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TSS, TDS AND TS OF EFFLUENTS FROM POTASSIUM HYDROXIDE AND CALCIUM HYPOCHLORITE BLEACHING

Chukwudebelu, J.A.[1] & Agunwamba, J.C.[2]
[1]*Chief Research Officer, Department of Chemical, Fibre& Environmental Technology, Federal Institute of Industrial Research, Oshodi, Lagos- Nigeria*
[2]*Professor, Department of Civil Engineering, University of Nigeria Nsukka, Enugu-Nigeria*

Abstract

The use of different raw materials and chemicals by pulp and paper industries during pulp and paper production has contributed immensely to the pollution load on the environment. This research used TCF (KOH) and Hypochlorite $(CaCIO)_2$ to bleach pulped agricultural residue (kenaf stem) to determine one with better environmental parameters. The dewatered kenaf was pulped with different concentrations of sodium hydroxide and formic acid at different time intervals. 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 were varied from 1hr, 2 hrs and 3 hrs at room temperature and TSS, TDS and TS of the bleaching effluents were compare for environmental quality. From physical pulp quality, 60% concentration and 2 hrs bleaching was selected and the effluent from that gave TSS 507.5 mg/L, TDS 2341.5 mg/l and TS 2849 mg/L for KOH and TSS 4492.5 mg/L, TDS 3707.5 mg/L and TS 8200 mg/L for $Ca(CIO)_2$. This result showed that the effluent from KOH bleaching has lower pollution load.

Keywords: *Total dissolved solid, Calcium hypochlorite, Bleaching, Kenaf pulp, Environmental quality.*

INTRODUCTION

Water is one of the essential requirements for life. Our water resources are depleting at an alarming rate due to increasing population. Industries play a major role in water pollution, Pulp and paper industry is considered as one of the most polluting industry due to the compounds they release into the environment (Bahar*et al*,. 2015). These compounds increase the toxicity of effluent substances as well as Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD) and Total Dissolved Solids (TDS) of the receiving aquatic resources, which consequently imbalances the aquatic life (Singh and Chandra, 2019). The most significant sources of pollution among various processing stages are wood preparation, pulping, pulp washing, screening and bleaching (Akan,2008). Among various processes, chemical pulping generates high amount of waste water.

Nowadays, bleaching of chemical pulps is achieved by two processes, *i.e*., the elemental chlorine-free (ECF) process and/or the total chlorine-free (TCF) one, in which bleaching is carried out essentially by using oxygen compounds (El-Sakhawy et al,. 1996). Which concept is preferred depends mainly on the desired final brightness of the pulp to be bleached, its properties, capital costs of bleaching chemicals, and concentration of chlorine-containing components in the effluent (Otůček and Říhová, 2016).

In countries with limited forest resources, the use of agricultural residues for pulp manufacturing offers a possibility to solve the lack of wood and also using totally chlorine-free bleaching will be a win-win for the environment (El-Sakhawy et al,. 1996).

Bleaching is engaged on the brown pulp obtained after pulping in order to meet the desired colour dictated by product standards(Parker et al,. 1990). Bleaching is a sequence of chemical treatments and washes of the pulp. The bleaching of pulp generates wastes. A substantial part of the waste is in liquid form. This effluent arises from the washing of pulp between some bleaching stages. It contains spent bleaching chemicals, degraded lignin, and other substances (Parker et al,. 1990). The particular sequence used mainly depends on the nature of the fibre (for example, softwood, hardwood, or non-wood), the type of pulping process applied, and the end use of the fibre. Regardless of the method of bleaching, the effluent may have certain characteristics which can damage the environment, such as suspended and dissolved solids and the capacity to deplete oxygen from the receiving waters (Parker et al,. 1990). Pulp and paper mills can take measures to reduce the formation of organochlorines, organic materials, heavy metals, suspended solids, and other potential pollutants in their bleaching wastes by modifying bleaching processes as well as the use of total chlorine free chemicals (Parker et al,. 1990.

Several bleaching agents, including chlorine, chlorine dioxide, hydrogen peroxide, oxygen, 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(Kaizar and Norli,2015).

Bleaching of pulp using conventional methods releases a range of pollutants, including organic products that have affected the water bodies and also the aquatic fauna as well as livelihood of the surrounding communities.Up to 85% of the total effluent volume is generated in the bleaching stage. The degree of delignification of the unbleached pulp, the

bleaching process, the washing loss, type of wood, final brightness desired, chemical and water consumption and the degree of plant closure are important indicators of wastewater characteristics (European Commission,2015 and Dalh,2008). The two main types of bleaching methods in use are elemental chlorine free (ECF), when no molecular or gaseous chlorine is dosed in the bleaching, and totally chlorine free (TCF) bleaching (European Commission. 2015). Owing to the differences between both the bleaching technologies and chemical composition of the bleaching effluents, it is necessary to study in order to predict and understand the environmental impact associated, and consequently to develop the most suitable treatment that decreases effluent loads and toxicity(María,2017)

Effluent quality is commonly judged on the basis of such aggregate characteristics as biochemical oxygen demand, chemical oxygen demand, total suspended solids (TSS), total solids (TS), total dissolved solids (TDS) turbidity, pH, color e.t.c. Total suspended solid (TSS) represents the solid particles mixed in water or effluent. Total dissolved solids (TDS) are measured as the mass of residue remaining when a measured volume of filtered water is evaporated. Total solids (TS) are the amount of solid present in dissolved and suspended form.

A significant number of studies pertaining to the chemical composition of bleaching effluents have been published. Several authors have worked inidentifying the chemical compounds in filtrates. More than 500 organic compounds have beenidentified in bleaching effluents so far. Most compounds identified in bleaching effluents are derived from lignin or other wood components, such as extractives or carbohydrates (Kague and Carlberg, 1996).

Lignin is an organic material. The lignin that remains after chemical pulping is
oxidised in the case of chlorine bleaching process. The effluent from the process contains a range of organochlorines. Some organochlorines break down quickly; and some, including dioxins and furans, have long lives.Organochlorines may be largely removed by treatment of effluent at the pulp mill, but it is not currently feasible to avoid discharging some into the environment with the effluent. Some organochlorines can also remain embedded in the pulp and, ultimately, in the paper products (Parker et al,. 1990). The effects of organochlorine discharges on people and on natural ecological systems are not fully understood or quantified. In this paper, soda and formic acid cooked pulps fromkenaf stemwere subjected to single stage bleaching with potassium hydroxide and calcium hypochlorite under laboratory

conditions to check the effects of chemicals, concentrations and time on the effluent quality with respect to solids.

MATERIALS AND METHODS

Kenaf stem was manually 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%. The dewatered Kenaf was pulped with different concentrations of sodium hydroxide and formic acid at different time intervals. 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 were 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 of size 0.027 to get the effluent used in the analyses. The tests were carried out in triplicate and each value is an average of three samples.

The effluent was analysed using the Standard Method for Examination of Water and Wastewater (APHA, 2005). The parameters determined were TSS, TDS and TS.

Kenaf stem Bleached pulp Bleaching effluent

Figure1. Samples of experimental materials

RESULTS AND DISCUSSION

Table 1: Effluent from-bleaching with 10g KOH-H2O2 and Ca (CIO)2 at 20%

Time(Hrs)	Chemicals/Parameters	TDS(mg/L)	TSS(mg/L)	TS(mg/L)
1	KOH	8726.5	367.5	9094
	Ca(CIO)2	4170.2	3832	8002.2
2	KOH	7477	360	7837
	Ca(CIO) 2	6770	1105	7875
3	KOH	4608	330	4938
	Ca(CIO) 2	5564.5	473	6037.5

The pulps obtained from 1hr, 2hrs and 3hrs bleaching with 20%, 60% and 90% concentrationswere examined physically and the pulp bleached with 60% concentration for 2 hrs gave the best. **Table 1** showed the values of TSS, TDS and TS of the effluent when the pulp was bleached with 20% concentration of potassium hydroxide and calcium hypochlorite at 1, 2 and 3 h intervals. The result showed that with potassium hydroxide (KOH-H_20_2), TSS decreased from 367.5 mg/L to 330mg/L as the time of bleaching increased which was not so significantly. This suggests that solid in the KOH solution was not degraded much with time and concentration. With Hypochlorite ($Ca(CIO)_2$), TSS values decreased significantly from 3832 g/L to 473 mg/L as the time of bleaching increased. From the study, TDS showed a decrease in value with increase in bleaching time in KOH bleaching effluent while TDS values increased with increase in bleaching time in $Ca(CIO)_2$ bleached effluent. TS values reflected the outcome of TSS and TDS for the two chemicals with results that showed reduction in values as the bleaching time increased. This may be indicative that chemicals and raw materials react differently.

Table 2: Effluent from bleaching with 10g KOH-H_2O_2 and Ca(CIO)2 at 60%

Time(Hrs)	Chemicals/Parameters	TDS(mg/L)	TSS(mg/L)	TS(mg/L)
1	KOH	2768	820	3588
	$Ca(CIO)_2$	5275	5090	10365
2	KOH	2341.5	507.5	2849
	$Ca(CIO)_2$	3707.5	4492.5	8200
3	KOH	1553	490	2043
	$Ca(CIO)_2$	291.5	3037.5	3329

In **table 2**, values of TSS, TDS and TS of effluent obtained from bleaching of kenaf pulp at 1h, 2hrs and 3hrs time interval at 60% concentration of KOH and ($Ca(CIO)_2$) was provided. The result showed that the whole solids showed decrease in values as the time of bleaching increased, this suggest that more organic matter was degraded with time. Most reduction was observed in the values of TDS in $Ca(CIO)_2$ bleaching that reduced from 5275 mg/L to 291.5 mg/L during the 3 hrs period. The highest values were obtained for TDS, TSS and TS from 1 hr bleaching with $Ca(CIO)_2$ bleaching effluent having higher solid values than KOH effluent.

Table 3:Effluent from bleaching with 10g KOH-H_2O_2 and Ca(CIO)2 at 90%

Time(Hrs)	Chemicals/Parameters	TDS(mg/L)	TSS(mg/L)	TS(mg/L)
1	KOH	2602	1970	4572
	$Ca(CIO)_2$	14522.5	4162.5	18685
2	KOH	2163.5	837.5	3001
	$Ca(CIO)_2$	13446	3961	17407
3	KOH	998.5	537.5	1536
	$Ca(CIO)_2$	13092.5	1887.5	14980

*Each value is an average of three samples.

From **table 3** which recorded the values of 90% bleaching, the result showed reduction in values of the solids as the bleaching time increased. This followed the same pattern with 20% and 60% with the highest reduction being observed in the values of TSS that reduced from 1970 mg/L to 537.5 mg/L during the 3 hrtime of bleaching. This is similar with the result reported by Nagdhi et al (2013) in which a value of 1800mg/L was obtained for TSS.

The TS of the three concentrations at the 3 hr periods followed the pattern of the TSS and TDS and decreased as the bleaching time increased. The highest TS (18685 mg/L) was reportedin the Ca(CIO)2 effluent after 1 hr bleaching with 90% concentration while KOH effluent from 3 hr bleaching at 90% gave the lowest value (1536 mg/L). This may be due to the reactions between the chemicals and the raw materials that determined the distribution of the solids.Nagdhi et al (2013) and Kesalkar et al, (2012) reported 3000mg/L and between 1365 – 1798mg/L respectively for TS.

All the concentrations with the two chemicals have their maximum TSS, TDS and TS after 1 hr and minimum after 3 hr bleaching which suggest that more organic matter was degraded with time.Higher values of TDS observed across the bleaching periods with different concentrations may be due to the high concentration of sodium and potassium which can cause increase in salinity of the wastewater (Chandra et al,. 2020). But generally, higher values of solids were reported from $Ca(CIO)_2$ bleaching effluentthan that of KOH effluent in all the processes.

This study investigated TSS, TDS and TS in the KOH and $Ca(CIO)_2$ bleaching effluentto determine their environmental quality. Solids are contaminants in an effluent and their high

value poses danger of pollution to the environment. In Nigeria, the standard set by the regulatory body (FEPA, 1991) put the maximum limit to be discharged to the environment for total dissolved solid is 2000 mg/L, total suspended solid is 30 mg/L while total solid is 2030 mg/L.

Table 4: Mean and SE of TSS (mg/l) over the concentrations, time and chemicals for Bleaching

Concentration	Time	Chemical	Mean + SE
20%[a]	1 Hour	Ca(CIO)2	3832 + 3430.88[a]
		KOH	7837 + 3430.88[a]
	2 Hours	Ca(CIO)2	1105 + 3430.88[a]
		KOH	9094 + 3430.88[b]
	3 Hours	Ca(CIO)2	473 + 3430.88[a]
		KOH	936 + 3430.88[a]
60%[b]	1 Hour	Ca(CIO)2	14980 + 3430.88[a]
		KOH	3588 + 3430.88[b]
	2 Hours	Ca(CIO)2	17407 + 3430.88[a]
		KOH	2849 + 3430.88[b]
	3 Hours	Ca(CIO)2	10365 + 3430.88[a]
		KOH	2043 + 3430.88[b]
90%[ab]	1 Hour	Ca(CIO)2	18685 + 3430.88[a]
		KOH	1221 + 3430.88[b]
	2 Hours	Ca(CIO)2	8200 + 3430.88[a]
		KOH	536 + 3430.88[b]
	3 Hours	Ca(CIO)2	3329 + 3430.88[a]
		KOH	4572 + 3430.88[b]

Table 5: ANOVA Table

Source	Sum of Squares	df	Mean Square	F	Sig.
Chemical	232054444.444	1	232054444.444	9.857	.006
Time	137025850.889	2	68512925.444	2.910	.080
Conc	130359500.222	2	65179750.111	2.769	.089
Chemical * Time	55919537.556	2	27959768.778	1.188	.328
Chemical * Conc	401358908.222	2	200679454.111	8.524	.002
Time * Conc	48529081.778	4	12132270.444	.515	.725
Chemical * Time * Conc	166987577.778	4	41746894.444	1.773	.178
Error	423753788.000	18	23541877.111		
Corrected Total	1595988688.889	35			
b. R Squared = .734 (Adjusted R Squared = .484)					

The Anova table above shows that while all the factors are not significant, only chemical – concentration interaction is significant ($p < 0.05$).

Table 6: Mean and SE of TS (mg/l) over the concentrations, time and chemicals for bleaching

Concentration	Time	Chemical	Mean + SE
20%[a]	1 Hour	Ca(CIO)2	360 + 2269.93[a]
		KOH	12875 + 2269.93[b]
	2 Hours	Ca(CIO)2	367.5 + 2269.93[a]
		KOH	16252.5 + 2269.93[b]
	3 Hours	Ca(CIO)2	330 + 2269.93[a]
		KOH	6037.5 + 2269.93[b]
60%[b]	1 Hour	Ca(CIO)2	490 + 2269.93[a]
		KOH	5090 + 2269.93[b]
	2 Hours	Ca(CIO)2	820 + 2269.93[a]
		KOH	4492.5 + 2269.93[a]
	3 Hours	Ca(CIO)2	507.5 + 2269.93[a]
		KOH	2037.5 + 2269.93[a]
90%[b]	1 Hour	Ca(CIO)2	537.5 + 2269.93[a]
		KOH	572.5 + 2269.93[a]
	2 Hours	Ca(CIO)2	837.5 + 2269.93[a]
		KOH	562.5 + 2269.93[a]
	3 Hours	Ca(CIO)2	1970 + 2269.93[a]
		KOH	550 + 2269.93[a]

Table 7: ANOVA Table

Source	Sum of Squares	df	Mean Square	F	Sig.
Chemical	198340277.778	1	198340277.778	19.247	.000
Time	25038179.167	2	12519089.583	1.215	.320
Conc	173646037.500	2	86823018.750	8.425	.003
Chemical * Time	34919926.389	2	17459963.194	1.694	.212
Chemical * Conc	222381776.389	2	111190888.194	10.790	.001
Time * Conc	36296145.833	4	9074036.458	.881	.495
Chemical * Time * Conc	24973431.944	4	6243357.986	.606	.663
Error	185493175.000	18	10305176.389		
Corrected Total	901088950.000	35			
R Squared = .794 (Adjusted R Squared = .600)					

The table above shows that chemical, concentration and chemical – concentration interaction were significant ($p < 0.05$) while the remainder were not.

Table 8: Mean ± Standard error of **TDS(mg/L**) of effluents from bleaching at different percentage of chemicals/ parameters

Parameters	**20 %**	**60%**	**90%**
KOH	6937.17 ± 1219.16	2220.83 ± 355.89	1921.33 ± 478.47
$Ca(CIO)_2$	5501.57 ± 751.16	3091.33 ± 1471.23	13687 ± 430.03

Table 9: Mean ± Standard error of **TDS (mg/L**) of effluents from bleaching at different time of chemicals/ parameters

Parameters	**1 hour**	**2 hours**	**3 hours**
KOH	4698.83 ± 2014.4	3994 ± 1742.26	2386.5 ± 1122.22
$Ca(CIO)_2$	7989.23 ± 3282.17	7974.5 ± 2875.05	6316.17 ± 3714.39

Table 10: ANOVA table

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	159682457.503[a]	5	31936491.501	2.335	0.106
Intercept	556419224.294	1	556419224.294	40.677	0.000
Concentration (%)	83422682.321	2	41711341.161	3.049	0.085
Time	13533428.354	2	6766714.177	0.495	0.622
Parameters	62726346.827	1	62726346.827	4.586	0.053
Error	164148467.493	12	13679038.958		
Total	880250149.290	18			
Corrected Total	323830924.996	17			
a. R Squared = .493 (Adjusted R Squared = .282)					

The ANOVA table showed no significant for the three factors but the interaction (intercept) was significant ($p < 0.05$).

CONCLUSION

These two chemical bleaching processes (KOH and $Ca(CIO)_2$) were compared for environmental quality with respect to solids. The method was bleaching with three different concentrations for 1hr, 2hrs and 3 hrs intervals. The pulp bleached with 60% concentrations of KOH and $Ca(CIO)_2$ for 2 hrs gave better pulp on physical examination. The results of the solids obtained from the analyses of the effluents from the 60% concentration for 2 hrs bleaching showed that KOH process has fewer solids in its effluent. Though, the process did not meet the effluent standard of Nigeria, but it is closer to it. From the statistical analysis, mainly chemical-concentration interactions are significant ($p > 0.05$) while others are not. There is need for further research into other effluent parameters for a robust conclusion.

Conflict of Interests

The authors have not declared any conflict of interests.

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