Characteristics of Effluent from Potassium Hydroxide and Calcium Hypochlorite Bleaching of Pulp from Kenaf Stem

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***Abstract*:**

Waste and wastewaters are generated from both pulp and bleaching processes of paper making. However, like many industrial processes it has impacted our environment and our health. A dewatered kenaf stem was bleached in the 20%, 60% and 90% concentrations of potassium hydroxide and calcium hypochlorite at time intervals of 1hr, 2hrs and 3hrs to compare the COD and BOD of their effluent for environmental friendliness. After examining the whole concentrations and the time intervals, 60% concentration of the chemicals at 2hrs bleaching gave better pulp on physical examination. When the COD of the effluent of two chemicals were analysed, potassium hydroxide effluent had a COD of 784mg/L while that of hypochlorite was 3240mg/L. Also the BOD of potassium hydroxide effluent was 16.88mg/L while that of hypochlorite effluent gave 18.75mg/L. The report of this study showed that bleaching of kenaf pulp with 60% potassium hydroxide for 2 hrs has lower COD than the use of hypochlorite while the two have almost the same BOD.

Keywords: *Biochemical oxygen demand, Bleaching, Chemical oxygen demand, Effluent quality, Kenaf pulp, Potassium hydroxide.*

INTRODUCTION

The generation and release of certain water pollutants from chemical pulp bleaching operations are affected by the choice of bleaching chemicals, and the industry's shift from chlorine bleaching to ECF bleaching has altered wastewater characteristics. Effluent quality is commonly judged on the basis of such aggregate characteristics as biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), total solids (TS), turbidity, pH, color e.t.c. Each reflects a measured effect of a combination of constituents, and not the concentration of one specific substance.

The increasing public awareness of the fate of these pollutants and stringent regulations established by the various authorities and agencies are forcing the industry to treat effluents to the required compliance level before discharging in to the environment [1]. Sundry studies have been conducted so far on this sector regarding the environmental impacts as well as the control of the pollutants [2]. In many modern mills, reduced inputs of toxic chemicals and improved wastewater treatment have resulted in significant reduction of effluent toxicity [3] and of environmental impacts [4]

Bleaching is engaged on the brown pulp obtained after pulping in order to meet the desired colour dictated by product standards. Bleaching is often undertaken, primarily for two purposes: first, to increase brightness; second, to remove residual lignin. Lignin can be thought of as the 'glue' holding the cellulose fibres of wood together;it accounts for up to 50 per cent of the weight of pulpwood, the basic feedstock for pulp manufacture [5]

Several bleaching agents, including chlorine, chlorine dioxide, hydrogen peroxide, ozone, etc. may be used either singly or in combination. It is in this step that lignin, phenols, resin acids, etc. get chlorinated and transformed into highly toxic xenobiotics.

In the late 1980's and early 1990's, there was increasing pressure to significantly reduce organochlorine discharges in pulp and paper mill effluents, as they were believed to be major contributors to toxicity observed in these effluents [6].

Since, the 1980's process improvements replaced elemental chlorine bleaching of wood pulps in developed countries, however, elemental chlorine is still widely used in developing countries [7]. The removal of elemental chlorine from bleaching processes resulted in a suggested reduction in effluent toxicity and also symptomatic changes but not absence of chronic impacts [8].

MATERIALS AND METHODS

Kenaf stem was chopped into 1 to 4 cm long, washed with warm water to remove dirt and dust. The washed kenaf was dewatered to a solid content of 40% to 45%. 5 grams of kenaf stem was taken in 400ml of cooking liquor in 1000ml flask at atmospheric pressure and pulped at 20%, 60% and 90% concentrations of formic acid and sodium hydroxide, cooking time was varied from 1hr, 2 hrs and 3 hrs at 95°C. At the end, the pulp from each cooking was bleached with 20%, 60% and 90% concentrations of potassium hydroxide and calcium hypochlorite and the bleaching time was varied from 1hr, 2 hrs and 3 hrs at room temperature. At the end of each bleaching, the sample was filtered with a fine mesh sieve to get the effluent used in the analyses.

The effluent was analysed using the Standard Method for Examination of Water and Wastewater [9]. The parameters determined were COD and BOD. COD was determined by closed reflux titrimetric method and BOD by measuring dissolved oxygen before and after incubation at 20^{C} for 5 days.

K*enaf stem* *dewatered kenaf stem* ***Pulp*** ***Bleached pulp*** ***Bleaching Effluent***

Calculation done to determine the BOD_5;

$$\frac{(DO_1 - DO_5)}{P} = BOD_5 \text{ mg/l}$$

DO_1 = initial dissolved oxygen

DO_5 = final dissolved oxygen (dissolved oxygen after five days)

P = fraction of sample (volume of sample/volume of sample bottle)

Calculation done to determine the COD;

$$\frac{V_t \times N \times 8000}{V_S} = COD \text{ mg/l}$$

Where V_t is the volume of titrant, N is normality of the standard Ferrous Ammonium Sulphate and V_s is volume of sample used.

Results and Discussion

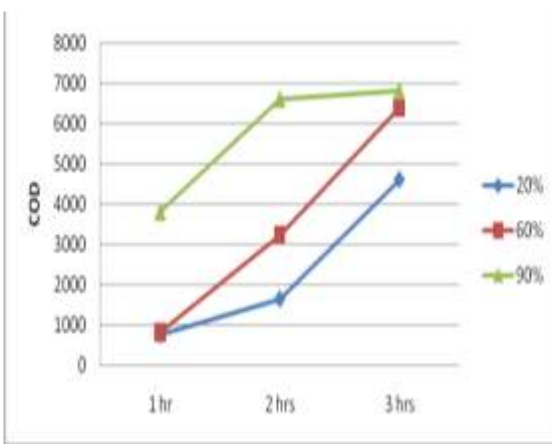

Fig. 1: Variation of COD with bleaching time and hypochlorite concentration

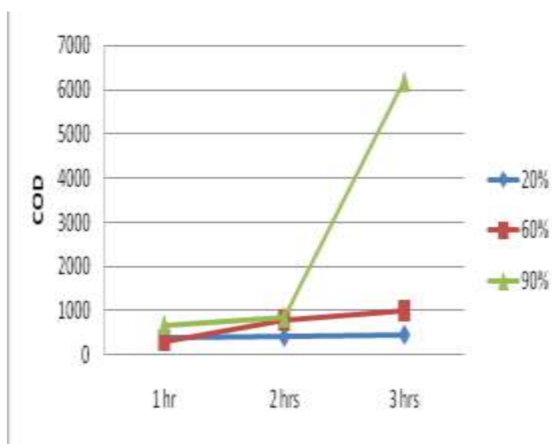

Fig. 2: Variation of COD with bleaching time and KOH-H_2O_2 concentration

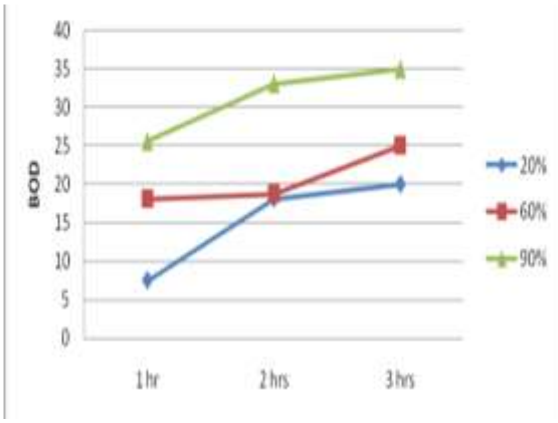

Fig. 3: Variation of BOD with bleaching time and hypochlorite concentration

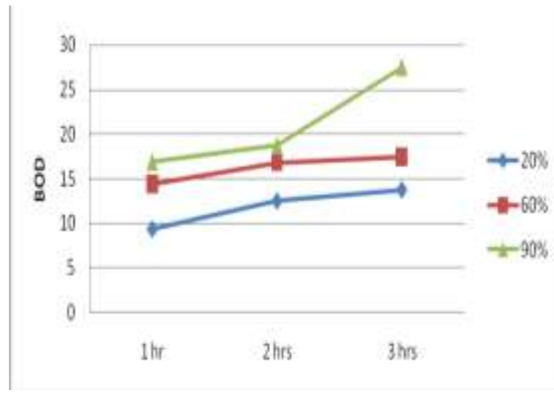

Fig. 4: Variation of BOD with bleaching time and KOH-H_20_2 concentration

Chemical Oxygen Demand (COD) represents the amount of oxygen required to oxidise all of the organic matters both degradable and non-degradable present in the sample. **Figures 1 - 4** showed the values of COD and BOD of the effluents when the pulp was bleached with 20%, 60% and 90% concentrations of formic acid/potassium hydroxide and sodium hydroxide/calcium hypochlorite at 3 hours interval.

It is a little bit difficult to explain this result due to some inconsistent variation which its cause is not clear yet. With sodium hydroxide/Hypochlorite bleaching; the COD values were between 762 – 6800 mg/L within the three concentrations during the 3 hour period. COD increased with increase in time and concentration when hypochlorite was used .This is the kind of relationship between time and concentration with regards to COD value as reported by [10]. Another finding was made by [11]Hu et al. (2015) in which COD value of between 60mg/L and 80 mg/L with ECF bleaching was recorded. The values of COD in this investigation were higher compared to [12] that reported 2300 mg/L COD and [13] recorded 61 mg/L.

Formic acid/KOH-H_2O_2 on the other hand also has highest COD values at 90% in 3 hours (20%/460 mg/L, 60%/996 mg/L, 90%/6200 mg/L) while [14] obtained values between 60 mg/L and 70mg/L. Formic acid/potassium hydroxide bleaching effluent recorded sharp increase in COD after 2 hours with 90% concentration. This could be that degradation increased with increase in time and concentration.

It was observed that at 3 hours, values of COD from KOH-H_2O_2 and Ca (CIO) $_2$ bleaching increased with increase in concentration with KOH maximum at 90% (6200 mg/L) while $Ca(CIO)_2$ maximum was 6800 mg/L at 90%. At 2 hours, KOH has COD maximum value of 846 mg/L at 90% while Ca (CIO) $_2$ maximum value was 6600 mg/L.

BOD (Biochemical Oxygen Demand) represents the amount of oxygen used by microorganism to decompose organic material. With sodium hydroxide(NaOH)/calcium hypochlorite ($Ca(CIO)_2$) , the BOD in the processes have their highest values at 3 hours bleaching for all concentration (20%/20 mg/L, 60%/25 mg/L, 90%/35 mg/L) with 60% having the least increment. BOD value in 60% concentration almost remained the same between 1 and 2 hours. Reference [15] reported BOD of 350 mg/L in effluent from soda/hypochlorite pulp bleaching.

As observed from formic acid (FAA)/potassium hydroxide (KOH) bleaching, effluent also had highest BOD values in 3 hours at all the concentrations (20%/13.75 mg/L, 60%/17.5 mg/L, 90%/27.5 mg/L).

The result showed that at 3 hours FAA/KOH has maximum BOD at 90% (27.5 mg/L) as well as NaOH/$Ca(CIO)_2$ with 90% (35 mg/L). At 2 hours bleaching, FAA/KOH and NaOH/$Ca(CIO)_2$ effluent gave maximum BOD of 18.75 mg/L and 33.13 mg/L respectively at 90% concentration. This result indicated that degradation increased with increase in concentration and time. Reference [16] worked on pulping agricultural residue with formic acid and bleaching with KOH but did not discuss these environmental parameters of the effluent.

Table 1:

Mean and SE of **COD (mg/l)** over the Concentrations, Time and Chemicals for Bleaching

Concentration	**Time**	**Chemical**	**Mean + SE**
20%^{a}	1 Hour	Ca(CIO)2	762 + 736.77^{a}
		KOH	460 + 736.77^{b}
	2 Hours	Ca(CIO)2	4600 + 736.77^{a}
		KOH	388 + 736.77^{b}
	3 Hours	Ca(CIO)2	1650 + 736.77^{a}
		KOH	408 + 736.77^{b}
60%^{b}	1 Hour	Ca(CIO)2	822 + 736.77^{a}
		KOH	996 + 736.77^{b}
	2 Hours	Ca(CIO)2	6800 + 736.77^{a}
		KOH	784 + 736.77^{b}
	3 Hours	Ca(CIO)2	6600 + 736.77^{a}
		KOH	312 + 736.77^{b}
90%^{b}	1 Hour	Ca(CIO)2	3800 + 736.77^{a}
		KOH	6200 + 736.77^{b}
	2 Hours	Ca(CIO)2	6400 + 736.77^{a}
		KOH	846 + 736.77^{b}
	3 Hours	Ca(CIO)2	3240 + 736.77^{a}
		KOH	678 + 736.77^{b}

Table 2

ANOVA Table

Source	Sum of Squares	df	Mean Square	F	Sig.
Chemical	61894933.778	1	61894933.778	57.012	.000
Time	10443254.222	2	5221627.111	4.810	.021
Conc	28285270.222	2	14142635.111	13.027	.000
Chemical * Time	56799056.889	2	28399528.444	26.159	.000
Chemical * Conc	9085430.222	2	4542715.111	4.184	.032
Time * Conc	35811596.444	4	8952899.111	8.247	.001
Chemical * Time * Conc	10527527.111	4	2631881.778	2.424	.086
Error	19541704.000	18	1085650.222		
Corrected Total	232388772.889	35			

R Squared = .916 (Adjusted R Squared = .836)

The Anova table above reveals that all the factors and all the interactions except the three (3) level interactions were significant ($p < 0.05$).

Table 3:

Mean and SE of **BOD (mg/l)** over the Concentrations, Time and Chemicals for Bleaching

Concentration	Time	Chemical	Mean + SE
20%[a]	1 Hour	Ca(CIO)2	20 + 6.25
		KOH	16.88 + 6.25
	2 Hours	Ca(CIO)2	35 + 6.25
		KOH	13.75 + 6.25
	3 Hours	Ca(CIO)2	18.13 + 6.25
		KOH	17.5 + 6.25
60%[a]	1 Hour	Ca(CIO)2	18.13 + 6.25
		KOH	12.5 + 6.25
	2 Hours	Ca(CIO)2	25.63 + 6.25
		KOH	9.38 + 6.25
	3 Hours	Ca(CIO)2	25 + 6.25
		KOH	16.88 + 6.25
90%[a]	1 Hour	Ca(CIO)2	7.5 + 6.25
		KOH	14.38 + 6.25
	2 Hours	Ca(CIO)2	33.13 + 6.25
		KOH	18.75 + 6.25
	3 Hours	Ca(CIO)2	18.75 + 6.25
		KOH	27.5 + 6.25

Table 4:

ANOVA Table

Source	Sum of Squares	df	Mean Square	F	Sig.
Chemical	321.007	1	321.007	4.109	.058
Time	384.635	2	192.318	2.462	.113
Conc	38.542	2	19.271	.247	.784
Chemical * Time	577.170	2	288.585	3.694	.045
Chemical * Conc	187.847	2	93.924	1.202	.324
Time * Conc	293.229	4	73.307	.938	.464
Chemical * Time * Conc	67.882	4	16.970	.217	.925
Error	1406.250	18	78.125		
Corrected Total	3276.562	35			

R Squared = .571 (Adjusted R Squared = .165)

Table above shows that only the time – chemical interaction is significant ($p < 0.05$) while the rest were not.

Conclusion

The data obtained from this work can be used to address the controversy on comparative environmental effects of TCF and ECF processes. Since potassium hydroxide with peroxide was able to adequately bleach the pulped stem, it can be used to reduce the environmental impacts of chlorine bleaching. When physically examined, the pulp bleached for 2 hours at 60% concentration has better appearance and the effluent from potassium hydroxide – hydrogen peroxide bleaching has less pollutant load with respect to BOD and COD. If kenaf stem can be turned into pulp and paper using environmentally less harmful process, it will increase the economic base of farmers. However, further work is needed to ascertain the behavior of other effluent characteristics.

Acknowledgements

I acknowledge the Federal Institute of Industrial Research, Oshodi, Lagos, Nigeria and University of Nigeria, Nsukka, for their support during the course of this work. There is no conflict of interest.

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