Research Article

Some Selected Physico-Chemical and Heavy Metal Properties of Palm Oil Mill Effluents

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Abstract

This study investigated the physico-chemical and heavy metals parameters found in palm oil milling effluents (POME). The POME samples were randomly collected aseptically from eight smallholders milling sites that generated POME out of the eleven visited at Elele, Rivers State, Nigeria. The physico-chemical and heavy metals parameters of the POME samples were determined using standard analytical procedures. The results of the physico-chemical analysis were obtained in the following range; pH (5.213 – 6.357), dissolved oxygen (DO) (2.567 – 4.127mg/l), biological oxygen demand (BOD) (254 – 1541mg/l), chemical oxygen demand (COD) (1231 – 2422 mg/l), phosphorus (P) (5.267 – 8.682 mg/l), potassium (K) (9.533 – 29.143mg/l), nitrogen (N) (7.550 – 20.653 mg/l) and oil and grease (41.667 – 98.167mg/l). Analysis of variance showed that there were significant differences ($P < 0.05$) in the pH, DO, COD, K, N, and oil and grease but no significant difference ($P > 0.05$) in BOD and phosphorous levels. The concentration of heavy metals in the POME samples were found in the following range; iron (1.8120 – 13.8127mg/l), Chromium (Cr) (0.6053 – 1.6683 mg/l), copper (Cu) (0.6143 – 1.6093mg/l), and cadmium (Cd) (0.0040 – 0.0231mg/l). Analysis of variance showed that there were significant differences ($P < 0.05$) in Cu, Fe and Cr level but no significant difference ($P > 0.05$) in Cd level. Due to the high BOD, COD and oil and grease levels in POME, it is preferable to recycle POME rather than discharge. This is the current practice in most of the oil mills at Elele.

Key words: heavy metal, palm oil milling effluents, physico-chemical parameters, smallholders.

1. INTRODUCTION

Nigeria is currently the fifth world's leading producer of palm oil (Nnorom, 2012). The palm oil industry is a major agro based enterprise in Nigeria especially in the southern part where palm oil trees are found both in the wild and plantations (Nwaugo et al., 2008). Palm oil processing is carried out using large quantities of water in mills where oil is extracted from the palm fruits. During the extraction process, about 50% of the water results in POME (palm oil mill effluents). It is estimated that for every 1 tonne of crude palm oil produced, 5.0-7.5 tonnes of water end up as POME (Ma, 1999; Ahmad *et al.,* 2003; Okwute and Isu, 2007; Wu et al., 2009). Raw POME consisting of complex vegetative matter is thick, brownish colloidal slurry of water, oil and solids including about 2% suspended solids originating mainly from cellulose fruit debris (Bek- Nielsen et al., 1999). These brownish and colloidal suspension of POME contain high concentration of organic matter, high amounts of total solids (40,500 mg/L), oil and grease (4,000 mg/L), chemical oxygen demand (COD) (50,000 mg/L) and biological oxygen demand (BOD) (25,000 mg/L) (Ma, 2000). The constituent of raw POME have been reported to be a colloidal suspension of 95-96% water, 0.6-0.7% oil and 4-5% total solids including 2-4% suspended solids and high concentration of organic nitrogen (Ma, 2000; Onyia et al., 2001; Ahmed et al., 2005). However it also contains appreciable amounts of plants nutrients such as nitrogen, potassium, magnesium and Calcium (Habib *et al.,* 1997; Muhrizal *et al.,* 2006). Also, toxic metals such as lead, can also be found in POME (Habib et al., 1997), but their concentrations are usually below sub-lethal levels (> 17.5µg/g) (James et al., 1996). Other heavy metals present in POME are cadmium, copper, chromium and iron. The raw or partially treated POME has an extremely high content of degradable organic matter, which is due in part to the presence of unrecovered palm oil (Ahmad et al., 2003).

POME, if untreated, contains high amounts of fatty acids, proteins, carbohydrates and other plant materials (Ngan et al., 1996; Chan and Chooi, 1982), which has the tendency of altering environmental parameters particularly BOD, DO, C/N ratio and COD level (Okwute and Isu, 2007). This highly polluting POME can cause pollution of waterways due to oxygen depletion, land use and other related effects (Sridhar and AdeOluwa, 2009; Awotoye et al., 2011; Okwute and Isu, 2007; Ahmad et al., 2003; Khalid and Wan Mustafa, 1992; Hartley, 1988). Discharged POME on aquatic ecosystem turns the water brown, smelly and slimy (Awotoye et al., 2011), which may kill fishes and other aquatic organisms and deny the human inhabitant of such region assess to good water for domestic uses (Ezemonye et al., 2007). Thus, while enjoying a most profitable commodity, palm oil, the adverse environmental impact from the palm oil industry cannot be ignored. Large and medium scale mills produce copious volumes of POME from the processing lines, (sterilizers, clarifying centrifuges and hydro cyclones). However, small-scale processors generate minimal effluents because majority of the wastewater are reused.

Apart from the sludge water itself which amounts to about 300 kg/tonne of bunches milled (or about 1.5 tonne/ tonne of palm oil), there are also about 175 kg of sterilizer condensate and between 40 and 140 kg of POME from the hydrocyclone or clay bath separators / tonne of bunches (Hartley, 1988). Since POME generally contain materials which are at concentrations above threshold values (Wu et al., 2009), they could be injurious to the environment. It becomes necessary that effluent water should be treated or purified prior to its discharge into the environment (Awotoye et al., 2011). In Nigeria, oil palm is processed mostly by smallholder processors, who typically recycle POME to recover more oil rather than discharging. Nevertheless, this study investigates the physico-chemical and heavy metals properties of small- scale palm oil processing effluents in Elele, Rivers State, Nigeria.

2. MATERIALS AND METHODS

2.1. Field Sampling

Eleven small-scale oil palm processing mills were visited for sample collection at Elele, River State Nigeria from 13th – 22nd April 2012. Out of the eleven mills visited, only eight generated POME. The POME generated was collected aseptically with sterile sampling containers. A total of twenty four POME samples, i.e. three replicate samples from each mill were collected for laboratory analysis. The process of POME generation from oil palm processing at these mills is basically the same and is presented in Fig. 1

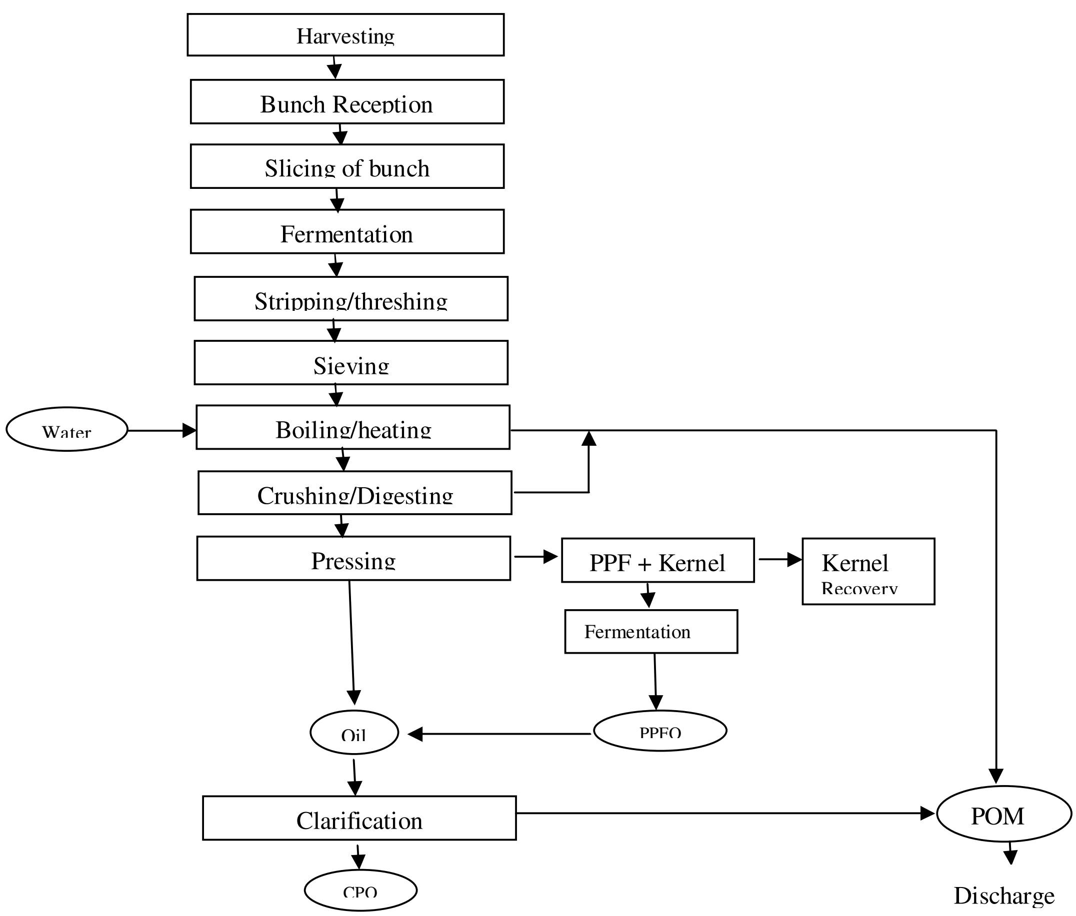

Fig 1: POME generation from oil palm processing by small-scale processors in Elele, River State, Nigeria. (POME = palm oil milling effluents; PPF = palm press fibre; PPFO = palm press fibre oil; CPO = crude palm oil)

2.2 Laboratory Analysis

2.2.1 Determination of physico-chemical parameters of POME

Determination of Ph: The pH was determined in–situ by the method described by Ademoroti (1996) using pH meter (HANNA HI 9820).

Determination dissolved oxygen (DO): The dissolved oxygen was determined in–situ using DO meter (Extech 407510A), using the scheme of Ademoroti (1996).

Determination of chemical oxygen demand (COD) by titration: COD was determined by titrimetric/dichromate oxidation method as described by Ademoroti (1996). The COD was calculated using the formula:

$$\text{COD (mg/l)} = \frac{(V_b - V_a) \times M \times 16000}{\text{Vol.of sample used}}$$

where;
V_b = ml of FAS used for blank
V_a = ml of FAS used for sample
M = Molarity of FAS

Determination of biochemical oxygen demand (BOD):

The biological oxygen demand (BOD) was determined using the method described by Ademoroti (1996) and APHA (1998). The 5-day BOD was computed from difference in the DO value of day 1 and day 5 multiplied by the dilution factor.

Nitrogen determination:

Total nitrogen was determined using Kjeldahl indophenols (colorimetric) method as described by Ademoroti (1996). A spectrophotometer (JENWAY 6505uv/vis) wavelength of 635nm was used and the value was obtained by extrapolation from standard calibration curve.

Determination of potassium (K):

Potassium was determined by flame photometer (Perkin-Elmer) as described by Ademoroti (1996). The spectrophotometer (JENWAY 6505uv/vis) was set at 768nm. By extrapolation the concentration of potassium is calculated using the formula:

$$\text{K (mg/l)} = \frac{\text{concentration reading on curve x D}}{\text{ml sample}}$$

Where; D = dilution factor

Determination of oil and grease: Oil and grease determination was carried out using gravimetric method after soxhlet extraction (APHA, 1998) and Ademoroti (1996). The total oil and grease is calculated using the formula:

$$\text{Oil and grease (mg/L) increase in weight of flask} = \frac{(\text{mg}) \times 1000}{\text{ml of sample}}$$

Determination of total phosphate by vanado-molybdo-phosphoric acid colorimetric method: Phosphate was determined by vanado-molybdo-phosphoric acid colorimetric method as described by Ademoroti (1996). Absorbance values were measured at 490nm using spectrophotometer (JENWAY 6505uv/vis). By extrapolation from the standard curve, the phosphate was calculated using the formula:

$$PO_4^{3-} \text{ (mg/l)} = \frac{(\text{mg}) \times 1000}{\text{ml of sample}}$$

Where; D = dilution factor

2.2.2 Determination of heavy metals (cadmium, copper, iron, chromium

The heavy metals were analyzed using Atomic Absorption Spectrophotometer (AAS) (APHA 301A) (model: 5100 PC, Perkin-Elmer, Boston, USA) (APHA, 1998).

2.3 Statistical Analysis

SPSS software version 17 (SPSS Inc, Chicago) was used to carry out the statistical analysis. A one-way analysis of variance was carried out at $\alpha = 0.05$, and Duncan's multiple range test was used to discern the source of the observed differences.

3 RESULTS AND DISCUSSION

The physico-chemical parameters of POME samples from small scale palm oil processing mills in Elele, Rivers state, Nigeria are presented in Table 1. The pH ranged from 5.213 – 6.357, being significantly different among the various mills ($P<0.05$). This result is close to the findings of other authors who reported the pH range of POME to be; 4 – 5 (Rupani et al*.,* 2010), 3.5 – 4.5 (Ma, 1999), 4.0 – 9.0 (Ma, 2000), 6.25 (O'Thong et al*.,* 2008), 5.34 (Awotoye et al., 2011), 4.7 (Ahmed et al., 2003). The value of pH recorded in this study is however lower i.e. more acidic than the IFC (2007) guideline value (pH 6 – 9) for effluent from vegetable oil processing. The low pH of the POME indicates that it is acidic (Hemming, 1977). The acidic nature of POME may have been influenced by the corrosion of iron used in processing (Jones, 1998), and organic acids found in fresh fruit. When the POME is discharged into the soil, it affects nutrient availability of the nearby plants (Okwute and Isu, 2007), because most plant grows and do better within a pH range of 6.5 – 7.5 (Hajek et al., 1990).

The oil and grease level in the effluent ranged from 41.667 – 98.167mg/l, though not significantly different ($P>0.05$) in most mills. Ma (2000) reported high concentration of oil and grease level in POME ranging from 4000 – 6000mg/l. The regulatory discharge limit of oil and grease in POME is 50mg/l (Ahmed et al., 2003) though IFC (2007) recommended a lower value of 10mg/l as limit of oil and grease from vegetable oil processing effluent.

The dissolved oxygen (DO) in the effluents of the mills were in the range of 2.567 – 4.127mg/l), being significantly different ($P<0.05$) among the mills, except for mills A, C and H that were not significantly different ($P>0.05$). Awotoye et al. (2011) reported that the dissolved oxygen of raw POME is 1.250mg/l. The relatively high DO reported in this study may be due to the high temperature and duration of bright sunlight, which influenced the percentage of soluble gases (O_2 & CO_2) in the effluent (Manjare et al., 2010). DO is an important parameter in POME quality assessment and reflects the physical and biological processes prevailing in the POME, it indicates the degree of pollution in water bodies (Murhekar, 2011).

The BOD obtained from the mill effluents were in the range of 254 – 1541mg/, being significantly different ($P<0.05$), except for mill E and F that are not significantly different ($P>0.05$). Prasertsan and Prasertsan (1996), Ma (2000), Wood et al. (1979) and Awotoye et al. (2011) reported BOD of POME to be 50000, 25000, 2080 and 123.675mg/l in their independent studies respectively. The BOD values recorded in this study was significantly lower than that of other authors, but higher than the IFC (2007) guideline value of 50mg/l for vegetable oil processing effluents. COD value obtained during the study was in the range of 1231 – 2422 mg/l, being significantly different among the various mills ($P<0.05$), apart from mill B, F, G and H that are not significantly different ($P>0.05$). Ma (2000), Wood et al. (1979) and Awotoye et al. (2011) presented the COD of POME as 50000, 10250 – 43,750, 5790 and 284.875mg/l in their various studies respectively. The value of COD recorded in this study was close to the results of other authors but several orders higher than the IFC (2007) guideline value of 250 mg/l for effluent from vegetable oil processing.

The potassium level in the mill effluents was in the range of 9.533 – 29.143mg/l, being significantly different ($P<0.05$), apart for mill B and G that are not significantly different ($P>0.05$). Wood *et al.* (1979) reported the potassium level in POME as 162mg/l. The phosphate concentration in the effluent was in the order of 5.267 – 8.682 mg/l, being significantly different ($P<0.05$) in the various mills, except for mill A, C, F and G that are not significantly different ($P>0.05$). This concentration is far lower than the results of Awotoye et al. (2011) that reported phosphate value of 165.65mg/l. The total nitrogen level in the effluent was in the range of 7.550 – 20.653 mg/l, though not significantly different in most mills. Other authors have reported higher values of 64 mg/l (Ma, 2000) and 750 mg/l (Wood et al., 1979). Total nitrogen is consistently found in high concentration in POME (Ho *et al.,* 1984, Habib et al., 1997; Muhrizal et al., 2006). IFC (2007) recommended guideline value for vegetable oil processing effluent is 10mg/l N.

Table1: Physico-chemical parameters of palm oil milling effluents

Mill	pH	DO, mg/l	COD, mg/l	BOD, mg/l	PO_4^{3-}, mg/l	K, mg/l	N, mg/l	Oil and grease, mg/l
A	5.860±0.087d	3.537±0.045bc	2312.667±19.722abc	312.333±65.743a	8.683±0.920bc	24.433±1.097de	13.303±0.582ab	85.893±8.073cd
B	5.613±0.030bcd	3.060±0.291ab	1498.333±29.018ab	254.333±16.597a	7.540±0.643abc	15.217±0.533abc	10.307±0.762a	98.167±16.623d
C	5.393±0.078ab	3.450±0.202bc	2422.000±48.138bc	288.667±19.411a	10.433±1.543c	20.340±2.844cd	13.950±3.931ab	58.517±3.494ab
D	5.630±0.117bcd	2.567±0.498a	1231.667±96.710a	513.333±14.474a	8.233±0.888abc	17.400±2.767bcd	14.483±2.468ab	45.773±1.709a
E	5.213±0.119a	4.127±0.240cd	3143.333±47.899c	1541.667±58.512b	7.757±1.614abc	29.143±4.234e	20.653±4.489b	41.667±3.676a
F	5.460±0.150abc	4.800±0.346d	1490.000±29.433ab	546.667±75.130a	6.467±0.546ab	11.633±1.822ab	10.600±1.097a	56.513±3.148ab
G	5.727±0.022cd	3.250±0.087abc	1838.333±42.065ab	378.333±2.603a	5.267±0.623a	16.767±0.219abc	7.550±0.535a	55.533±2.790ab
H	6.357±0.109e	3.850±0.189bc	1672.667±35.559ab	294.333±23.024a	8.000±0.400abc	9.533±1.378a	13.507±0.775ab	72.267±1.913bc

Each value is expressed as mean ± standard error (n = 3). Different letters in each column indicate significant differences at $P < 0.05$ according to the Duncan Statistics

Table 2: Heavy metal parameters of palm oil milling effluents

Mill	Cd	Cu	Fe	Cr
A	0.0184±0.0005b	1.6093±0.0433d	1.8120±0.0741a	1.6123±0.1503d
B	0.0231±0.0057b	1.2120±0.0933c	2.6666±0.0853b	1.6683±0.0582d
C	0.0199±0.0065b	N/D	4.4740±0.2178d	1.0727±0.0549c
D	0.0028±0.0006a	N/D	4.5767±0.2367d	N/D
E	0.0137±0.0030ab	N/D	13.8127±0.3835e	N/D
F	0.0040±0.0006a	0.0840±0.0028b	4.6873±0.0637d	0.8327±0.0326b
G	0.0068±0.0004a	0.0625±0.0027b	3.5580±0.0874c	0.6998±0.0251ab
H	0.0075±0.0030a	0.6143±0.0131a	3.5883±0.1167c	0.6053±0.0044a

(ND = not detected; Cd = cadmium; Cu = copper; Fe = iron; Cr = chromium)

Each value is expressed as mean ± standard error (n = 4). Different letters in each column indicate significant differences at $P < 0.05$ according to the Duncan Statistics

The heavy metal parameters of POME in the study area are presented in Table 2. The concentration of heavy metals in the POME samples were found in the following range; iron (1.8120 – 13.8127mg/l), Chromium (0.6053 – 1.6683mg/l), copper (0.6143 – 1.6093mg/l), and cadmium (0.0040 – 0.0231mg/l). The cadmium level is significantly not different in most mills. Wood et al. (1979) reported 0.001mg/l cadmium in POME. Traces of copper level was detected in few mills, while it was not detected in mill C, D and E. Wood et al. (1979) and Ma (2000) reported 0.09mg/l and 0.89mg/l copper level in POME respectively. The iron level is significantly different ($P<0.05$) among the different mills, aside from mill C, D and F that are not significantly different ($P>0.05$). Wood et al. (1979) and Ma (2000) reported the level of iron in POME as 11 and 46.6mg/l respectively. The chromium level is significantly different ($P<0.05$) among the mills, apart from mill D and E that it was not detected. Wood et al. (1979) found from their study that the level of chromium in POME is 0.01mg/l. The concentration range of the heavy metal indicates lack of uniform distribution of metal in POME; however same variations of this magnitude have also been reported by Obodo (2002). The variations observed were probably due to various factors such as trace metal contents of the crops, contamination from the engine during digestion process (Abulude et al., 2007). The degree of hardness of the water used in processing might affect the dissolution of heavy metals (Adeyeye and Ayejuyo, 2002).

4: CONCLUSION

Environmental issues are increasingly becoming important in economic activities. In view of this, the physico-chemical and heavy metal content of POME from eight palm oil mills in Elele, Rivers State, Nigeria was studied. The following parameters pH, DO, BOD, COD, P, K, N, oil and grease, Cd, Cu, Fe and Cr were analyzed using standard methods. Apart from Cu and Cr, the results were found to be above the guidelines recommended for vegetable oil processing effluents by International Finance Corporation and other international and local agencies in Nigeria. Due to the high concentrations of oil and grease, BOD and COD in the oil palm processing effluents, discharging it into the environment could cause pollution hence it is preferable to recycle rather than discharging.

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