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ASSESSMENT OF LEACHABLE TOXIC METALS IN GLAZED CERAMIC DINNERWARE'S IN IBADAN, SOUTHWESTERN NIGERIA

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Abstract
This study investigates the presence and leaching potential of some toxic metals (Pb, Ni, Cd and Cr) from ceramic dinnerware's commonly found in Nigerian households. A total of 104 ceramic cups-32, bowls-36 and plates-36 of different colours where subjected to metal leaching using 4% acetic, 1% citric, 1% lactic acids and hot water across a period of 1 to 5days. Average leached Pb from cups, bowls and plates range between 0.026±0.01 to 0.047±0.04 mg/L while leached Ni range between 0.033±0.03 to 0.056±0.02mg/L. Cadmium and chromium levels were relatively insignificant and undetected. Concentrations of Pb and Ni from the ceramic wares were related to colour and leaching time. Blue, brown and green ceramics were found to potentially leach more metals and concentration increase with increasing leaching time. Average Pb levels in wares for the four leaching solutions were within Food and Drug Administration action level of 0.5-3.0mg/L, but slightly exceeding Standard Organization of Nigeria's permissible limit of 0.01mg/L. In conclusion, the ceramic wares pose little or no potential health risk. However, constant monitoring is essential to avert associated health risk arising from prolong contact of consumables (foods and drinks) with glazed ceramic wares.

Keywords: Acetic; acid; dinnerware; heavy metals; leaching.

Introduction
Cases of toxic metal poisoning is a subject of global concern which is threatening both man and its environment. Frequent and continuous usage of glazed ceramic wares in dispensing foods constitute one such concern and may pose serious health risk (Gonzalez & Craigmill, 1996; Sheets, 1998: Omolaoye, Uzairu, & Gimba, 2010; Samlofo, 2017). Ceramics are materials made from naturally occurring clay or earth prepared by the action of heat and subsequent cooling (Reed, 1995). Glazing of ceramics often enhances its appearance but has recently proved toxic due to presence of toxic heavy metals (Beale, Craigmill, & Wetzlich, 1991; Sheets, 1996: Aderemi, Adenuga, Oyekunle, & Ogunfowokan, 2017). The use of metal based oxides for glazing ceramics, primarily lead and cadmium has come under scrutiny in relation to negative health and environmental impacts. The amounts of heavy metals which migrate from ceramics to food is dependent not only on quality of glaze but also more particularly on temperature at which the ceramic was fired, type of food and duration of contact. Hence, heating ceramic utensils increases leaching, as does acidic foods or drinks and prolong usage. Many ceramics and other food-ware products may contain lead and other toxic metals if improperly manufactured. Prolonged or

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repeated food contact can result in chronic poisoning. Lead has been a common component in glazing materials for ceramic dishes, bowls, pitchers, plates and other earthenware since the beginnings of civilization (Rothweiler, Cabb, & Gerstenberger, 2007). Recent studies by Carmen, Clara, Samuel, José, Eduardo, José, María, & Juan, (2011) and Samlofo (2017) have shown that handcrafted glass-clay containers are a health risk because they can be contaminated by heavy metals, which can be transferred to food, thus reaching the human body to potentially cause illness.

In Nigeria glazed ceramics are common daily household items used for serving different foods and drinks at varying temperatures (hot or cold) and moisture content. Large amount of this cheap and popular dinner wares are locally produced and most imported without appropriate regulations and quality assurance monitoring. Coloured metal pigments are often used for these glaze production to enhance appearance. As such, exposure to heavy metal poising cannot be over-rule. Glazed ceramic ware is traditionally and widely used in Ibadan for serving hot/cold foods and drinks. Most of the drinks are known to have very low pH values such as fruit juice; therefore, leaching of heavy metals may be of concern. Presently, there's limited research data that extensively addresses the release of toxic metals from dinnerware surfaces and possible effects of such on human health and environment. Similarly, there's need to maintain internationally accepted methods of testing these wares for toxic metals release, and define permissible limits for leaching of the metals. In view of these, this study assesses levels of leachable toxic metals in glazed ceramic wares in Ibadan, southwestern Nigeria, and evaluate effect of colored glazed ceramics on metal leachability using standard ASTM C738-81 and BS 6748 combine methods. It should be noted that toxic metal levels specified in this study are not meant to be regarded as maximum levels of the metals to which exposure can be considered safe.

Material and Methods

Sampling and Preparation

A total of 104 glazed ceramic wares samples (cups-32, bowls-36 and plates-36) were collected from local markets within the Ibadan metropolis, southwestern Nigeria with sampling coordinates between N (07º 23′ 19.5″), E (003º 52′ 21.4″) and N (07º 25′ 18.7″), E (003º 51′ 87″). The capacity of wares ranged between 350 to 800mL. Inner colour shades collected were cups-blue, brown, green, cream and black; bowls- blue, brown, green, cream and black; plates-blue, brown, green and red. Samples were properly kept in cool, clean and dry room, free from dust and metallic contaminants. Samples were kept clean and free from grease or other matter likely to affect the test. Standard test solutions of 4% v/v acetic acid, 1% w/v citric acid, 1% v/v lactic acid and hot water were prepared for the leaching experiment. This simulates various acidic foods, drinks and temperature variation often associated with use of ceramic wares. The pH and temperature values of test solutions are presented in Table 1.

Leaching Experiment

The method used for leaching of toxic metals from ceramic wares was a modified combination of British Standard procedure, BS 6748 (BSI, 1986) and that of American Society for Testing Materials ASTM C738-81 (ASTM, 1982). The ceramic wares to be tested were cleaned and dried. A 100mL portion of 4% acetic acid was first transferred into each cleaned vessels, covered with

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aluminum foil and set aside for 24hrs (1 day) at ambient temperature (25-28^0 C). After 24hrs, the content was made to mark in a 100mL standard flask and transferred to polyethylene bottles for metal analysis. This process was repeated for 2, 3, 4 and 5 days. Leaching test was also carried out for 1% citric acid, 1% lactic acid and hot water following the same procedure for acetic acid. The leaching experiment was carried out in duplicates with precision of about 5%. Concentrations of Pb, Ni, Cr and Cd were determined in the leachates using flame atomic absorption spectrophotometer Varian SpectrAA 600. Commercial BDH stock standards were used for instrument calibration. Reagent blanks were prepared and analyzed along each leaching solution. Analar grade reagents were used for all preparations

Statistical Data Analysis

Data collected were subjected to descriptive statistical analysis by determining the average of values. Test of significance were conducted on mean concentrations of Pb, Ni, Cd, Cr in sample vessel for different colors and test solutions. Comparison and trend analysis was done by multiple line graphs and statistical correlation was performed to check significant relationships using Pearson's correlation coefficient.

Table 1: pH and temperature values for test solutions

Extractant	**pH value**	**Temperature ^{0}C**
Acetic acid 4% (v/v)	2.98±0.3	25.0±2
Citric acid 1% (w/v)	2.98±0.2	25.0±2
Lactic acid 1% (v/v)	3.41±0.3	25.0±2
Hot water	6.90±0.1	100±2

Result and Discussion

Effect of leaching solutions on leaching potentials of metals

As shown in Table 1, all extractions were carried out in acidic medium with a pH range of 2.98±0.2 to 3.41±0.3, with exception of hot water which had pH of 6.90±0.1, though at a higher temperature. This agrees with the modified combination of ASTM C738-81 (ASTM, 1982) and that of BS 6748 (BSA, 1986). Out of 104 sampled ceramic dinnerware's used for extraction (cups-32, bowls-36and plates-36), only about 6% had Pb and Ni and over 90% had Cd and Cr levels below detection limits. Table 2 shows average concentration of metals from leaching experiment. Generally, Pb and Ni were mostly leached from the ceramic wares in order of Ni>Pb. Leachability of Cd and Cr from ceramic wares were generally below detection limit. These data are an indication of possible usage of Ni and Pb based glazed during ceramic making and firing. Acetic and citric acids happen to leached more concentration of Pb and Ni from cup, bowl and plates comparatively to lactic acid and hot water. These trends could be related to the leaching solution pH values. Lower pH tends to enhances leaching of metals against higher pH. Lactic acid and hot water represent conditions mostly applicable for domestic usage; therefore, levels of Pb and Ni leached from the ceramics may be an indication of health concern. Leached Pb and Ni from the four leaching solution were about the same for the three sample ceramic wares (cup, bowl and plates) suggesting that raw materials used could play a significant role in leached metal levels.

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From Figures 1 and 2, leaching potential of Pb and Ni from ceramic cups, bowls and plates were found to progressively increase with time for all four leaching solutions. A strong indication that longer contact time of any ceramic ware with acidic solutions or foods, even hot water will significantly affect and influence the degree of leachable toxic metals. Statistical t-testing (*p=0.05*) show no significant differences between Pb and Ni concentrations in cups, bowls and plates for each of the four leaching solutions. A strong positive correlation was similarly observed between Pb and Ni in cups (0.997), bowls (0.794) and plates (0.861). Average Pb levels (0.027±0.01 to 0.047±0.04mg/L) in cups, bowls and plates from this study arising from the four leaching solutions was much lower than Food and Drug Administration limits of 0.5-3.0mg/L (Tisler, 1978)), but higher than Standards Organization of Nigeria 0.01mg/L recommended level (SON, 2007). Lead has also been previous found to leach from glazes ceramic dinnerware's in concentrations high enough to constitute a health hazard (Mohammed et al., 1995; Sheets, 1997; Aderemi, et. al., 2017). Colourants used in glaze contain the same kind of pigments used in ordinary oil and water colours; hence they contain basic compounds of lead, nickel and chromium. Some studies have shown a clear correlation between the uses of lead-glazed ceramic ware and elevated blood lead levels (Belgiad, 2003). Glazed pottery, especially craft and home-made kind which has not been kilned at a significantly high temperature or has been made with poorly formulated frits is capable of releasing toxic metals into foods and drinks at level higher than permissible limits (WHO, 1993). Some ceramic ware raw materials can also contain significant levels of metals which could affect quality of made dinner wares. One such study has reported levels of 0.15 µg/g and 0.13 µg/g Cr as leachates in rice cooked in new and old clay pots respectively in Nigeria (Ojezele, Ojezele, & Adeosun, 2016), while another study reported as high as 1031 µg/g of Cr in some geophagy clay deposits in Nigeria (Wood & Hackman-Duncan 2014; Samlafo 2017).

Table 2: Average concentration (mg/L) of metals from leaching experiment

Type	**Washing solution**	**Pb**	**Ni**	**Cd**	**Cr**
Cup	Acetic acid	0.047±0.04	0.044±0.03	0.006±0.01	0.00*
	Citric acid	0.041±0.03	0.041±0.03	0.004±0.01	0.00
	Lactic acid	0.031±0.02	0.036±0.03	0.005±0.01	0.00
	Hot water	0.027±0.02	0.033±0.03	0.002±0.003	0.00
Bowl	Acetic acid	0.037±0.01	0.055±0.02	0.0002±0.0004	0.00
	Citric acid	0.034±0.01	0.050±0.02	0.001±0.002	0.00
	Lactic acid	0.026±0.01	0.047±0.02	0.00	0.00
	Hot water	0.029±0.01	0.042±0.02	0.00	0.00
Plate	Acetic acid	0.033±0.01	0.056±0.02	0.00	0.00
	Citric acid	0.029±0.01	0.053±0.02	0.00	0.00
	Lactic acid	0.028±0.01	0.041±0.02	0.00	0.00
	Hot water	0.027±0.01	0.038±0.02	0.00	0.00

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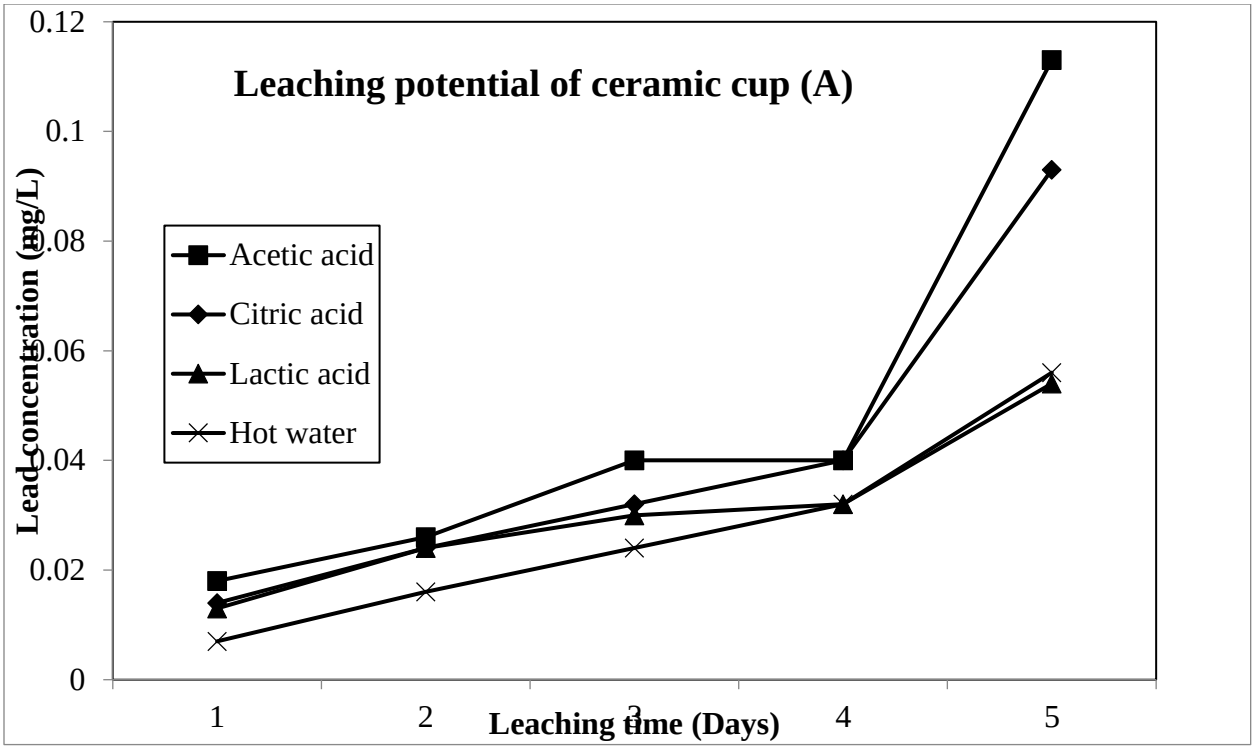
* Below detection limit



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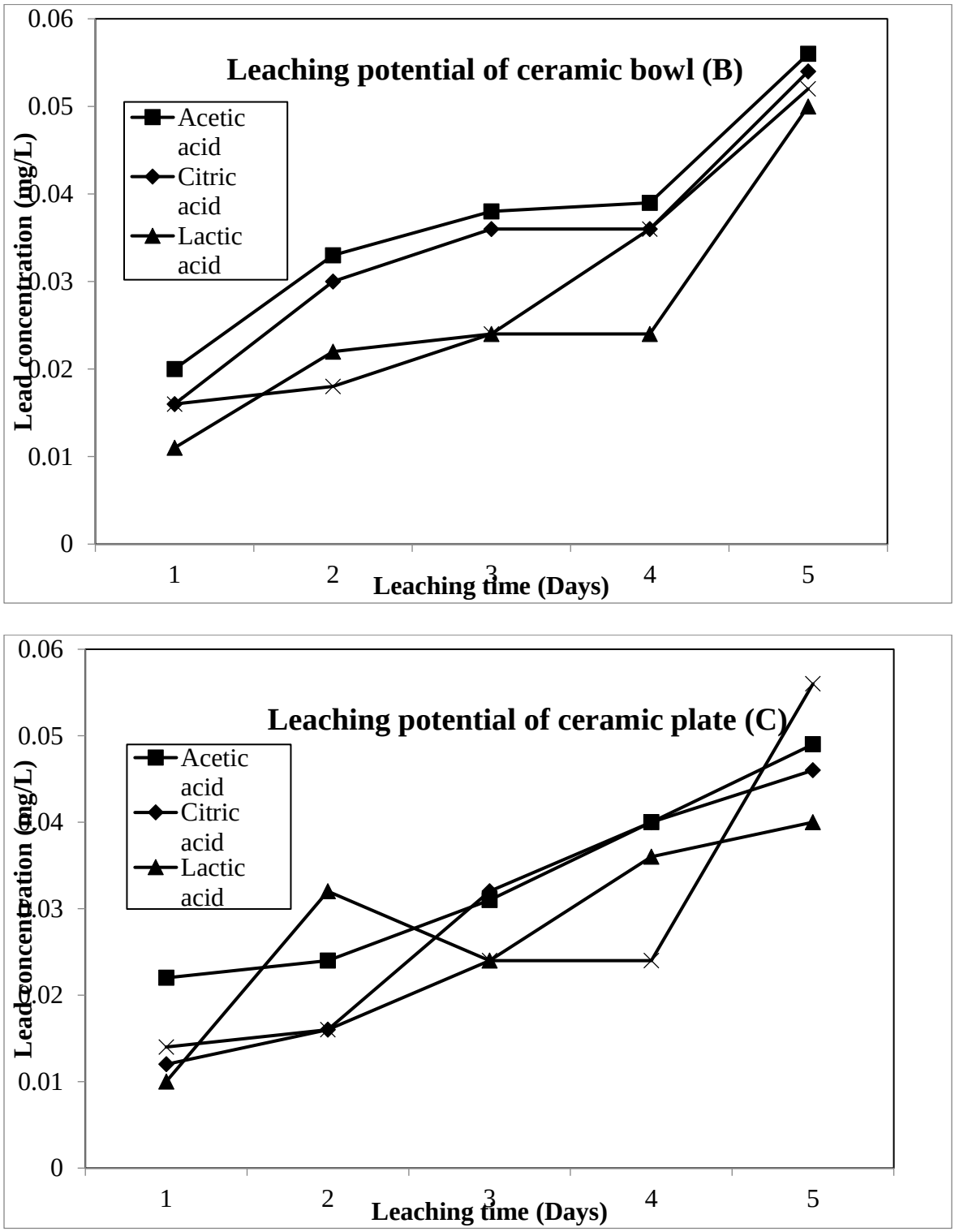

Figure 1: Leaching potential of Pb in cup (A), bowl (B) and plate (C) with time

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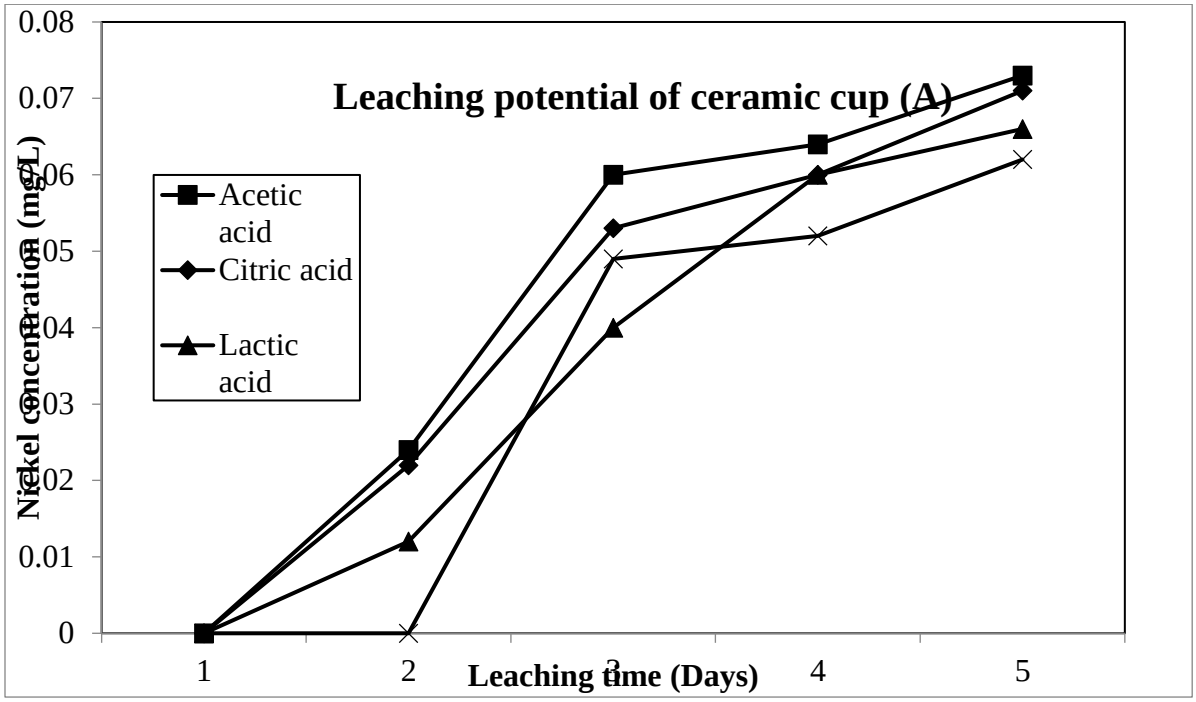

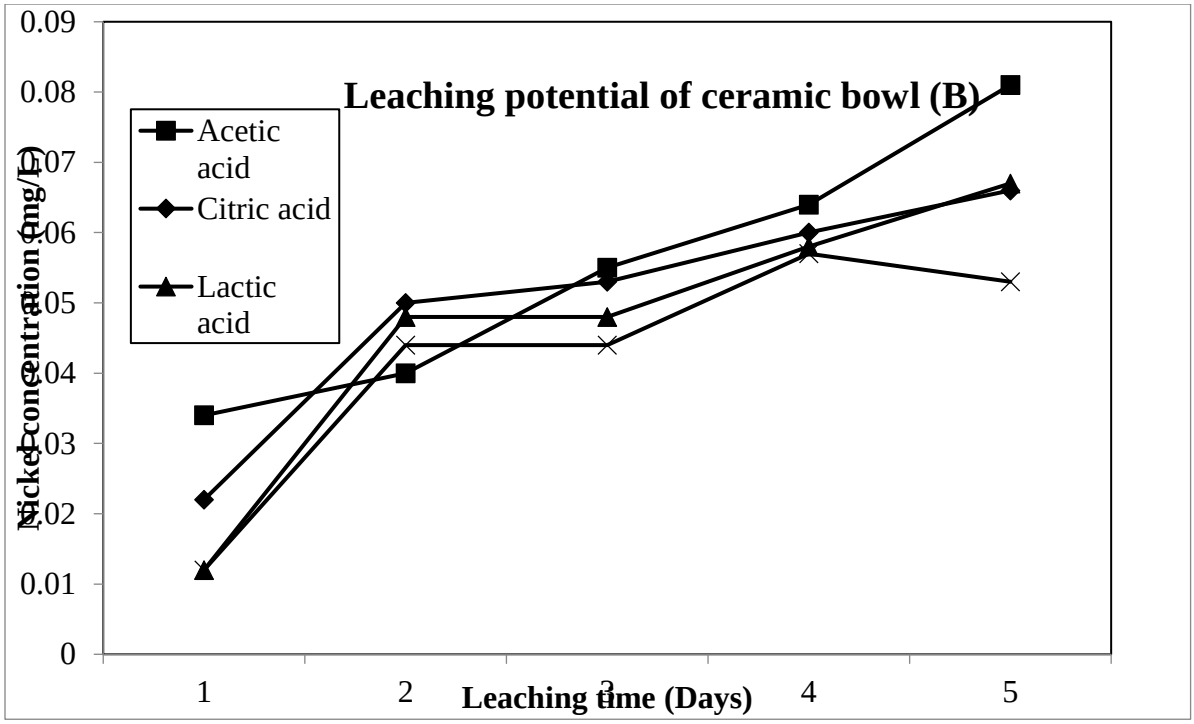

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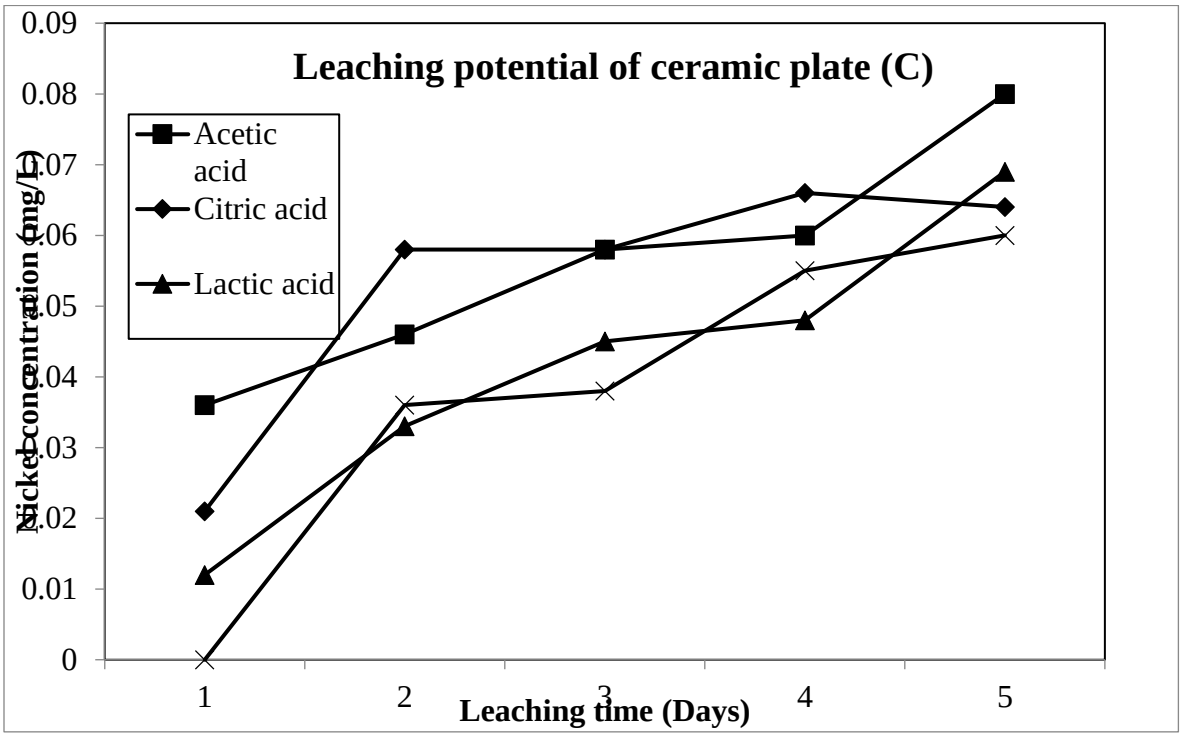

Figure 2: Leaching potential of Ni in cup (A), bowl (B) and plate (C) with time

Effect of color on leaching potential of metals

Table 3 shows average concentrations of metals in different colour ceramic cups, bowls and plates. For cups; blue, brown and green colours happen to leach the highest amount of Pb and Ni whose concentrations are relatively about the same. Cadmium levels in the different cup colours were relatively insignificant. Cream and black colours showed no appreciable levels of metals. In bowls; blue, brown and green leached more of Pb while blue green and cream leached more of Ni. Concentrations of Pb and Ni in these colored bowls were similarly about the same. Ceramic plates on the other hand, recorded the highest levels of Pb and Ni in only colours blue and brown. From Table 3, it's clearly obvious that ceramic cups, bowls and plates with colours; blue, brown and green, has great potential to leach Pb and Ni. Several studies have similarly concluded that Pb and Ni are released more from blue colours than any other color (Sheet, 1997; Buldini, 1997; Omolaoye et al., 2010). Cadmium and lead are the main components of ceramic colors. In most of the colours, lead oxide and cadmium compounds are used as a flux and pigments in the manufacture of red, orange and yellow colours, respectively (Ajmal, Khan, Nomani, & Ahmed,, 1997). Numerous pieces of contemporary glazed pottery dinnerware have been shown to release excessive amounts of Pb, greater than 1000µg/ml in several instances and extended use with frequent scouring increased the Pb release (Wallace, Kalman, & Bird, 1985). Glazed dinner wares with colorful paints are very popular in Ibadan; therefore, regular consumption of beverages from cheap dinner wares can be extremely harmful especially for growing children, pregnant women,

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or women of child bearing age. Researchers have found a high concentration of lead and cadmium in double distilled water that leached from both old and new glazed, colourful ceramic cups heated in the microwave (convection mode) at 140 degree Celsius for 2.5 minutes (Fernandes, 2019). This problem arises when surfaces of dinner wares are not manufactured under strict quality control. Acidic pH of food as well as temperature at which foods are served also influences the migration of metals from ceramics. Comparing results of this study with relevant standards, the average level of Pb leached from all colours of the cups, bowls and plates are within the FDA action level of 0.5-3.0mg/L, but clearly exceeding SON standard of 0.01mg/L Pb. Statistical t-testing showed no significant difference between Pb and Ni levels in the difference colours of cups, bowls and plates.

Table 3: Average concentration (mg/L) of metals in different colored ceramic wares

Type	**Color**	**Pb**	**Ni**	**Cd**	**Cr**
Cup	Blue	0.032±0.02	0.038±0.03	0.004±0.01	0.00
	Brown	0.040±0.03	0.045±0.03	0.0006±0.001	0.00
	Green	0.034±0.02	0.038±0.02	0.0002±0.0004	0.00
	Cream	0.012±0.03	0.00	0.00	0.00
	Black	0.005±0.01	0.00	0.00	0.00
Bowl	Blue	0.021±0.02	0.042±0.03	0.00	0.00
	Brown	0.034±0.02	0.005±0.01	0.00	0.00
	Green	0.038±0.02	0.046±0.02	0.004±0.001	0.00
	Cream	0.002±0.01	0.051±0.02	0.00	0.00
	Black	0.00	0.00	0.00	0.00
Plate	Blue	0.023±0.01	0.050±0.01	0.00	0.00
	Brown	0.032±0.01	0.054±0.02	0.00	0.00
	Green	0.006±0.01	0.006±0.01	0.00	0.00
	Red	0.002±0.01	0.005±0.01	0.00	0.00

Conclusion

This study provides an inside into possible health problems that may arise on domestic usage of colored ceramic dinner wares. Results showed that, lead and nickel were the only metals found to leach from ceramic cups, bowls and plates obtained within the Ibadan metropolis. The leached levels of Pb and Ni were about the same across the different leaching solutions (acetic acid, citric acid, lactic acid and hot water) although acetic and citric acids were slightly higher. The color of ceramic wares was similarly found to influence levels of Pb and Ni leached. Blue, brown and green colors recorded highest Pb and Ni levels. Lead and nickel levels increased with increasing contact time with leaching solutions. It can be concluded that the dinnerware sold in Ibadan metropolis and possibly other markets only contain lead and nickel but not in amount high enough to cause any serious toxic effect to humans. Results obtained in this study was only limited to Ibadan metropolis, however, ceramic wares are very much popular in other cities of Nigeria. There is need for constant monitoring of all popular dinner wares (local or imported) across the country for quality compliance to avoid possible health issues.

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