Asian Journal of Chemical Sciences

Volume 13, Issue 1, Page 46-55, 2023; Article no.AJOCS.97343
ISSN: 2456-7795

Effect of Different Types of Chemicals, Cooking Time and Chemical Concentration on the Quality of Sludge and Pulp Appearance

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

Article Information

DOI: 10.9734/AJOCS/2023/v13i1232

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/97343

Original Research Article

Received: 05/01/2023
Accepted: 07/03/2023
Published: 28/03/2023

ABSTRACT

Pulp and paper production process releases different types of wastes into the environment and pulp mill sludge is one of the major wastes from pulp and paper mill. The environmental awareness has led to more attention being given to the process of paper production and the raw materials and chemical usage. In this study, we analyzed the effect of chemical, concentration and cooking time on the characteristics of sludge and physical appearance of pulp obtained from pulping kenaf stem. The stem was pulped with 20%, 60% and 90% concentrations of formic acid and sodium hydroxide at 1 hour, 2 hours and 3 hours intervals to determine the parameters of their sludge as well as pulp

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appearance. The parameters considered include carbon, nitrogen, turbidity, phosphorus, ash and moisture. Sludge from sodium hydroxide pulping showed lowest value (0.02) of carbon with 60% concentration and highest (4.30) with 90% after 1hr cooking. Formic acid sludge that reported zero carbon with 20% concentration gave lowest value (1.77) at 60% after 1hr and highest value (8.73) after 3hrs with 90% concentration. Both formic acid and sodium hydroxide sludge recorded highest values (0.29 & 39.77) of nitrogen at 60% concentrations. The sludges of the two chemicals were most turbid at 90% and less at 60% concentrations with highest phosphorus values at the same concentrations. Both sludges reported lowest moisture contents at 60%. Sodium hydroxide showed highest ash at 20% after 1hr cooking while the highest value for formic acid was recorded at 90% after 3hrs cooking. The 60% formic acid at 2 hours gave a better pulp on physical examination and the sludge from the same process can also be reused.

Keywords: Sludge; formic acid; phosphorus; carbon; ash; sodium hydroxide; turbidity.

1. INTRODUCTION

"The management of wastes, in particular of industrial waste, in an economically and environmentally acceptable manner is one of the most critical issues facing modern industry, mainly due to the increased difficulties in properly locating disposal works and complying with even more stringent environmental quality requirements imposed by legislation. In addition, in recent years the need to achieve sustainable strategies has become of greater concern, also because some traditional disposal options, such as landfill, are progressively restricted, and in some cases banned, by legislations. Paper industry is a strategic industry in many countries but in the same time, the production of paper consumes high quantities of energy, chemicals and wood pulp" [1].

Pulping is a process in which the raw material is treated mechanically or chemically to remove lignin in order to facilitate cellulose and hemicellulose fiber separation and to improve the papermaking properties of fibers. Significant solid wastes from pulp and paper mills include bark, reject fibers, wastewater treatment plant sludge, scrubber sludge, lime mud, green liquor dregs, boiler and furnace ash.

"Sludge is produced during paper manufacturing and its content depends on the raw materials, bleaching chemicals, and the manufacturing process" [2]. "These sludges and other wastes from pulp and paper mills represent a major environmental cost for the mill operators. Over the last few years, the problem of efficient disposal and management of organic solid wastes has become more rigorous due to the rapid increase in population, intensive agriculture, and industrialization" [3].

"To maintain a cleaner environment, waste disposal has become an issue of vital importance. Attempts should be made to recycle, re–use and utilize waste. 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" [4,5].

The primary sludge is generated in the largest quantities. [6] and [7] stated that the production of 1 ton of paper generates about 30 kg of primary sludge.

"The complete process of production of both pulp and paper leads to the creation of multiple waste- and by-products, with around 87% of these materials being classified as Pulp and Paper Mill Sludge (PPMS), whilst the other 13% is accounted for by impurities, waste chemicals and gaseous emissions" [8].

"Primary and secondary sludges are sometimes combined and at operations where both pulp and paper mills are integrated at the same site sludge from both mills is sometimes combined" [9].

These combined sludges are generally referred to as mixed PPMS. Any of these sludges can be commonly referred to as PPMS. The PPMS generated at pulp and paper mills can be categorised into Primary and Secondary sludges. Primary sludge refers to the material generated by the initial clarification of raw paper/pulp mill effluent via flotation or sedimentation and primary sludge may undergo further treatment. This commonly involves biological decomposition through aerobic activated sludge systems, aeration and mixing to oxidise, or a successive combination of these or other methods to

Table 1. The reported physicochemical properties of primary, secondary and mixed PPMS [12] (and references therein; [13-19]

Parameter	Paper mill		Pulp mill		Mixed paper and pulp mill		Deinking sludge
	Primary	Secondary	Primary	Secondary	Primary	Secondary	
Dry matter (% w/w)			22.9–33.0	47.3	15–57	1–47	19–60
Ash content (% solids)			33.10	24.39	10–15	10–20	20
Nitrogen (ppm)	2390–5400	4680	38	2560	450–2800	11000-77000	7000–36000
Phosphorous (ppm	31400		167	370	100–600	2500–28000	2200–7400
Potassium (ppm)	3170				200–900	780–7000	300–3300
C :N ratio	138.92–289.47	86.21			111:1–943:1	8:1–50:1	13:1–31:1
pH	7.58		6.6–8.0	6.8–8.2	5.0–11.0	6.0–8.5	3.8–8.5
Organic matter (% w/w)	75.1	4 0.2	36–47.8	11–76.1			

generate a more processed waste material known as secondary sludge. As the economic costs of PPMS disposal are increasing, and with the growing desire to re-cycle and re-use resources within a more circular economy, land spreading continues to offer a suitable and potentially environmentally positive alternative to landfilling or incineration and should be encouraged where possible [10].

The physicochemical properties of PPMS produced at different mills can vary (Table 1) depending on the raw materials used, the treatment processes employed at the mill, and the nature of the end product (i.e. grade of product produced influences the level of treatment and nature of additives [11].

Previous studies have also highlighted that variations in sludge properties can arise even when comparing sludges from different mills that employ similar processes and/or produce similar products" [20]. "Therefore, individual characterisation of sludges is crucial if informed decisions are to be made about their suitability for land application and are currently already conducted in many countries" [21].

"During the production of paper and board, virgin or recovered timber and possibly a portion of recycled paper and board go through a series of processes at pulp mills to separate out the cellulose fibres and so produce a cellulose rich product known as pulp" [22].

"Although mechanical pulping is still used in some areas, most large-scale pulping operations now use a chemical pulping process based on heat and pressure plus either an alkali treatment (the most prevalent is known as the Kraft process) or an acidic treatment (known as the sulphite process)" [18,19].

"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" [20].

The quantity of waste sludge produced at paper and pulp mills using virgin materials only is relatively low, but this quantity increases (typically 2–4 fold; [21,22] where recycled paper is used in the production process. This increase in sludge production is due to the increased number of impurities.

This work investigated the qualities of pulping sludge with respect to time and chemical concentration interactions under laboratory conditions considering carbon, nitrogen, phosphorus, turbidity, ash, moisture and C: N ratio.

2. 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 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.

2.1 Determination of Nitrogen Content

The nitrogen content of the sample was determined by using Kjedahl technique [23]. The method involves digestion of samples, the distillation of digests, and titration of distillate.

Calculation: % N = T ×14.01 × Molarity of HCL (0.1) x 100 x10/Weight of sample taken (2g) x 1000

Where T = (sample titre – blank titre)

Determination of Carbon content: The colorimetric method of [24] was used to calculate the total carbon

Moisture (mol/wt) (%) = weight of wet sample – weight of dry sample/weight of wet sample x 100

Ash Content

$$\% \text{ Ash (wet basis)} = M_{ASH}/M_{WET} \times 100$$

M_{ASH} = Weight of ash

M_{WET} = Original weight

The phosphorus content is calculated according to following formular [25]:

$$W_P = C \times V / m \times mt$$

W_P = content of phosphorus in g/l

C = concentration of phosphorus measured in the extraction solution, mg/l

V = Volume of the volumetric flask, ml

m = mass of the test sample

mt = dry mass of the test sample

Turbidity

Turbidity is commonly measured in Nephelometric Turbidity Units (NTU) with turbidimeter which is an electronic hand-held meter.

C:N ratio is measured by dividing carbon by the nitrogen.

THREE WAY ANOVA was used for the analysis of the data.

Fig. 1. Sludge from formic acid

Fig. 2. Sludge from sodium hydroxide

Fig. 3. Pulp from Formic acid

3. RESULTS AND DISCUSSION

Table 2 presents the characteristics of sludge obtained during pulping of kenaf stem with 20%, 60%, and 90% concentrations of Sodium hydroxide and Formic acid. The parameters considered include carbon, nitrogen, phosphorus, turbidity, moisture, ash and C: N ratio. There was no sludge from pulping with 20% formic acid therefore, no values for carbon, nitrogen, phosphorus, turbidity, moisture and ash for the three-hour intervals as shown in Fig. 4. The parameters were detected in the sludge after pulping with 20% sodium hydroxide. Carbon and nitrogen content were highest (0.17 % & 1.67%) after 1hr cooking with sodium hydroxide. The value of turbidity which measures water clarity increased with time from 11.73NTU to 47NTU and this may be due to increased particles as the digestion progressed. Phosphorus content also increased with time from 1.24 – 5.56mg/100ml which can be attributed to release of phosphorus content of the raw material during the reaction process [26]. The mild increase in the value of carbon after 3hr cooking may be attributed to esterification as shown by [27]. Moisture reported highest value after 2hrs while ash was highest after 3hrs cooking.

The sludge obtained from cooking with 60% concentrations of formic acid and sodium hydroxide reported all the parameters with different variations as presented in Fig. 5. Carbon from sodium hydroxide sludge remained almost the same during the 3hr periods while carbon from formic acid sludge showed highest value (8.7) after 2hrs cooking. The nitrogen content of sludge from sodium hydroxide increased sharply from 18.1 to 39.77 during the 3hr cooking which may be due to the presence of triethylamine as reported by [28-30]. Nitrogen from formic acid sludge did not follow a particular pattern having its highest value after 2hr cooking. The turbidity content of sludges from both sodium hydroxide and formic acid increased with increase in cooking time as both reported highest values (31.43 & 32.32NTU) after 3hrs. The report showed that the value of phosphorus increased with time in sodium hydroxide sludge while formic acid sludge reported highest value (3.33mg/100ml) after 2hrs. The moisture content of sludge from sodium hydroxide sludge decreased with time while sludge from formic acid did not show any particular pattern with respect to moisture, having the lowest value after 2hrs. Both sludge from sodium hydroxide and formic acid pulping reported the highest values of ash after 2hrs cooking.

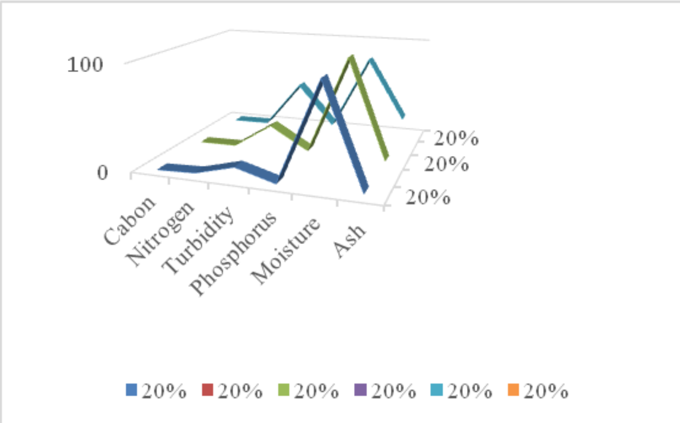

Fig. 4. 20% Concentrations of FA and NaOH

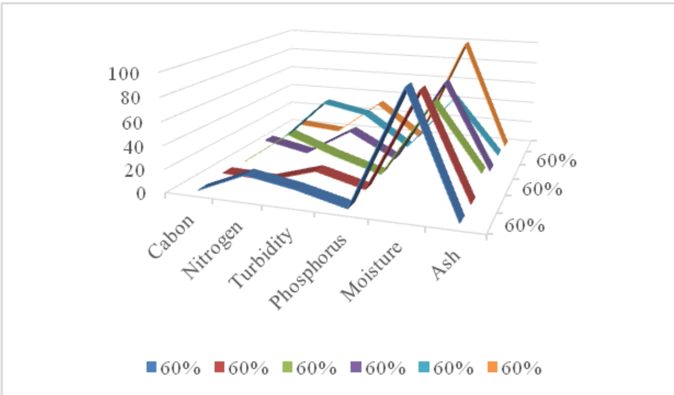

Fig. 5. 60% Concentrations of FA and NaOH

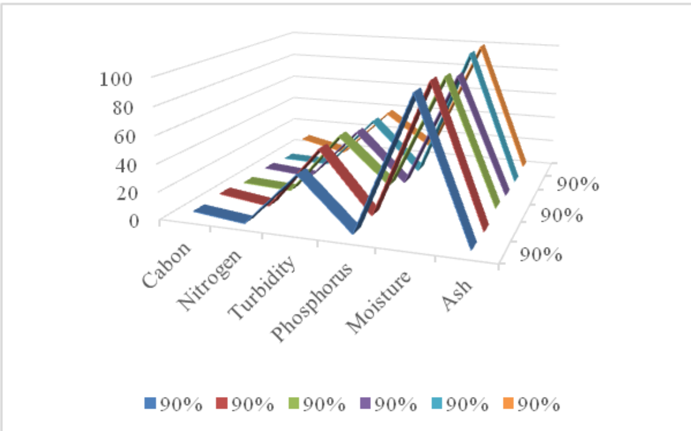

Fig. 6. 90% Concentrations of FA and NaOH

Table 2. Mean and SE of Sludge of Kenaf over the concentration, time and chemical factors for pulping

Concen-tration	Time	Chemical	Carbon (%) Mean + SE	Nitrogen (%) Mean + SE	C: N Ratio	Turbidity (NTU) Mean + SE	Phosphorus (mg/100ml) Mean + SE	Moisture (%) Mean + SE	Ash (%) Mean + SE
20%	1 Hour	NaOH FA	0.17+ 0.06	1.67 + 1.01	9:1	11.73 + 0.20	1.24 + 0.02	96.37 + 0.12	2.13 + 0.03
	2 Hours	NaOH FA	0.07 +0.06	0.63 + 1.01	9:1	24.93 + 0.35	3.24 + 0.02	98.2 + 0.06	1.27 + 0.03
	3 Hours	NaOH FA	0.11 + 0.06	0.67 + 1.01	6:1	47 + 0.15	5.56 + 0.03	80.27 + 0.03	19.03 + 0.03
60%	1 Hour	NaOH	0.02 + 0.06	18.1 + 1.02	26:1	11.1 + 1.92	0.76 + 0.45	99.47 + 0.17	0.45 + 0.04
		FA	1.77 + 0.09[a]	0.25 + 0.01[b]	7:1	13.02 + 0.11	2.1 + 0.05	88.66 + 0.01[b]	0.16 + 0.04
	2 Hours	NaOH	0.02 + 0	29.4 + 0.66	865:1	14.28 + 0.48	1.74 + 0.14	69.15 + 1.89	12.43 + 4.05
		FA	8.70 + 0.06[b]	0.29 + 0.00[b]	30:1	25.33 + 0.02[b]	3.33 +0.05	77.50 + 0.02[a]	1.47 + 0.04
	3 Hours	NaOH	0.03 + 0	39.77 + 2.98[b]	1325:1	31.43 + 0.27[a]	3.28 + 0.02[b]	53.70 + 0.06[a]	3.43 + 0.03[b]
		FA	3.57 + 0.09[a]	0.13 + 0.00[b]	27:1	32.32 + 0.10[b]	2.13 + 0.03[a]	98.93 + 0.00[b]	0.59 + 0.02[a]
90%	1 Hour	NaOH	4.30 + 0.06[b]	0.14 + 0.00[a]	30:1	39.07 + 0.02[a]	2.33 + 0.12[a]	99.54 + 0.00[a]	1.63 + 0.01[a]
		FA	5.2 + 0.06	0.18 + 1.01	7:1	46.42 + 0.23[b]	2.10 + 0.00[a]	99.89 + 0.01[b]	0.16 + 0.12[b]
	2 Hours	NaOH	2.30 + 0.06[a]	0.23 + 0.00[a]	10:1	46.21 + 0.01[b]	12.53 + 0.03[b]	95.65 + 0.01[b]	4.15 + 0.02[b]
		FA	3.37 + 0.03	0.28 + 1.01	12:1	40.04 + 0.05[a]	3.33 + 0.03[a]	89.49 + 0.01[a]	1.47 + 0.01[a]
	3 Hours	NaOH	1.23 + 0.12[a]	0.13 + 0.00[a]	9:1	39.85 + 0.01[b]	2.17 + 0.03[a]	99.77 + 0.03[b]	1.07 + 0.00[a]
		FA	8.73 + 0.03[b]	0.22 + 0.01[b]	39:1	38.07 + 0.01[a]	12.13 + 0.03[b]	99.64 + 0.02[a]	2.56 + 0.00[b]

NB: NaOH was significantly different from FA at 5% level of significance where superscripts differ

The report of sludge from 90% concentration of sodium hydroxide showed a decreasing value (4.30 to 1.23) of carbon from 1hr to 3hr cooking (Fig. 6). Carbon from formic acid sludge has its highest value (8.73) after 3hr cooking and lowest value (3.37) after 2hr cooking. Nitrogen content of sludge from both chemicals did not show significant change during the 3hr period but have their highest values (0.23 & 0.28) after 2hr cooking. The turbidity in sodium hydroxide did not follow a particular pattern having the highest value after 2hrs while decreased with time in formic acid. Phosphorus content of formic acid sludge increased with time while that in sodium hydroxide had the highest value after 2hrs. Moisture content of both sludges were high during the 3hr period. The value of ash in formic acid sludge increased with time while sodium hydroxide sludge had the highest ash after 2hrs.

The C:N ratio of organic residues is important because it influences the rate at which a residue decomposes and the amount of nitrogen recycled from the residue. The lowest C:N ratio (low carbon, high nitrogen) was reported during cooking with 20% concentration of chemicals followed by 90% while highest values of C: N ration (high carbon, low nitrogen) was obtained with 60% concentration.

The content of parameters of the sludge from this research showed lower values compared with the ones from craft and sulphite pulping in Table 1. However, to the best of my knowledge, no report has been found so far that studied the parameters of sludge from formic acid and sodium hydroxide pulping

4. CONCLUSION

There was no report of the parameters when cooked with 20% concentrations of formic acid due to low concentration of formic which was unable to break down the stem to produce sludge. The 20% concentration of sodium hydroxide reported high values in most of the parameters with under pulped stem. With 60% concentrations lower values of parameters were recorded except for carbon and nitrogen with properly pulped stem. Chemicals at 90% concentrations showed some high values of the parameters with over pulped stem. Considering the physical quality of the pulp and values of the parameters, 60% concentration of the chemicals at 2hr cooking are recommended. Looking at the two chemicals, formic acid is better because it can easily be recovered from the system and reused without causing harm to the environment while the sludge can be used for soil enrichment. More research is still needed in this area.

ACKNOWLEDGEMENT

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

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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