OPTIMIZATION OF COAGULATION-FLOCCULATION AND OZONATION PROCESSES FOR THE TREATMENT OF KRAFT PULP MILL EFFLUENT

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A study on the effect of ozonation and coagulation- flocculation processes on kraft pulp mill effluents has been carried out. The objectives were to determine (1)best chemical combination for coagulation-flocculation, (2)optimum pH for ozonation and to evaluate (3)suitability of ozonation as pre and post treatment of coagulation-flocculation. Removal efficiencies of color, turbidity and phenolic compounds were investigated under different conditions. Results indicated that initial acidic pH in the effluent is more favorable for ozonation at the experimented O₃ flow rate. Use of 0.1g/L AlCl₃.2H₂O with 0.05g/L polyacrylamide gives the maximum reductions of color, turbidity and phenolic compounds in the effluent. Coagulation-flocculation followed by ozonation is a better system for the treatment of kraft pulp mill effluent. This system can reduce all the three parameters by about 90%.

Key Words: ozonation, coagulation-flocculation, kraft pulp mill effluent, color, phenolic compounds, turbidity

1. INTRODUCTION

The pulp and paper industry is a major industrial sector utilizing a significant amount of water during processing. It also contributes to the environmental pollution significantly. The effluents from the industry cause slime growth, thermal impacts, scum formation, color problems and loss of aesthetic beauty in the environment. They also increase the amount of toxic substances in the water causing death to the zooplankton and fish, profoundly affecting the terrestrial ecosystem¹.

Different processes are employed for the making of paper and there is a significant difference in quality of wastewaters from the pulp and paper making operations. This is due to the diversity of processes and chemicals used². The black alkaline liquor released by paper mills contributes only 10–15% of

the total wastewater, but contributes approximately to 95% of the total pollution load of pulp and paper mill effluents³.

Lignin and its derivatives are difficult to degrade naturally because of the strong linkages within their molecular structures⁴. Due to this fact, even though the conventional biological treatment processes are effective in decreasing the organic matter in the effluents, they have little effect on decolorization of the effluents.

Advance Oxidation Processes (AOPs) are being researched and used for the treatment of these refractory compounds. In AOPs' hydroxyl radicals (OH[•]) are generated and used as the oxidizing agent. OH[•] is a powerful oxidizing agent with an oxidation potential of 2.33V and exhibits a faster rate of oxidation reaction compared to that of conventional oxidants, such as hydrogen peroxide or potassium

permanganate⁴⁾.

Ozonation is one of the existing AOPs which is being widely used for disinfection. Theoretically ozone is able to oxidize both inorganics and organics to their highest oxidation states, depending on the molecular selectivity and decay rates. The decomposition rate of ozone is affected by the presence of inorganic/organic species in the reaction medium. Ozone reacts with organic compounds dissolved in water through either direct ozone attack or indirect free radical attack. The radical oxidation is less selective and predominates under basic conditions, while direct oxidation is more selective and predominates under acidic conditions⁵⁾.

A major limitation of the ozonation process is the relative high cost of ozone generation coupled with the very short half life period of ozone. Therefore it is always necessary to generate ozone at site.

Chemical coagulation-flocculation followed by settling is a probed technique for the treatment of high suspended solids wastewater especially those formed with colloid matter. Coagulation is mainly induced by inorganic metal salts, e.g. aluminium and ferric sulphates and chlorides. Polyelectrolytes of various structures, e.g. polyacrylamides (PAA), chitosan, polysaccharides, polyvinyl and many others are usually used as flocculants to enhance the formation of larger flocs in order to improve the rate of settling⁶⁾.

Several researchers have carried out studies on ozonation⁴⁾⁷⁾⁸⁾ and coagulation- flocculation⁶⁾⁹⁾ using effluents originated by different types of pulp and paper manufacturing processes. But information on the combined treatment of the above two methods are limited. Ramos¹⁰⁾ has evaluated the effect of chemical precipitation and ozonation conditions on the decolorization kinetics in the residual water of a paper industry.

Kraft pulp effluent is the residual coming from the kraft pulping process in which wood chips are treated at high temperature with cooking chemicals, NaOH and Na₂S. Therefore the effluent contains residuals of cooking chemicals, lignin compounds as well as extractives and hydroxyl acids coming from the raw materials¹¹⁾. A normal procedure exercised in most modern pulp mills is concentration in multiple effect evaporators, followed by incineration, smelting and causticization to recover 85% of the cooking chemicals¹²⁾. Most of the organic substances in kraft pulp effluent are burnt off, however dilute effluent mostly coming from pulp washing always result in refractory wastewater.

The present work focuses on the application of ozonation in the treatment of kraft pulp mill effluent in combination with coagulation-flocculation; especially for the reduction of color, turbidity and phenolic

compounds. The objectives were to determine (1) best chemical combination for coagulation-flocculation, (2) optimum pH for ozonation and to evaluate (3) suitability of ozonation as pre and post treatment of coagulation-flocculation.

2. MATERIALS AND METHODS

(1) Materials

The wastewater samples for the experiments were sourced from a kraft pulp mill in Ehime Prefecture, Japan. Al₂SO₄.14H₂O, AlCl₃.2H₂O and CaCl₂.2H₂O were used as coagulants while PAA and sodium alginate were used as flocculants. All the chemicals used were of analytical reagent grade and used without further purification.

Ozonizer OZM 5006 (Nomura Electronics Co. Ltd. Japan) with a flow rate of 0.2g/m³ (76mg/hr) was used as the ozone generator.

(2) Methods

Wastewater samples were initially analyzed for the determination of COD(chemical oxygen demand), SS(suspended solids) and TDS(total dissolving substances) according to the standard methods of examination of water and wastewater¹³⁾. The average values of three samples are tabulated in **Table 1**.

Table 1 The average characteristics of the kraft pulp mill effluent

Parameter	Value
pH	11.5
COD (g/L)	160.1
SS (g/L)	5.5
TDS (g/L)	170.7
Dissolved inorganic solids (g/L)	73.8
Dissolved Ca ²⁺ (g/L)	1.2
Dissolved Na ⁺ (g/L)	338.7

Prior to ozonation or coagulation-flocculation, kraft pulp mill effluents were filtered using Advantec No.2 filter papers. Effluents for the experiments were prepared by diluting the filtered effluent by 1000 times using distilled water. This diluted solution is equivalent to the residual effluent released by the manufacturing process. This effluent is not having enough organic or chemical compounds for chemical or energy recovery. Every experiment was done in triplicate.

UV/Vis absorption spectra in a UV/Vis spectrophotometer (Hitachi U-2810) were obtained at wavelengths of 465nm, 450nm and 280nm to monitor the removal efficiency. These wavelengths correspond to different properties of wastewater;

i.e. 465nm corresponds to visible color¹⁴⁾, 450nm corresponds to turbidity, 280nm is related to aromatic groups like phenols, which are usually present in these kinds of effluents¹⁵⁾.

a) Coagulation–flocculation of the effluent

Coagulation-flocculation experiments were conducted using different chemical combinations, at different dosages and initial effluent pH levels. Details of those combinations are tabulated in **Table 2**. The experiments were performed in jars, using sample volumes of 200mL. Sample pH values were adjusted using small volumes of concentrated H₂SO₄. After pH adjustment, coagulant was added at varying dosages. It was then followed by the addition of flocculant at varying dosages. All the samples were immediately stirred rapidly for 30 seconds. They were then stirred slowly for 5 min and allowed to settle down for 2 hrs. UV/Vis spectrophotometer absorption values were taken initially before addition of chemicals and at every 30 min period during settling down.

Table 2 Different conditions for coagulation-flocculation experiments

Coagulant	Coag. dose (g/L)	Flocculant	Floc. dose	pH
Al ₂ SO ₄ .14H ₂ O	0	PAA	0.01g/L	10
	0.06		0.05g/L	5
	0.08	Sodium alginate	0.01%	3
	0.1			
AlCl ₃ .2H ₂ O	0	PAA	0.05g/L	10
	0.1	Sodium alginate	0.01%	5
	0.5			3
CaCl ₂ .2H ₂ O	0	Sodium alginate	0.05% 0.01%	10
	0.1			5
	0.2			3
	0.3			

b) Ozonation of the effluent

Ozonation was performed in a reactor with a capacity of 250mL. The ozone stream was continuously introduced to the sample as bubbles through a glass filter at the bottom of the reactor. Ozone flow rate was 0.2g/m³ (76mg/hr). Effluent samples were ozonated for 3hrs and UV/Vis spectrophotometer absorption values were taken initially as well as at every 30min period during ozonation.

c) Ozonation as pre and post treatment to coagulation-flocculation

Experiments were conducted aiming at evaluating the suitability of ozonation as a treatment method before or after coagulation-flocculation. As for first approach, coagulation-flocculation was done

according to the method described in section **a)** for 500mL of diluted effluent. The chemicals used were 0.1g/L AlCl₃.2H₂O and 0.05g/L PAA at pH5. After allowing 2hrs for settling, the supernatant was separated and ozonated for 3hrs.

As for the other approach, the diluted effluent at pH5 was ozonated for 3hrs. Ozonated effluent was then treated with 0.1g/L AlCl₃.2H₂O and 0.05g/L PAA according to the method described in section **a)** and allowed to settle for 2hrs.

3. RESULTS AND DISCUSSION

(1) Coagulation-flocculation of the effluent

Maximum removal efficiencies obtained by coagulation-flocculation experiments are summarized in **Table 3**.

Table 3 Maximum removal efficiencies by coagulation-flocculation.

Coagulant+ Flocculant	Al ₂ SO ₄ .14H ₂ O+ 0.05g/L PAA	AlCl ₃ .2H ₂ O+ 0.05g/L PAA
Coagulant dose(g/L)	0.1	0.1
pH	4	5
% removal of color	83	89
% removal of turbidity	85	89
% removal of phenolic compounds	78	83

In the coagulation process, the aggregation of colloidal particles occurs through charge neutralization and sweep-floc effects. The pH range of 4–5.5 is appropriate for charge neutralization between the positively charged coagulant and negatively charged colloids. On the other hand, as for metal coagulants, such as Al or Fe salts, their ability of removing turbidity is achieved mainly by the adsorption of amorphous solid state aluminium hydroxide, Al(OH)_{3(S)}. For the formation of Al(OH)_{3(S)}, the pH range of 6-8 is favorable because the Al ions require sufficient alkalinity to form it. Thus in the combined action of charge neutralization and sweep-floc point of view, pH 5-8 is the optimal range for turbidity reduction⁹⁾.

As per the results obtained, the optimum pH for coagulation-flocculation exists in the range of 4-5. This establishes the fact that in coagulation-flocculation of kraft paper mill effluent, charge neutralization, which is dominant in the acidic pH, plays an important role in forming the settleable floc. The chemical combination of 0.1g/L AlCl₃.2H₂O and 0.05g/L PAA at pH5 gives the maximum reduction in color, turbidity and phenolic compounds in the diluted effluent, with efficiencies 89%, 89% and 83%, respectively.

(2) Ozonation of the effluent

Fig.1 and Fig.2 show the percentage reductions of phenolic compounds and color during the 3hrs of

ozonation. Change of pH during ozonation is shown in Fig.3.

Fig.1 Effect of pH on the percentage reduction of phenolic compounds during ozonation

Fig.2 Effect of pH on the percentage reduction of color during ozonation.

Fig.3 Change of pH during ozonation.

Reduction percentage of phenolic compounds increases with lowering pH. The maximum removal after 3hrs of ozonation is 70% and the minimum is 52% at pH of 3 and 10, respectively. This result shows that ozonation performs better in terms of degradation of phenolic compounds under acidic conditions, which is in agreement with the published results¹⁶⁾.

Variation of color and turbidity has a similar trend. At the end of 3hrs ozonation reduction of color at pH 3, 5, 7, and 10 are 79%, 80%, 75% and 67%, respectively. This also confirms the fact that ozonation has higher efficiency at low initial pH of the effluent.

Experimental results show that the rates of decomposition of phenolic compounds as well as reduction of color are high within an initial hour. Thereafter the rate lowers, showing a tendency to become almost constant at some point of time. This observation can be explained in the following way.

The decolorization and decomposition of phenolic compounds occur in two distinct regions: (1) the first region is, an initial hour where reduction efficiency is high and (2) the other region is, after an hour, gradual reduction of reduction efficiency⁴⁾. The higher initial reduction rate is due to the higher reactivity of ozone with the relatively fragile compounds in effluent. Less availability of easily oxidizable structures makes further ozonation sluggish.

The pH values of samples decrease with ozonation and converge to a value of around 2 after 3 hrs of ozonation (Fig.3). Degradation of phenolic compounds into acyclic, acidic compounds such as muconic acid^{17) 18)} can be the reason for this characteristic in pH reduction. Muconic acid is supposed to be easily formed within first hour, then further decomposed into other acidic compounds, such as oxalic acid etc.

and finally converted to carbon dioxide. But the latter reactions seem to be much slower than the former reaction. It may be a reason why the samples having higher initial pH indicate a rapid decrease of pH during ozonation although decomposition of phenolic compounds is larger at lower initial pH (Fig.1).

(3) Ozonation kinetics

Kinetic investigations on the decomposition reactions of phenolic compounds by ozonation have found to be of the first order with almost constant reaction coefficients^{19) 20) 21)}. These experimental analyses have been conducted using aqueous solutions of different types of phenols. Since the pure compounds follow first order reaction kinetics, the compounds available in kraft mill effluent can also be assumed to follow the same order.

Decomposition kinetics of phenolic and color compounds were investigated, assuming the reactions have the first order kinetics. Fig.4 and Fig.5 show the graphs of $\ln[A_0/A]$ vs time t . In Fig.4 A_0 and A correspond to initial phenolic compound concentration and phenolic compound concentration at any time t , respectively. Fig.5 represents the same parameters related to color.

Fig.4 shows near linear characteristics and it proves that the decomposition of phenolic compounds existing in the kraft pulp mill effluent have approximately the first order reaction kinetics in this experiment.

However according to Fig.5 the decomposition of color compounds hardly fit to the first order variation. The existence of compounds other than the phenolics which contributes to the color of the solution can be the reason of this deviation. Even though the phenolic compounds follow the first order reaction kinetics the others might not behave in the similar manner.

Fig.4 Change of the concentration of phenolic compounds at pH 10.

Fig.5 Change of the concentration of color compounds at pH 10.

(4) Ozonation as pre and post treatment to coagulation-flocculation

Percentage reduction of phenolic compounds and color is shown in Fig.6 and Fig.7, respectively. Fig.6 corresponds to coagulation- flocculation followed by ozonation, while Fig.7 corresponds to ozonation followed by coagulation- flocculation.

As seen in Fig.6, the reduction of phenolic compounds by coagulation-flocculation followed by ozonation is 93% - out of which coagulation-flocculation accounts for 83%, while 10% is due to ozonation.

When ozonation is followed by coagulation-flocculation, as shown in Fig. 7, the reduction of phenolic compounds is 59%. Out of it, the initial ozonation accounts for 57%, while coagulation-flocculation accounts for only 2%.

The meaning of results obtained above can be interpreted as follows: During coagulation-

flocculation and settling, high molecular weight organic compounds end up in the sediment. The low molecular weight compounds that remain in the supernatant are further oxidized during ozonation²²⁾ leading to higher reduction of phenolic compounds. On the other hand, initial ozonation degrades phenolic compounds into low molecular weight compounds, which are less removable by coagulation-flocculation.

According to Fig.6 and Fig.7, it is apparent that what brings in the reduction of effluent color is whatever the initial treatment step, regardless of whether it is coagulation-flocculation or ozonation.

There is virtually no effect on color reduction from the second treatment method that follows. In addition, when coagulation-flocculation is the second method, there is a decrease in the clarity after adding chemicals, due to the formation of flocs.

Fig.6 Percentage reduction of color and phenolic compounds with initial coagulation-flocculation (0-2 hrs) followed by ozonation (2-5 hrs).

Fig.7 Percentage reduction of color and phenolic compounds with initial ozonation (0-3 hrs) followed by coagulation-flocculation (3-5 hrs).

4. CONCLUSIONS

The results of the study can be summarized as below.

More than 80% of reductions in color, turbidity and phenolic compounds can be achieved by using 0.1g/L $\text{AlCl}_3 \cdot 2\text{H}_2\text{O}$ with 0.05g/L PAA at pH 5.

After coagulation-flocculation, 1 hr settling period is sufficient enough to settle almost all the flocs formed.

Ozonation is more effective in the treatment of kraft pulp mill effluent under acidic conditions.

Decomposition of phenolic compounds in the effluent by ozonation has a first order reaction kinetics.

In the case of treating kraft paper mill effluent, ozonation is more suitable after the chemical coagulation-flocculation. This sequence of combined treatment is capable of producing colorless and phenolic compounds-free effluent.

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