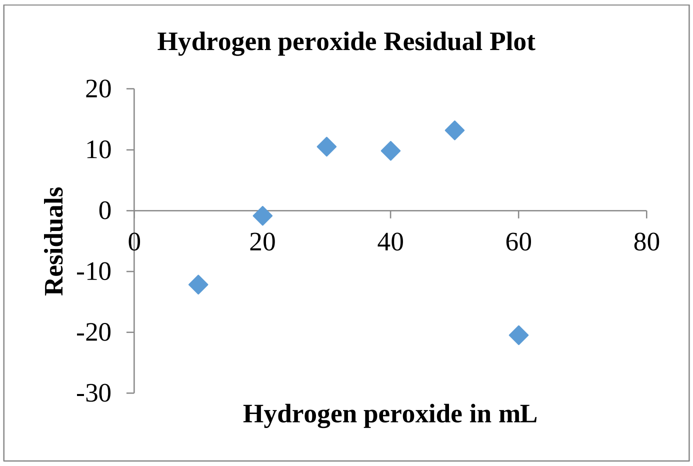

Figure 6: Residual plot for different Hydrogen peroxide concentration

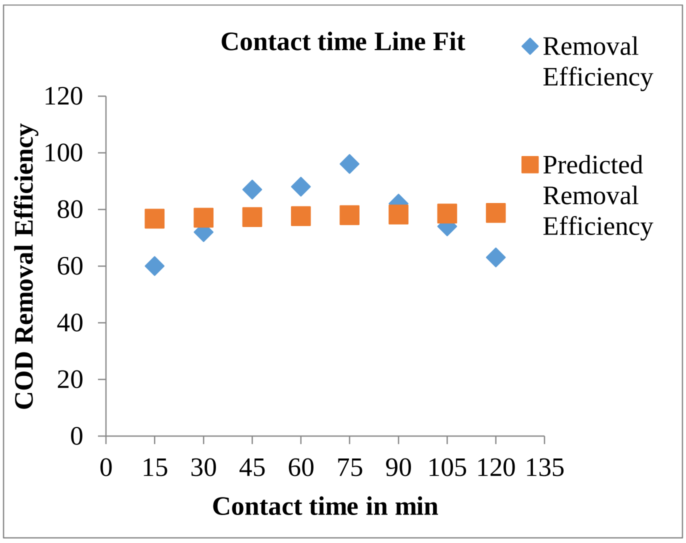

Figure 7: COD Removal Efficiency for different contact time

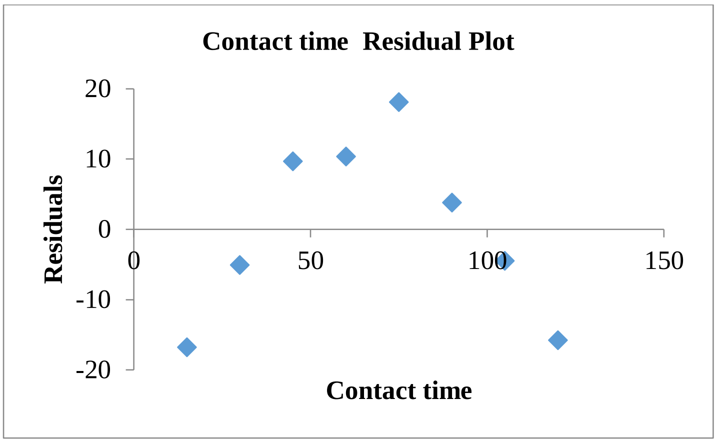

Figure 8: Residual plot for different contact time

Effect of Contact time: The batch reactor study was conducted to optimize the contact time for the maximum COD removal from the paper and pulp industry effluent. This study was done by varying the reaction time from 15 minutes to 135 minutes keeping the pH as 3, quantity of $FeSO_4$ as 140 mL and the hydrogen peroxide as 50 mL. The COD removal efficiency is calculated after every 15 minutes and the corresponding values are noted down and is shown in fig. 7. COD reduction efficiency recorded after 135 min is in decreasing trend which is due to the conversion of H_2O_2 into H_2O and O_2[1,20]. The faster degradation of organic compounds in the initial stage is mainly attributed to the reactions between hydroxyl radicals and pollutants, then the reaction rate is decreased when the pollutant concentration is reduced and more intermediate products are generated[8].

The removal efficiency varied between 76 and 78% for every 15 minutes when simulated for regression analysis from 15 to 135 minutes. However, the experimental results showed that the efficiency gradually increased and it reached a maximum of 96 % at the contact time of 75 minutes. The P-value and standard residuals implied that the data was not following null hypothesis and it was within the level of significance.

Conclusion

The present study investigated the performance of Fenton oxidation in a batch mode for treating wastewater from the paper and pulp industry and the process parameters that influenced the reaction. The following conclusions were noted from this experiment:

i. The maximum reduction of COD is obtained at pH 3, 140 mL of $FeSO_4$, 60 mL of H_2O_2 and contact time of 75 minutes. At pH 3, the reduction efficiency is 95%, 89% for 140 mL of $FeSO_4$, 91% for 60 mL of H_2O_2 and 96% at 75 minutes.

ii. The results of linear regression analysis show that it follows alternative hypothesis and it confirms that the efficiency of COD reduction depends on the process parameters such as pH, $FeSO_4$ concentration and H_2O_2 concentration. It is also inferred that there exists a linear relation between the process parameters and the COD reduction efficiency.

iii. The efficiency obtained at the optimized experimental conditions nearly confers with the state pollution control board discharge norms and it can be further enhanced by coupling with the other treatment technology to produce synergistic effects.

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