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Potentiodynamic Corrosion Evaluation and Heavy-Metal Contamination in Wet Grinding Machine processed Pepper and Maize media

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Abstract

This work studied the corrosion of component parts of the wet-grinding machine (WGM), the workhorse of local food processing for Nigerian families, with a view to quantifying the surreptitious food contamination through corrosion of the machine's metallic components. Potentiodynamic method was utilized for the quick capture of corrosion rates before the onset of fermentation and its accompanying problematic pH swings. Corrosion of key machine components was studied inside WGM-processed pepper and maize. Heavy-metal contamination of the pepper/maize was investigated with Particle Induced X-Ray Emission (PIXE). Elemental composition of the machine's component parts was determined using Energy-Dispersive X-Ray Fluorescence (EDXRF). The maize medium was found to be the more corrosive, with corrosion rates that ranges from 1.4481 mm/year (grinding stone) to 6.1838 mm/year (hopper). For the pepper medium, corrosion rate ranges from 0.057699 mm/year (shaft) to 0.37587 mm/year (grinding stone). The low corrosion rate observed in pepper medium may be due to its high concentration of Vitamin C, which is well-known for inhibitory properties. The maize medium could not benefit from any inhibitory effect of starch due to the presence of fibres which occludes the surface, filtering away the starch. WGM-processed pepper/maize showed very high increases in concentration of heavy metals. Fe increased by 1100% and Mn by 64% in WGM-processed pepper; Fe increased by 295% and Ti by 185% in the WGM-processed maize. EDXRF analysis of the hopper, a non-wearing part, indicated the presence of Rb, also present in the WGM-processed pepper. This is an indication that the contaminants likely originated from corrosion action and not wear.

Keywords: contaminants, corrosion, heavy-metal, potentiodynamic and wet-grinding.

1.0 INTRODUCTION

African societies still engage in artisanal, downstream processing of food staples such as pepper and maize at neighborhood food processors and in local markets using the ubiquitous wet-grinding machine (WGM). Many enthusiastic arguments abound about the health merits of quickly processing and consuming pepper and maize, without a need for preservatives. However true these may be, there is an often-overlooked dark side to processing food at artisanal level with locally fabricated machines. The effect of corrosion on the constructional materials of the processing equipment may lead to silent food poisoning within an unsuspecting populace due to the infusion of the processed pepper and maize with heavy metals resulting from corrosion byproducts. This situation comes with a high degree of concern, given the that consumption of pepper and maize processed with WGM is a lifelong activity by many people in Africa; even minute levels of heavy metal infusion into the human body could have dire long-term cumulative consequences.

Corrosion is the deterioration of a material or its properties due to reaction with the environment (Budinski, 1983) and it is a problem in a lot of industries. It is of particular concern in the food processing (Jekayinfa *et al.,* 2005) and pharmaceutical industries where in addition to the loss of production time for maintenance and risk of equipment failure, there is the additional risk of product contamination by corrosion products (Omobowale, 2010). It is thus very important to select corrosion-resistant constructional material most appropriate for the expected type of corrosive environment occurring in the production plant (Nash, 2007).

The use of the local WGM is a popular way of processing agricultural staples such as pepper, maize, beans and guinea corn in African communities as it offers a convenient alternative to the traditional grinding stone. Fabrication of the WGM involves the joining of various types of metals by different welding processes. Ideally, the most suitable metal alloy for fabrication is stainless steel because of its high resistance to corrosion. Over the years in Nigeria and Africa in general, there has been an increase in the local fabrication of WGM using materials that are not stainless steel to reduce cost and make the machines more affordable. These machines have been mainly fabricated from mild steel and cast iron. However, most foods are acidic (McSwane *et al.,* 2003) and since steels are electrochemically active in acidic media (Reddy et al, 2016), these constructional materials are susceptible to corrosion in processed food environment (Miret *et al.,* 2003).

The corrosion of mild steel in processed food media has been studied by many workers (Rajagopal and Iwasaki, 1992). Corrosion of grinding plates in wet-grinding machine was studied my Andrews and Kwofie (2010), using ground maize as the corrosive environment. They not only discovered progressive increments in corrosion rate with time, but also increments in pH, over a 15-day period. Also, Ofoegbu et al (2011) studied the corrosion of mild steel (uncoated), galvanized steel and stainless steel (304L) over a period of 98 days in ground melon, cassava pulp, mashed palm fruit, tomato pulp, and black-eyed bean pulp. Their investigation showed that tomato pulp was the most corrosive media, expectedly, stainless steel exhibited highest corrosion resistance while, uncoated mild steel exhibited the least resistance.

However, a notable characteristic of the cited works is the use of the weight-loss method. While this method may be amenable to the study of corrosion in other media, it is problematic for agricultural staples such as pepper and maize due to action of microorganisms which causes fermentation and deterioration of the media over time. This leads to pH swings over the long time period required to realize the weight-loss method, a scenario unlikely to provide an accurate view of the corrosion occurring in the WGM. Furthermore, a quick understanding of the corrosiveness nature of the pepper and maize whilst they are still fresh is unrealizable using the weight-loss method.

This work reports the use of potentiodynamic corrosion study approach to investigate the effect of WGM on freshly prepared maize and pepper corrosive medium. Maize and pepper arguably are the most widely processed staples in Africa, particularly in Nigeria.

2.0 MATERIALS AND METHOD

The materials and methodology used in this work are presented under the following sub-sections.

2.1. Materials

2.1.1 WGM construction materials

A partially exploded view of a typical locally fabricated WGM is presented in Figure 1. Samples of constructional materials were cut from the main sections of the WGM namely: (i) Hopper (ii) Grinding plate (iii) Pipe (iv) Supporting plate (v) Shaft. The samples were each connected with electrical leads and mounted with slow-setting epoxy in custom-machined Teflon® cups. The mountings were done in such a manner as to expose geometrically well-define surface areas of the samples for exposure to the corrosion media.

2.1.2 Processing of pepper/maize

The two staples studied in this work are pepper and maize. These were selected because they are amongst the most widely locally processed staples using the WGM. The pepper and maize were bought fresh from the local market and were divided into groups A and B. Group A was hand-mashed and oven dried. Group B was ground using a WGM; a small quantity was oven-dried while the rest was used as media for the corrosion investigation.

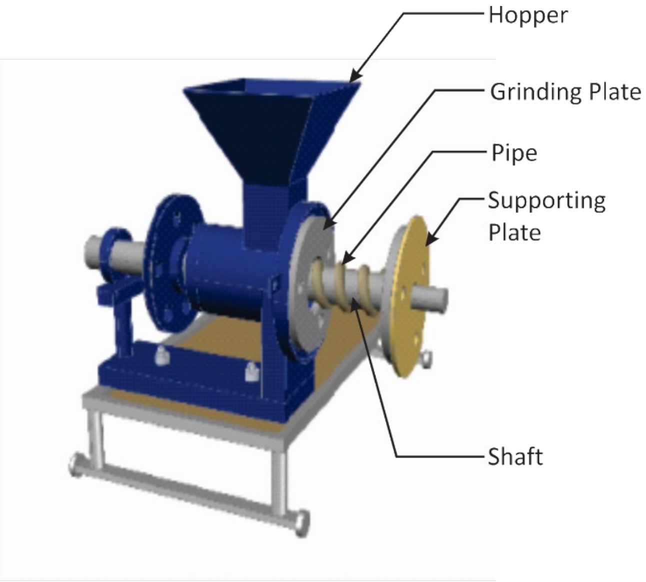

Figure 1: A partially exploded view of typical locally fabricated WGM showing key parts selected for analysis

2.2 Compositional Analysis

i. X-Ray Fluorescence (XRF): Compositional analysis of constructional material cut from each of the main sections of the WGM (Figure 1) was carried out using X-ray Fluorescence (XRF). This was carried out with an Energy Dispersive XRF using a Cu K_α radiation at Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Osun State.

ii. Particle Induced X-Ray Emission (PIXE): Compositional analysis was conducted on oven-dried samples from Group A and Group B using PIXE. The infusion of heavy metals into processed staple was investigated using Particle Induced X-ray Emission (PIXE). These were performed in a 1.7 MeV Pelletron Accelerator at CERD, Obafemi Awolowo University, Ile-Ife, Osun State.

2.3 Preparation of the Corrosion Cell and Potentiostatic Investigation

The corrosion cell setup includes each of the previously mounted WGM samples serving in turn as working electrodes, a copper wire reference electrode while amorphous graphite was the counter electrode. The potentiostat used was a PGSTAT 101 by AutoLab® available at Prototype Engineering Development Institute (PEDI), Ilesha Osun State. All potentiostatic investigations were done at a scan rate of 0.01 mV/s. The pH of the processed pepper and maize was monitored throughout the investigation. The experiment was carried out once for each of the WGM sample parts and the maize/pepper media.

3.0 RESULTS AND DISCUSSION

The results from the potentiostatic investigations, compositional analyses and inferences from them are presented in the following sections.

3.1 Potentiodynamic Investigation

The potentiodynamic polarization investigation revealed the corrosion rate of the various WGM components in the machine-ground pepper and maize. These are presented in Tables 1 and 2 respectively. The measured pH of the fresh machine-ground pepper was 5.9 while the pH of the maize was 5.1.

Table 1. Corrosion rates of WGM components in Pepper

Samples	Corrosion rate (mm/year)
Sample A (grinding stone)	0.37587
Sample B (pipe)	0.37143
Sample C (supporting plate)	0.24816
Sample D (hopper)	0.18082
Sample E (shaft)	0.057699

Table 2. Corrosion rates of WGM components in Maize

Samples	Corrosion rates (mm/year)
Sample A (grinding stone)	1.4481
Sample B (pipe)	3.4043
Sample C (supporting plate)	3.6589
Sample D (hopper)	6.1838
Sample E (shaft)	3.3491

From the tables, it could be seen that corrosion rate is much higher in maize which has the higher pH. This seem to indicate that the higher pH value of the maize medium favors increased corrosion rates of the WGM parts in maize medium as compared to the pepper medium. Parts from samples D and E that exhibited higher resistance to corrosion in pepper medium had much higher corrosion rates in the maize media.

The potentiodynamic polarization curve for the samples in pepper medium are presented in Figures 2 to 6, while plots for the samples in maize medium are presented in Figures 7 to 11. The measured pH of the pepper in this work is 5.9. The pH of Chili pepper generally ranges between 4.97 and 6.17. This is influenced by storage period and mode of storage (Samira et al. 2013). Pepper is rich in Vitamin C (Ascorbic acid). It contains about 143 mg per 100g (USDA, 2018); that is, 250% of Recommended Daily Intake (RDI). Vitamin C is an efficient corrosion inhibitor in steel (Fuchs-Godec *et al.,* 2015). It may thus be inferred that the relatively low rate of corrosion observed in Table 1 for samples exposed to pepper is because of the inhibitory properties of the significant proportion of Vitamin C in pepper.

In contrast the maize medium is more acidic, with the measured pH of 5.1. The value is within the reported value of 5.5 by Assohoun et al. (2013) and 4.9 reported by Onyeka et al. (2019) indicating its acidity is higher than that of the pepper medium. Maize contains much lower Vitamin C than pepper, only 17 % of the RDI (Streit, 2018). Hence the WGM samples are unlikely to benefit much from the inhibitory effect of Vitamin C inside the maize medium. Also, maize contains significant proportion of starch, and according to Nwanonenyi et al. (2016), starch is capable of imparting substantial inhibitory effect on mild steel. It must be noted that this observation was reached when millet starch which was processed to be fibre-free. The maize used in this work did not undergo any additional processing including sieving after grinding in the WGM. This was done so as to be closely representative of the actual condition of processed samples in the WGM. It thus contained significant fiber content. It is highly likely the constructional materials of the WGM would not benefit much from any inhibitory effect of the starch because of the presence of fibres which would compete for space on the sample surface, effectively filtering out the starch. This combination of effects, it is believed, resulted in the consequent significantly higher corrosion rate in the maize medium.

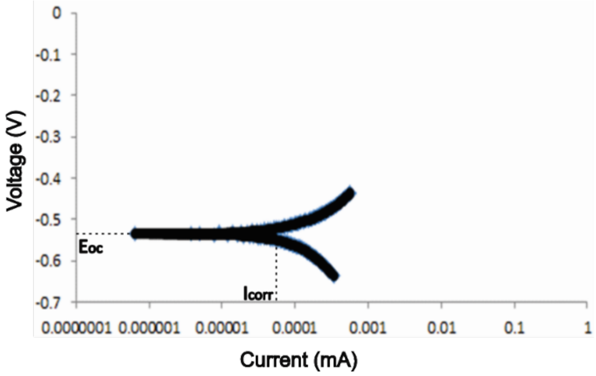

Figure 2: Sample A in pepper slurry

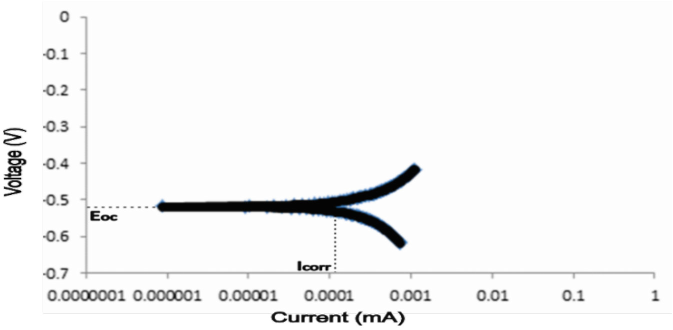

Figure 3: Sample B in pepper slurry

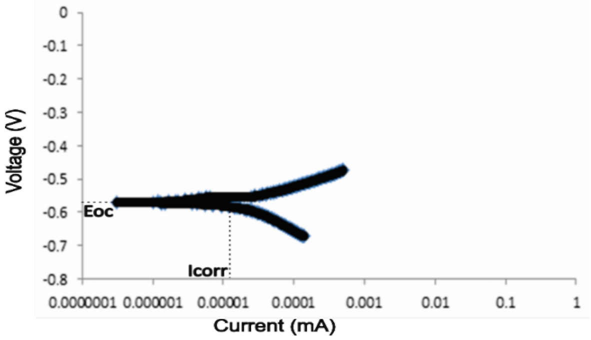

Figure 4: Sample C in pepper slurry

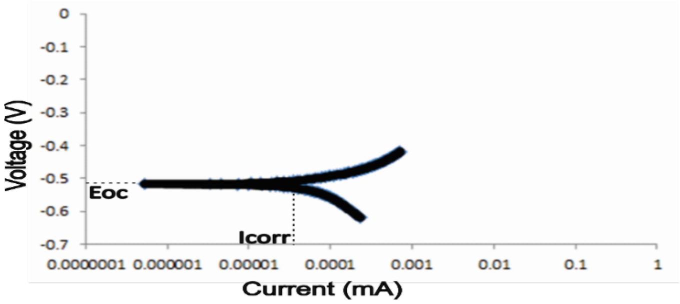

Figure 5: Sample D in pepper slurry

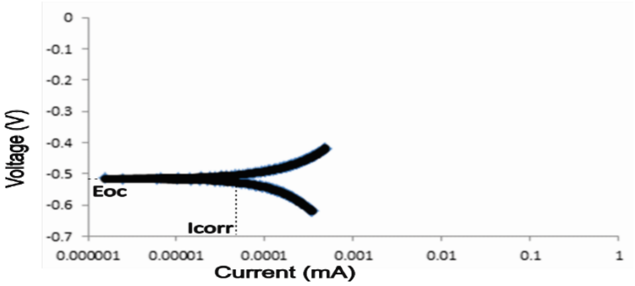

Figure 6: Sample E in pepper slurry

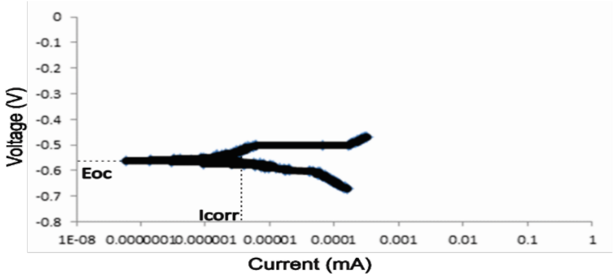

Figure 7: Sample A in maize Slurry

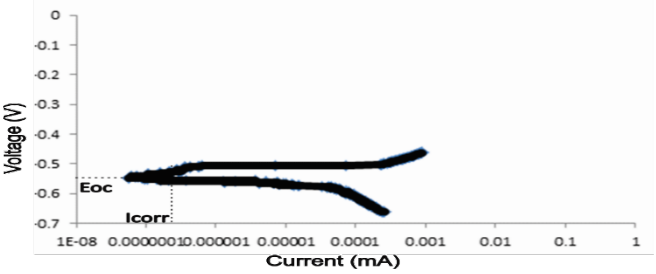

Figure 8: Sample B in maize Slurry

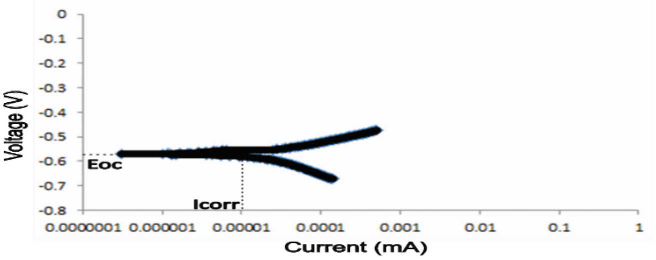

Figure 9: Sample C in Maize Slurry

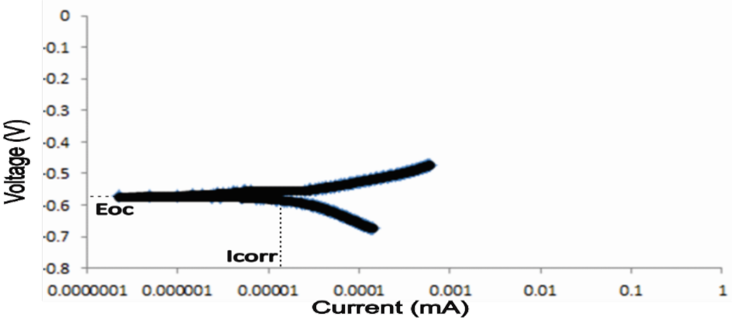

Figure 10: Sample D in Maize Slurry

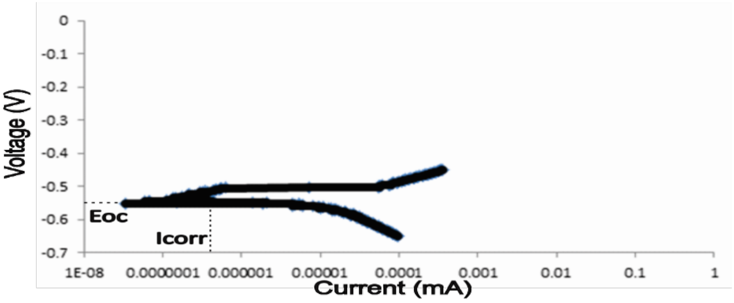

Figure 11: Sample E in Maize Slurry

3.2 PIXE Analysis of Farm-Fresh and WGM Processed Pepper/maize

The outcome of the PIXE analysis of the farm-fresh maize (Group A) and WGM processed maize (Group B) samples are presented in Tables 3 and 4 respectively. The PIXE analysis of the farm-fresh pepper (Group A) and WGM-processed pepper (Group B) are presented in Tables 5 and 6.

From Table 4, there is an infusion of the processed maize with Calcium, Manganese and Copper, which were not present in the farm-fresh maize. The processing in the WGM has caused a very significant reduction in the concentration of many of the elements in the farm-fresh maize. These reductions in % concentration is: Mg (93%), Al (49%), Si (24%), P (95%), S (87%), Cl (87%), K (97%), Cr (39%). These are very significant depletions in nutritional value. However, of greater concern are the increases in the % concentration of Zn (144%), Ti (185%), and Fe (295%) in the WGM processed maize.

From Table 6, the WGM-processed pepper medium has now been contaminated by two new elements, Nickel and Rubidium. These were not present in the fresh pepper. Also, the processing of the pepper in the WGM has led to very significant reductions in the concentrations of elements in the farm-fresh pepper. The percentage reductions in the % concentration of these elements is: Mg (18%), Al (5%), Ca (2 %), Ti (24%). These represent depletion in nutritional value. Also, it was noticed that there are significant percentage increments in the concentration of the other elements like Si (2%), P (0.21 %), S (13 %), Cl (22 %), K (8 %), Mn (64 %), Zn (0.24 %), Fe (1100 %) in pepper processed by the WGM.

Although the values in Tables 3 to 6 are in parts per million (ppm), the cumulative effects of the daily ingestion of these processed pepper/maize in the WGM over the course of a lifetime should be of concern. In the tables, the “LOD” is the Limit of Detection, which is the lowest concentration of the respective elements that can be reliably detected.

Table 3. PIXE Analysis of Farm-Fresh Maize

Element	Concentration (ppm)	LOD
Mg	1550.6	30.8
Al	1339.5	12.0
Si	4856.2	12.2
P	5125.2	20.4
S	1640.5	16.8
Cl	867.4	15.8
K	8412.6	15.1
Ti	23.6	4.7
Cr	23.4	2.9
Fe	318.2	4.3
Zn	23.6	2.0

Table 4. PIXE Analysis of WGM-processed Maize

Element	Concentration (ppm)	LOD
Mg	109.1	14.8
Al	680.7	4.4
Si	3701.8	4.6
P	267.6	10.1
S	208.4	7.8
Cl	112.8	6.0
K	244.1	4.1
Ca	451.7	2.3
Ti	67.3	790e-3
Cr	14.2	1.2
Mn	11.0	2.0
Fe	1259.7	3.3
Cu	45.3	2.5
Zn	57.5	2.7

Table 5. PIXE Analysis of Farm-Fresh Pepper

Symbol	Concentration (ppm)	LOD
Mg	2548.0	422.4
Al	3114.8	373.7
Si	1755.3	192.5
P	5270.3	131.4
S	3070.2	88.6
Cl	1938.8	76.9
K	29990.2	55.4
Ca	2319.0	182.7
Ti	42.9	13.7
Mn	15.7	6.7
Fe	186.1	6.0
Zn	41.6	8.4

Table 6. PIXE Analysis of WGM-processed Pepper

Symbol	Concentration	LOD
Mg	2090.6	497.6
Al	2962.1	403.6
Si	1797.8	194.4
P	5281.5	143.8
S	3455.6	98.9
Cl	2368.9	79.7
K	32383.8	33.8
Ca	2274.0	199.4
Ti	32.8	16.3
Mn	25.7	9.7
Fe	2233.4	4.7
Ni	12.5	2.3
Zn	41.7	4.3
Rb	105.1	55.7

3.3 XRF Analysis of the selected parts of the WGM

Compositional analysis carried out on the grinding stone and hopper of the WGM is presented in Tables 7 and 8. The major limitation of Energy Dispersive X-ray Fluorescence is its difficulty in detecting light elements such as Aluminum in the periodic table. Whilst the elemental range for EDXRF goes from sodium to uranium (Brouwer, 2010), light elements (atomic number < 16) are difficult to identify (Declercq *et al.,* 2019). Fluorescence from lighter elements has low energy (<3 keV) and will mostly be reabsorbed by the sample or blocked by the air between the sample and the detector (Portable Spectral Services, 2019). The fluorescence from elements must reach the detector in such an abundance that enables it to be distinguished from the background noise and generate a meaningful response. Hence this group of elements is absent in the table. From Table 8, the presence of Mn, Cu, and Mo can be seen. These are often added to cast irons to improve its Austenability. The presence Ni-Cu for instance is capable of increasing hardness substantially without causing a loss in its ductility while Mo-Ni-Cu will increase hardness even more with only some loss of ductility (Konca *et al.,* 2017).

Most of these elements have found their way into the processed samples in significant quantities. It is quite possible that the presence of some of the elements in the processed samples might have been as a result of wear action or corrosion. In particular, the shaft (auger) in the WGM is subjected to wear and tear when in use in respect to usage years of the machine (Shakiru and Babasola, 2014). However, it must be noted an element like Rubidium is from the hopper (see Table 7) which normally should experience little or no wear due to the absence of the action of contacting metal surface on it. The only way it seems it may have found its way into the processed samples may have been through corrosion.

Table 7. XRF analysis of mild steel (hopper)

Elements	Concentration (ppm)
K	31250
Ca	3794
Ti	7530
Mn	19745
Fe	415683
V	388
Ni	700
Cu	1354
Ge	379
Br	200
Rb	1032

Table 8. XRF analysis of cast iron (grinding plate)

Elements	Concentration (ppm)
K	3973
Ca	36520
Ti	1023
Mn	66412
Fe	370976
V	299
Ni	281
Cu	283
Ge	144
Br	117
Rb	160
Mo	36
Zr	115

4.0 CONCLUSION

This work has revealed that significant corrosion of all the key components of the WGM occurs in both processed pepper and maize. While corrosion was relatively low in processed pepper due to the inhibitory effects of its high content of Vitamin C, it was much more severe in processed maize. It was inferred that the fibre occlusion of the sample surface in the un-sieved maize medium caused the filtering out the starch, effectively denying the samples of the inhibitory effect of starch. Furthermore, it was discovered that there is a substantial loss of nutritional content in the pepper and maize after processing. This is of concern as it undermines the health benefits derivable from them.

PIXE analysis of both fresh and WGM-processed pepper and maize confirmed an alarming level of heavy metal contamination. For instance, Fe experienced over 1000% increase in concentration in WGM-processed maize. The health consequences of a daily intake of these high concentrations of heavy metals contaminants over a lifetime should be a source of concern.

While some of the contamination may be due to wear, it is believed that given the higher rate of corrosion and the presence of contaminants from non-wearing parts of the WGM, most of the contamination is likely due to corrosion. This work should spur policymakers into formulating regulations on WGM material selection and design details that will safeguard the health of the public.

REFERENCES

Andrews, A. and Kwofie, S. (2010). Corrosion of cast iron mill plates in wet grinding, Leonardo Electronic Journal of Practices and Technologies,17, 97 – 108.

Assohoun, M. C. N., Djeni, T. N., Koussémon-Camara, M., and Brou, K. (2013). Effect of fermentation process on nutritional composition and aflatoxins concentration of doklu, a fermented maize-based food. Food and Nutrition Sciences, 4, 1120-1127.

Brouwer P. (2010). Theory of XRF: Getting acquainted with the principles. PANaytical B. V. Almelo, Netherlands, 62 pages.

Budinski, K. G. (1983) Engineering materials, properties and selection. Reston Publishing Company Inc. A Prentice-Hall Company.

Declercq Y., Delbecque N., De Grave J., De Smedt P., Finke P., Mouazen A. M., Nawar S., Vandenberghe D., Van Meirvenne M. and Verdoodt A. (2019). A Comprehensive Study of Three Different Portable XRF Scanners to Assess the Soil Geochemistry of An Extensive Sample Dataset. Remote Sens. 2019, 11, 2490; doi:10.3390/rs11212490

Fuchs-Godec, R., Pavlovic, M. G., and Tomic, M. V. (2015). The inhibitive effect of vitamin C on the corrosive performance of steel in HCL solution – Part II. International Journal of Electrochemical Science, 10, 10502-10512.

Jekayinfa, S. O., Waheed, M. A., Adebiyi, K. A. and Adebiyi, F. T. (2005) Effect of Cassava Fluid on corrosion Perfomance of Mild Steel. Anti-Corrosion Methods and Materials. 52(5), 286 – 292.

Konca, E., Tur, K. and Koç, E. (2017). Effects of alloying elements (Mo, Ni, and Cu) on the austemperability of GGG-60 ductile cast iron. Metals, 7, 320; doi:10.3390/met7080320

McSwane D., McSwane D. Z., Rue N. R., Linton R. (2003). Essentials of food safety and sanitation. Prentice Hall.

Miret, S., Simpson, R. J. and Mckie, A. T. (2003). Physiology and molecular biology of dietary iron absorption, Annual Review of Nutrition, 23, 283 – 301.

Nash, R. (2007) Battling corrosion in the food processing industry, pump & systems, foodprocessing section, **Source:** www.pump-zone.com, **Date accessed:** July 27, 2011.

Nwanonenyi, S. C., Madufor, I. C., Uzoma P. C., and Chukwujike, I. C. (2016). Corrosion inhibition of mild steel in sulphuric acid environment using millet starch and potassium iodide. International research journal of pure and applied chemistry.

Ofoegbu, S. U., Ofoegbu, P. U., Neife, S. I., and Okorie, B. A. (2011). Corrosion behaviour of steels in Nigerian food processing environments, Journal of Applied Science & Environmental Management, 15(1),135-139.

Omobowale, M. O. (2010). Problems facing local manufacturers in the Nigerian agro-allied machine fabrication industry, African Technology Development Forum (ATDF). 7(3/4), 3 -8.

Portable Spectral Services (2019). Detecting light elements with portable XRF.Source: https://www.portaspecs.com/detecting-light-elements-with-portable-xrf/ . Date Accessed: 16th January 2020

Rajagopal, V., and Iwasaki, I. (1992). Corrosion Properties of Cast Iron Ball Materials in Wet Grinding, Corrosion, 48(2), 124 – 132.

Reddy, C. M., Sanketi, B. D. and Kumar S. N. (2016). Corrosion inhibition of mild steel by Capsicum annuum fruit paste, Perspectives in Science, 8, 603—605.

Samira, A., Woldetsadik, K., and Workneh, T. S. (2013). Postharvest quality and shelf life of some hot pepper varieties. Journal of Food Science Technology, 50(5):842–855.

Shakiru, S. O., and Babasola, O. D. (2014). Assessment of dry and wet milling using fabricated burr mill. Food Science and Quality Management., 31, 1 – 11.

Streit, L. (2018). Is corn good for you? Nutritional facts and more. **Source:** https://www.healthline.com/nutrition/is-corn-good-for-you **Date accessed:** September 8th, 2019.

United States Department of Agriculture (USDA) (2018). National nutritional database for standard reference – Basic Report 11819, Peppers, hot chilli, red, raw. **Source:** https://ndb.nal.usda.gov/ndb/foods/show/3436?format=Abridged&reportfmt=pdf&pdfQvs=%7BQv%3D1%7D7&ds=Standard+Reference. **Date accessed:** September 8th, 2019.