Assessment of Leaching of some Heavy Metals from Domestic Ceramic Wares

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ABSTRACT

The aim of this study is to assess the possible leaching of heavy metals from ceramic wares into different solutions. Ceramic spoon, pot, soup bowl, plate, mug and cup were leached in batch process using hot water and 4 % solutions of glacial acetic acid, HCl acid, NaOH and Na_2CO_3 respectively. Chromium, manganese, lead, cadmium, zinc and copper which were incorporated as glazes in the ceramic wares were determined in the leachates using atomic absorption spectrophotometric technique. The metal concentrations in the leachates ranged between 101.565-233.010 mg/kg for chromium, 44.333-1449.047 mg/kg for manganese and 0.235-6.260 mg/kg for copper. The levels of manganese and copper in the ceramic wares analyzed were above the permissible limits of World Health Organization (WHO) and Society of Glass and Ceramic Decorators. The levels of chromium in the wares with the exception of mug were also above the permissible limits. The results highlight that hot drinks, acidic and alkaline solutions can easily induce leaching of metals from ceramic wares at concentrations higher than permissible limits. The results also indicate 4 % NaOH solution as the most aggressive leachant while hot Lipton tea was the least aggressive. Alkaline leachant solution leached Cu and Cr metals more than other solutions, though statistical analysis of the data did not indicate any significant difference between the leachant solutions. The highest percentage of metals leached were 96 % (Cr), 92 % (Mn) and 86 % (Cu) from pot and soup bowl respectively. Consumption of stored food and drinks from these ceramic wares may be associated with health implications owing to the toxicity of the metals at elevated concentrations.

INTRODUCTION

Ceramics wares are materials made from naturally occurring clay or earth materials. Most traditional ceramic products were made from clay or clay mixed with other materials. Table wares and decorative ceramics are generally still made using the same method. Traditional ceramic raw materials include clay minerals such as kaolinite; more recent materials include aluminium oxide, commonly known as alumina. Historically, metals such as lead were used as glazes in the production of ceramic wares to add luster, protect the surface and enhance durability[1]. Most table ware manufacturers use unleaded glazes when producing table ware patterns, but design requirements occasionally mandate the use of decorative borosilicate enamels containing some heavy metals[2]. The incorporation of heavy-metal borosilicate enamels in ceramic products brings to fore heavy metals in ceramic materials. If ceramic items are baked at the wrong temperature, the glazing will not have the desired sealing properties and lead can leak into food and drinks at low pH[3].

Leaching is a method used to remove soluble components from a solid matrix. Leaching methods are often categorized by whether the leaching fluid is a single addition (static extraction tests) or is renewed (dynamic tests). Methods can also be classified as batch leaching in which the sample is placed in a given volume of leach solution, as column or flow through systems, and as bulk or flow around systems for monolithic samples[4]. Heavy metals may leach from ceramic materials or vessels into the food or liquid. Acidic food like tomatoes will increase the leaching for certain types of cookware and alkaline foods particularly when using polished aluminium wares[5].

According to Omolaoye *et al.* (2010)[1], all ceramics wares contain heavy metals in varying concentrations. About 60 % of ceramic wares have Pb concentration higher than 500 $\mu g g^{-1}$, whereas cadmium levels are generally low. Clemens (2011)[6] studied leaching of metals from iron sauce pan, aluminium pot, aluminium and iron skillet and reported that leaching of metals occurred in acidic medium sufficiently.

MATERIALS AND METHODS

Sample Collection

Ceramic samples in the form of cup, mug, soup bowl, plate, spoon, and pot were randomly selected from available products and purchased from the Central Market in Kaduna, Nigeria.The ceramic Plates were made by Stoneware ceramic company. Cup and spoon were made by S.M.P ceramic company while soup bowl, pot and mug were made by EMEL and Seammi ceramic companies respectively, all of which are based in China.

Sample preparation for total heavy metal

Ceramic samples were crushed and pulverized into fine powder using cell cylindrical steel metal, pistil and mortar. The cell was thoroughly washed and dried to avoid contamination. The powdered samples were sieved using 250 µm sieve size and kept in a clean dry plastic container prior to analysis.

Digestion of ceramics for total heavy metals

To 2g of each sample in a Teflon beaker, 10 cm^3 of 60 % hydrofluoric acid, 10 cm^3 of Conc. Nitric acid and 1 cm^3 of conc. H_2SO_4 were added. The beaker was covered and allowed to stand for 5-6 minutes. The content was heated to 60 ^OC for 15 minutes on hot plate and stirred in fume cupboard to expel NO_2. The mixture was heated on a water bath for 75 minutes at 110 ^OC until near dryness. The digest was allowed to cool and filtered through Whatman 41 filter paper into 50 cm^3 graduated plastic bottles. The filtrate was diluted to the mark using distilled water. The digest solutions were analyzed by atomic absorption spectrophotometry (AAS).

Preparation of stock solutions and working standards

Metal Stock solutions of 1000 ppm were prepared for each metal and working standards were prepared for each metal by serial dilution of the stock solution. Working standard solutions of 0.5-2.5 ppm (manganese, cadmium, lead), 1-5 ppm (copper) and 0.5-2 ppm (chromium and zinc were prepared.

Preparation for Leaching Reagents

4 % glacial acetic acid, 4 % HCl acid, 4 % NaOH, 4 % Na_2CO_3 solutions were used as leaching reagents.

Leaching test

The batch process described by Kim (2011)[4] was adopted for the leaching experiments. 2g of each ceramic material was weighed into 50 cm^3 clean dry plastic containers and 10 ml of leaching reagent was added into the separate containers and were allowed to stand for 24 hrs. After 24 hrs, the contents were filtered using Whatman 41 filter paper and the filtrate was analyzed using AAS.

RESULTS AND DISCUSSION

The concentrations of heavy metals in the ceramic materials are presented in Table 1. The results of total heavy metal analysis of the ceramic wares studied are presented in Table 1. The results indicate the varying concentrations of metals in the different ceramic wares.

The Cr concentrations for all the ceramic wares were above permissible limits[7,8] of 2.3 mg/L. Spoon and Mug showed the highest Cr concentration of 233.01 mg/kg and 213 mg/kg respectively. These values are consistent with concentration of Cr obtained in ceramic wares by Ajmal *et al*. (1997)[9]. The results suggest that the ceramic wares may be a potential source of Cr contamination of foods and drinks.

Table 1: Heavy metal concentrations in digests of ceramic wares (mg/kg)

Ceramic	Pb	Cr	Cd	Mn	Zn	Cu
Pot	32.3775	101.565	0.4125	47.25	1033.3675	2.3375
Soup bowl	140.905	175.6825	1.1400	88.4125	61.0625	0.2350
Plate	67.420	86.7575	3.630	44.3325	1603.8475	0.6875
Cup	134.0175	148.610	0.6925	1449.047	123.6775	4.2975
Mug	13.7075	213.6975	0.1325	44.970	90.4275	6.2600
Spoon	119.1925	233.010	0.335	201.7775	110.7775	5.055

The concentration of Cr leached by distilled water, lipton tea and 4 % NaOH as leachant solutions were also above the permissible limits of WHO. Chromium was not leached by the other leachant solutions. Percentage Cr leached from the ceramic wares using different leachant solutions were 96 % from pot, 76 % from cup, 74 % from soup bowl, 60 % from plate, 59 % from mug and 56 % from spoon.

The concentrations of metals after leaching of ceramics with different solutions are shown in Tables 2, 3, 4, 5, 6, 7 and 8.

The results for Cu for all the ceramic wares analyzed were within the permissible limit of WHO of 2 mg/L for drinking water and 10 mg/L in all food. The Cu concentrations obtained were similar to the Cu reported by Jerzy (1998)[10] in ceramic wares. Cu was leached into lipton tea, 4 % NaOH, 4 % acetic acid. 4 % Na_2CO_3 and Hot distilled water, though, the Cu in 4 % Na_2CO_3 and hot water leachate solutions were within the limits of WHO. The highest concentration of Cu was 4.725 mg/kg in hot water and 11.325 mg/kg in 4 % NaOH. These further indicate how alkalinity and temperature may facilitate the leaching of heavy metals. The percentage of Cu leached from the wares using different leachant solutions were; 86 % from mug, 69 % from plate, 65 % from spoon and 37 % from mug.

Table 2: Concentrations of metals after leaching with 4 % HCl Acid (mg/kg)

Ceramic	**Pb**	**Cr**	**Cd**	**Mn**	**Zn**	**Cu**
Pot	5.800 (18)	ND	ND	ND	35.075 (3)	ND
Soup Bowl	16.325 (12)	ND	ND	ND	16.40 (27)	ND
Plate	30.150 (45)	ND	ND	ND	36.55 (2)	ND
Cup	27.225 (20)	ND	ND	ND	36.35 (29)	ND
Mug	12.425 (91)	ND	ND	ND	38.20 (21)	ND
Spoon	34.20 (29)	ND	ND	25.425 (12)	41.075 (37)	ND

( ) = % Metal Leached;   ND = Not detected

The concentrations of Mn detected in all the ceramic wares analyzed were above the limit of 0.5 mg/L in foods set by WHO. The Cup showed a high value of 1449 mg/kg. Ajmal *et al.* (1997)[9] reported a range of 135-853 mg/l for Mn. But Omolaoye *et al.* (2010)[1] reported the concentrations of Mn in the range between 2533--6783 mg/kg. The high leachate concentration of Mn in all the ceramic materials indicated the propensity with which it can easily be leached into foods within a reasonable contact time thereby promoting exposure to manganese poisoning. The Mn was leached into lipton tea and 4 % HCl but was below detection limit in other leachant solutions. This result agrees with Lewus *et al.*, (1998)[11] and Zou and Dai (2012)[12] on migration limit of manganese in ceramic wares. The percentage of Mn leached from the ceramic wares using different leachant solutions were 94 % from pot, 92 % from soup bowl, 32 % from mug and 3 % from cup.

Table 3 Concentrations of metals after leaching with 4% Acetic Acid (mg/kg)

Ceramic	**Pb**	**Cr**	**Cd**	**Mn**	**Zn**	**Cu**
Pot	35.10 (85)	ND	6.025	ND	34.775 (3)	9.35
Soup Bowl	22.875 (16)	ND	8.20	ND	13.075 (21)	ND
Plate	65.575 (97)	ND	ND	ND	33.05 (2)	ND
Cup	31.975 (24)	ND	ND	ND	40.05 (32)	ND
Mug	13.375 (91)	ND	14.40	ND	23.875 (26)	10.55
Spoon	66.80 (56)	ND	ND	ND	36.05 (33)	18.80

( ) = % Metal Leached, ND = Not detected

Table 4: Concentrations of metals in ceramic materials after leaching with 4% NaOH (mg/kg)

Ceramic	**Pb**	**Cr**	**Cd**	**Mn**	**Zn**	**Cu**
Pot	29.975 (93)	82.075 (81)	ND	ND	16.55 (2)	ND
Soup/Bowl	52.65 (37)	6.075 (3)	ND	ND	13.175 (22)	ND
Plate	57.925 (85)	15.275 (18)	ND	ND	10.40 (1)	ND
Cup	61.45 (46)	28.225 (19)	0.475 (68)	ND	17.50 (14)	ND
Mug	ND	ND	ND	ND	10.725 (12)	11.325 (37)
Spoon	60.05 (50)	104.575 (45)	ND	ND	15.775 (14)	ND

( ) = % Metal Leached, ND = Not detected

Table 5: Concentrations of metals in ceramic materials after leaching with 4 % Na_2CO_3 (mg/kg)

Ceramic	**Pb**	**Cr**	**Cd**	**Mn**	**Zn**	**Cu**
Pot	27.825 (86)	ND	ND	ND	7.775 (1)	ND
Soup Bowl	45.275 (32)	ND	ND	ND	3.45 (6)	ND
Plate	33.00 (49)	ND	ND	ND	8.975 (1)	0.925 (69)
Cup	48.85 (36)	ND	11.125	ND	7.80 (6)	ND
Mug	11.85 (86)	ND	10.20	ND	8.15 (9)	ND
Spoon	44.00 (37)	ND	11.15	ND	6.35 (6)	ND

( ) = % Metal Leached, ND = Not detected

Table 6: Concentrations of metals in ceramic materials after leaching with hot distilled water (mg/kg)

Ceramic	Pb	Cr	Cd	Mn	Zn	Cu
Pot	28.375 (86)	ND	12.875	ND	12.875 (1)	ND
Soup Bowl	22.45 (16)	ND	10.90	ND	10.90 (18)	ND
Plate	33.975 (50)	ND	ND	ND	10.20 (1)	ND
Cup	40.75 (30)	ND	10.20	ND	10.20 (8)	ND
Mug	3.85 (26)	ND	11.375	ND	11.375 (13)	4.725 (86)
Spoon	27.55 (23)	ND	12.10	ND	12.10 (11)	2.95 (58)

( ) = Percentage of Metal Leached, ND = Not detected

Table 7: Concentrations of metals in ceramic materials after leaching with Lipton tea solution (mg/kg)

Ceramic	Pb	Cr	Cd	Mn	Zn	Cu
Pot	13.852 (43)	0.700 (1)	1.700	44.575 (94)	16.775 (2)	ND
Soup Bowl	23.575 (17)	58.771 (33)	2.15	162.50 (92)	15.375 (25)	ND
Plate	ND	ND	6.65 (91)	ND	13.175 (1)	ND
Cup	23.425 (17)	44.70 (30)	0.30 (60)	37.850 (3)	13.65 (11)	ND
Mug	18.865 (88)	53.775 (25)	3.80 (30)	14.476 (32)	12.50 (14)	ND
Spoon	10.225 (9)	59.275 (25)	1.275 (80)	ND	51.825 (47)	8.275 (65)

( ) = Percentage of Metal Leached, ND = Not detected

Table 8: Concentrations of metals in ceramic materials after leaching with Distilled water (mg/kg)

Ceramic	Pb	Cr	Cd	Mn	Zn	Cu
Pot	36.00 (88)	97.70 (96)	ND	ND	7.30 (1)	ND
Soup Bowl	36.00 (26)	129.975 (74)	ND	ND	3.625 (6)	ND
Plate	38.925 (59)	127.525 (60)	ND	ND	7.175 (1)	ND
Cup	36.475 (27)	112.45 (76)	ND	ND	4.60 (4)	ND
Mug	15.60 (57)	125.525 (59)	ND	ND	8.125 (9)	ND
Spoon	52.50 (44)	131.35 (56)	ND	ND	6.625 (6)	ND

( ) = %Metal Leached, ND = Not detected

Pearson correlations among the metals in the ceramic samples were determined to examine their interrelation. The data indicated a weak correlation between Cd and Cr (-0.643); Mn and Cd (-0.171); Zn and Mn (-0.334) and Cu and Zn (-0.479) as shown in Table 8. The negative correlation observed between these metals indicated that the metals were probably not from the same source and that the presence of one metal does not significantly affect the presence of the other. Similarly, the positive correlations between the metals probably suggest similar sources.The data was further subjected to t-test analysis to ascertain if any, the significant difference in the results for 4 % HCl and 4 % acetic acid; 4 % NaOH and 4 % Na_2CO_3; alkaline and acidic leachant solution and Hot and distilled water. The results indicate no significant difference in the mean leaching of both acids even though 4% HCl acid leached more of the metals. The two acid leachants, 4 % acetic acid and 4 % HCl showed a similar pattern in the leaching of the metals, although, HCl acid leached metals in higher percentage than other solutions. This indicates how the acidity affects the leaching of metals from the ceramic wares.

Table 9: Correlation Matrix and Pearson Correlation among Heavy Metals

	Pb	**Cr**	**Cd**	**Mn**	**Zn**	**Cu**
Pb	1.00					
Cr	.208	1.00				
	(.692)					
Cd	.047	-643	1.00			
	(.930)	(.169)				
Mn	.505	-0.023	-.171	1.00		
	(.306)	(.966)	(747)			
Zn	.417	-.0853	.758	-.334	1.00	
		(.031)	(.080)	(.518)		
Cu	.085	.541	-6.22	.488	-.479	1.00
	(.873)	(0.268)	(.187)	(.326)	(.377)	

(γ=0.05)

CONCLUSION

Heavy metals in the form of borosilicates are incorporated as glazes in the production of ceramic domestic wares. The results of the leachate studies clearly show that all the ceramic wares analyzed leached heavy metals and in some cases at concentrations beyond the permissible limits of WHO. The results also revealed that temperature, acidity and alkalinity enhanced leaching of metals from the ceramic wares. The alkaline medium leached the metals more than any other leachant solutions used in this study. Pearson correlation indicated a week correlation among the metals while t-test analysis showed no significant differences in the concentration of heavy metals leached by the leachant solutions.

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