International Journal of Environmental Sciences & Natural Resources
ISSN: 2572-1119

Juniper Publishers
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Research Article
Volume 26 Issue 5 - January 2021
DOI: 10.19080/IJESNR.2021.26.556196

Int J Environ Sci Nat Res

Nitrogen and Carbon Characteristics of Sludges from Formic Acid and Sodium Hydroxide Pulping of Kenaf Stem

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Submission: November 24, 2020; **Published:** January 04, 2021

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Abstract

Sludge is produced during paper manufacturing. In this study, kenaf stem was pulped with formic acid and sodium hydroxide at 20%, 60% and 90% concentrations for a cooking period of 1,2 and 3h at 96oC under atmospheric pressure. The effluent from the pulping processes was filtered to get the sludge. The sludge was analysed for carbon and nitrogen. The sludge content from 20% pulping has nitrogen and carbon from sodium hydroxide, sludge from 60% pulping has carbon and nitrogen from both chemicals with more nitrogen while 90% pulping has more carbon. Considering the pulped stem, it showed under pulped, normal and over pulped with respect to 20%, 60% and 90%. Therefore, looking at the normal pulp at 60% concentration with the two chemicals, formic acid has moderate values of carbon and nitrogen compare to sodium hydroxide that showed high nitrogen content. Formic acid pulping is considered here because it can easily be recovered after pulping and the sludge used as manure.

Keywords: Kenaf; Sludge; Formic acid; Sodium hydroxide; Nitrogen; Carbon; Pulp

Introduction

The paper mill and pulp industry produce enormous quantities of paper and pulp products each year. It is the sixth largest polluting industry after the oil, cement, leather, textile, and steel industries, and many environmental contaminants are associated with the discharge of paper and pulp mill sludge [1]. Paper manufacturing is a complex industry involving multiple processes where different products are produced and large quantities of waste of primary, biological or de–inking origin are generated, waste water treatment sludge, primary sludge, and secondary sludge among them [2,3].

Pulp and paper mill production is growing every year worldwide. As a consequence, the amount of generated waste is increasing, along with increasing concern [4].

Sludge is the final solid waste recovered from the wastewater treatment process in pulp and paper mills. Sludge discharged from paper mills is divided into four categories:

a) primary sludge (PS), which comes from the production of virgin wood fiber;

b) de-inking paper sludge (DPS), which comes from the process of removing inks from recycled paper;

c) secondary sludge (SS; activated sludge), which comes from the secondary wastewater treatment system; and

d) combined primary and secondary sludge [5].

The sludge composition generally comprises organic matter, nitrogen and phosphorus, which can be used as macronutrient fertilizers in agriculture [6]. Nitrogen is important for growth of plant, its food processing and creation of chlorophyll. Carbon is the main part of soil organic matter and it aids soil to have water-retention capacity, form and fertility.

The sources of solids in a treatment plant vary according to the type of plant and its method of operation [7,8]. The amount and chemical composition, as well as the geotechnical properties of paper mill sludge depend on the paper grade being manufactured, specific fresh water consumption, the wastewater cleaning technique applied and the type of raw materials (e.g. wood, fillers). Thus, the chemical composition of paper mill sludge produced by one mill is often significantly different from that of another [9,10].

Many parameters have been introduced and tests developed to measure specific properties of sludge in relation to particular

methods of treatment. Conventional sludge characteristics can be grouped in physical, chemical and biological parameters. Physical parameters give general information on sludge processability and handlability. Chemical parameters are relevant to the presence of nutrients and toxic/dangerous compounds, so they become necessary in the case of utilization in agriculture. Biological parameters give information on microbial activity and organic matter/pathogens presence, thus allowing the safety of use to be evaluated [11].

Natural and anthropogenic environmental changes greatly influence the behaviour of metallic pollutants in sludge, as the form in which they occur may be change. Such external factors can include pH, temperature, the redox potential, organic matter decomposition, leaching, ion exchange processes and microbiological activity [12].

The pulp and paper industry consumes enormous amounts of water and natural resources and is also one of the largest effluents generators. Before the 1970s, wastewaters from the pulp and paper mills were normally discharged directly to the rivers or lakes, without any treatment or even a rough primary treatment. The high organic loads and solid content in the effluents affected the aquatic ecosystem in several ways such as localized damage to the benthic community, oxygen depletion in large areas and numerous changes in fish reproduction and physiology [13].

This study sets out to find out the effects of chemical, concentration and time interactions under laboratory conditions on the quality of sludge considering nitrogen and carbon from two chemical pulping processes.

Materials and Methods

Kenaf stem was pulped with formic acid and sodium hydroxide at 20, 60 and 90% concentrations for a cooking time of 1, 2 and 3h at 95°C under atmospheric pressure. At the end of each period, the sample was filtered with a fine mesh sieve of size 0.027mm to get effluent and the effluent was filtered with a filter paper to get the sludge used in the analyses. The sludge samples were then air-dried and screened to remove other contaminating materials. The screened raw materials were ground and placed in an airtight container to balance the moisture content and then used for chemical analysis. The tests were carried out in triplicate and each value is an average of three samples.

Determination of nitrogen content

Nitrogen content of the sample was determined by using Kjedahl technique [14]. The method involves digestion of samples, distillation of digests and titration of distillate.

$$Calculation: \%N = \frac{T \times 14.01 \times Molarity\ of\ HCl\ (0.1) \times 100 \times 10}{Weight\ of\ sample\ taken\ (2g) \times 1000}$$

Where T = (sample titre – blank titre)

Determination of carbon content

Colorimetric method of [15] was used to calculate the total carbon (Figure 1).

Figure 1: Processes used in getting sludge.

Results and Discussion

Table 1 presents the values of carbon and nitrogen from sludge obtained from pulping kenaf stem with 20% concentration of FA and NaOH. The sludge from formic acid pulping with 20% formic acid at three-hour intervals did not show any presence of carbon and nitrogen. Carbon and nitrogen were detected in the sludge from sodium hydroxide pulping at three-hour intervals in a decreasing concentration. The highest concentrations of carbon (0.17%) and nitrogen (1.67%) were obtained after 1-hour pulping while the lowest (0.07 & 0.63) were after two hours pulping. The increase of carbon content after three hours pulping may be as a result of esterification reaction as reported by [16].

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Table 1: Sludge from pulping with 20% FA and NaOH.

Time(Hrs)	Chemicals/ Parameters	Carbon (%)	Nitrogen (%)
1	FA	0	0
	NaOH	0.17	1.67
2	FA	0	0
	NaOH	0.07	0.63
3	FA	0	0
	NaOH	0.11	0.67

Nitrogen content of sludge from NaOH has close values and showed a little increase from 2 hours (0.63%) to three hours (0.67%). According to [17], the little increase in nitrogen may be due basic character of amine and hydrogen as triethylamine which took part in the reaction.

Table 2 shows the values of carbon and nitrogen in the sludge from pulping kenaf stem at 60% formic acid and sodium hydroxide. Carbon was detected throughout the 3-hour pulping with 60% formic acid, but the value did not follow a particular pattern because the highest value (8.7%) was obtained at 2 hour pulping followed by 3 hour (3.57%), while the lowest was at 1 hour (1.77%). With sodium hydroxide, carbon did not show a significance difference but only a minimal increase (0.03%) at 3-hour pulping. Nitrogen content in the sludge from formic acid is lower than that from sodium hydroxide which shows high percentage of nitrogen. The nitrogen values increased (18.1 -39.77) with time during sodium hydroxide pulping which may be due to the presence of triethylamine as reported by [17], while nitrogen in formic acid pulping sludge shows low values with minimal variations throughout the pulping period with the highest (0.29%) recorded after 2 hours pulping.

Table 2: Sludge from pulping with 60% FA and NaOH.

Time(Hrs)	Chemicals/ Parameters	Carbon(%)	Nitrogen(%)
1	FA	1.77	0.25
	NaOH	0.02	18.1
2	FA	8.7	0.29
	NaOH	0.02	29.4
3	FA	3.57	0.13
	NaOH	0.03	39.77

Table 3 reported the values of nitrogen and carbon contained in the sludge obtained during pulping of kenaf stem with 90% formic acid and sodium hydroxide at three-hour period. The values of carbon from both chemicals during the three-hour pulping were higher than those obtained from 20% and 60% pulping with sludge from formic acid pulping having the highest values (3.37-8.73%). The highest carbon (8.73%) was obtained after 3-hour pulping with formic acid while sodium hydroxide gave highest value (4.3%) after 1-hour pulping. Nitrogen content from both formic acid and sodium hydroxide pulping have close values (0.13 - 0.28) with formic acid showing a little higher value. This result has a little similarity with [18] that reported 0.9% for nitrogen Table 4.

Table 3: Sludge from pulping with 90% FA and NaOH.

Time(Hrs)	Chemicals/ Parameters	Carbon (%)	Nitrogen (%)
1	FA	5.2	0.18
	NaOH	4.3	0.14
2	FA	3.37	0.28
	NaOH	2.3	0.23
3	FA	8.73	0.22
	NaOH	1.23	0.13

*Each value is an average of three samples.

(Source: Author's lab work).

Table 4: Mean and SE of Sludge over the concentration, time and chemical factors for pulping.

Concentration	Time	Chemical	Nitrogen (%)	Carbon (%)
			Mean + SE	Mean + SE
20%	1 Hour	NaOH	1.67 + 1.01	0.17 + 0.06
		Formic Acid		
	2 Hours	NaOH	0.63 + 1.01	0.07 + 0.06
		Formic Acid		
	3 Hours	NaOH	0.67 + 1.01	0.11 + 0.06
		Formic Acid		
60%	1 Hour	NaOH		0.02 + 0.06
		Formic Acid	0.25 + 1.01	1.77 + 0.06
	2 Hours	NaOH	29.4 + 1.01	0.02 + 0.06
		Formic Acid	0.29 + 1.01	8.7 + 0.06
	3 Hours	NaOH	39.77 + 1.01	0.03 + 0.06
		Formic Acid	0.13 + 1.01	3.57 + 0.06
90%	1 Hour	NaOH	0.14 + 1.01	4.3 + 0.06
		Formic Acid	0.18 + 1.01	5.2 + 0.06
	2 Hours	NaOH	0.23 + 1.01	2.3 + 0.06
		Formic Acid	0.28 + 1.01	3.37 + 0.06
	3 Hours	NaOH	0.13 + 1.01	1.23 + 0.06
		Formic Acid	0.22 + 1.01	8.73 + 0.06

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The Table 5 & above shows Anova table that all the factors and interactions were significant ($p < 0.05$) except time.

Table 5: Mean and SE of Nitrogen (%) Sludge over the concentration, time and chemicals for pulping.

Concentration	Time	Chemical	Mean + SE
20%[a]	1 Hour	NaOH	1.67 + 1.01
		Formic Acid	
	2 Hours	NaOH	0.63 + 1.01
		Formic Acid	
	3 Hours	NaOH	0.67 + 1.01
		Formic Acid	
60%[b]	1 Hour	NaOH	
		Formic Acid	0.25 + 1.01
	2 Hours	NaOH	29.4 + 1.01[a]
		Formic Acid	0.29 + 1.01[b]
	3 Hours	NaOH	39.77 + 1.01[a]
		Formic Acid	0.13 + 1.01b
90%[a]	1 Hour	NaOH	0.14 + 1.01[a]
		Formic Acid	0.18 + 1.01[a]
	2 Hours	NaOH	0.23 + 1.01a
		Formic Acid	0.28 + 1.01[a]
	3 Hours	NaOH	0.13 + 1.01[a]
		Formic Acid	0.22 + 1.01[a]

Source	Sum of Squares	df	Mean Square	F	Sig.
Conc	2777.239	2	1388.619	456.523	0
Time	15.019	2	7.509	2.469	0.103
Chemical	1744.485	1	1744.485	573.518	0
conc * Time	67.507	4	16.877	5.548	0.002
Conc * chemical	1779.17	1	1779.17	584.921	0
Time * chemical	41.24	2	20.62	6.779	0.004
Conc * Time * chemical	41.87	1	41.87	13.765	0.001
Error	85.168	28	3.042		
Corrected Total	6261.417	41			

ANOVA Table

R Squared = .986 (Adjusted R Squared = .980).

The Anova table above shows that all the factors and interactions were significant ($p < 0.05$) except time.

Table 6 & above shows Anova table that both all the factors and interactions were significant ($p < 0.05$).

Table 6: Mean and SE of Carbon (%) Sludge over the concentration, time and chemicals for pulping.

Concentration	Time	Chemical	Mean + SE
20%[a]	1 Hour	NaOH	0.17 + 0.06
		Formic Acid	
	2 Hours	NaOH	0.07 + 0.06
		Formic Acid	
	3 Hours	NaOH	0.11 + 0.06
		Formic Acid	
60%[b]	1 Hour	NaOH	0.02 + 0.06[z]
		Formic Acid	1.77 + 0.06[b]
	2 Hours	NaOH	0.02 + 0.06[a]
		Formic Acid	8.7 + 0.06[b]
	3 Hours	NaOH	0.03 + 0.06[a]
		Formic Acid	3.57 + 0.06[b]
90%[c]	1 Hour	NaOH	4.3 + 0.06[a]
		Formic Acid	5.2 + 0.06[b]
	2 Hours	NaOH	2.3 + 0.06[a]
		Formic Acid	3.37 + 0.06[b]
	3 Hours	NaOH	1.23 + 0.06[a]
		Formic Acid	8.73 + 0.06[b]

Source	Sum of Squares	df	Mean Square	F	Sig.
Conc	39.047	2	19.523	1993.978	0
Timehr	6.27	2	3.135	320.186	0
Chem	137.358	1	137.358	14028.89	0
conc * Time	53.824	4	13.456	1374.305	0
conc * chem	5.078	1	5.078	518.584	0
Time * chem	30.617	2	15.308	1563.487	0
conc * Time * chem	50.736	2	25.368	2590.91	0
Error	0.294	30	0.01		
Corrected Total	381.458	44			

ANOVA Table

R Squared = .999 (Adjusted R Squared = .999).

Table above shows that both all the factors and interactions were significant ($p < 0.05$).

Conclusion

The sludge content from 20% pulping has nitrogen and carbon from sodium hydroxide, sludge from 60% pulping has carbon and nitrogen from both chemicals with more nitrogen while 90% pulping has more carbon. Considering the pulped stem, it showed under pulped, normal and over pulped with

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respect to 20%, 60% and 90%. Therefore, looking at the normal pulp at 60% concentration with the two chemicals, formic acid has moderate values of carbon and nitrogen compare to sodium hydroxide that showed high nitrogen content. Formic acid pulping is considered here because it can easily be recovered after pulping and the sludge used as manure. However, further research is recommended with more focus on other sludge parameters.

Acknowledgement

The support from the Federal Institute of Industrial Research, Oshodi, Lagos, Nigeria and University of Nigeria, Nsukka, during this work is well appreciated.

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