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Study of the Effects of Selected Heavy Metals in Wrapping Sheets and Food Products

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Abstract

Paper is light, cheap, easy to use and discard or recycle, and quite environmentally friendly which makes it a popular food packaging material in Nigeria especially used paper. In this study, 5 different food packaging papers (foil, ink pen, printed, plain and newspapers) were used to wrap bean cake at varying temperatures (room temperature, 45 ^{o}C, 65 ^{o}C and 85 ^{o}C) for 30 minutes using Atomic Absorption Spectroscopy. The packaging papers were analyzed for levels of toxicity of 10 heavy metals (Pb, Ni, Cr, Mn, Cu, Zn, Co, As, Hg and Fe).The quantities of the selected heavy metals in the papers were compared with permitted values published by the European Council for food contact materials where Pb, Ni, As, Co and Cr were observed to be more than the permitted concentration in the samples, while Fe, Cu, Zn and Mn were observed within the permitted concentration. The food samples have concentration range of; Ni (BDL – 0.03 ppm), Pb (BDL – 0.03 ppm), Co (BDL), Ar (BDL) and Cr (BDL – 0.05 ppm) with maximum legal concentrations of 0.02 ppm, 0.01 ppm, 0.01 ppm, 0.1 - 0.2 ppm and 0.05 ppm respectively. Comparison of the determined concentrations of heavy metals in the food packaging papers with permitted standards for food contact materials suggests that the presence of these contaminants may be associated with health hazards but the migration of these heavy metals to the food sample were observed to be in low concentrations and below the permissible level of the WHO/FAO standard for food, except for a few concentrations of lead and nickel which were above the permissible limit. Even at low concentration, heavy metals are toxic to biological cells as they do not undergo biodegradation. Consequently, they accumulate in humans, leading to various diseases and disorders, even when present in low concentrations. But based on the migration ability of these heavy metals from the food packaging paper to the food product, the best packaging paper is foil paper with very low concentration of metals migrating compared to other papers.

Keywords: Heavy Metals, Bean cake, Paper Packaging, Toxicity, Health

INTRODUCTION

The use of paper as a packaging material dates back to the 17th century (Kirwan, 2003). After coating or waxing, their applications extend to the packaging and serving of wet and fatty foods (Geueke, 2018). Paper is commonly used in making corrugated boxes, milk cartons, folding cartons, paper plates and cups, bags and sacks, as well as wrapping paper.

Migration is the transfer of chemical compounds from or to the packaging film that occurs upon contact with the food. The migration phenomenon in packaged foods may happen in

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two directions simultaneously, i.e., from packaging material to the food product and vice versa (Mousavi *et al.*, 1998). This is influenced by a number of factors which are; the nature of packaging materials, nature of food, duration of contact, temperature of contact, type of contact, migrant concentration in packaging and migrant characteristics (Hron *et al.*, 2012).

Jo and Jeong (2007), Park *et al.* (2018), Conti and Botrè (2007), Mertoglu-Elmas and Cinar (2018), Sood and Sharma (2019), Cieplinski (2004), and Kim *et al*. (2008) studied the concentration of heavy metals in virgin and recycled paper and paperboard using food simulant (Acetic acid) and it was discovered that that metals like Pb, Cd, Zn, Ni, Cu Cr, Al, As, B, Ba,, Fe, Mn, Te, Ti, V etc were present. These metals were attributed to the presence of additives, residues related to printing inks (Kim *et al*., 2008), adhesives or stickies, constituents arising from paper not used in food contact applications, etc (Marcelo, 2008). In Europe, the concern about the examination of packaging materials with regard to the content of toxic substances has substantially grown after introduction of the EC Directive (94/62/EC), which limits the level of the toxic heavy metals in packaging materials (Ali *et al*., 2020).

Health-related risks from heavy metals present in paper needs to be carefully considered and thoroughly monitored to prevent contact and potential migration of carcinogenic chemical compounds into food (Sood and Sharma, 2019); such carcinogens need to be eliminated to: increase food safety, reduce health related risks (Tangahu *et al*., 2011) from these carcinogens, increase consumers' satisfaction and confidence and increase sells for food vendors (Nouri *et al*., 2011). This research seeks to study the migration of selected heavy metals between packaging papers and food, and provide better ways of packaging food product.

METHODOLOGY

A total of 5 paper packaging materials (newspaper, foil paper, printed paper, plain paper and ink pen paper) and beans were collected in Lapai, Niger State Nigeria. The bean cakes were prepared by washing 1 kg of beans, grinding into paste and addition of ingredients such as maggi, salt, pepper and onion. A table spoon of the sample was scooped and deep fried with groundnut oil. The food products (fried bean cakes) were wrapped with each of the packaging materials at room temperature, 45^{o}C, 65^{o}C and 85 ^{o}C for 30 minutes.

The samples were digested for metal analysis using the dry ashing method according to AOAC (2006). The digested samples were analyzed for the presence of lead, nickel, mercury, chromium, manganese, copper, iron, cobalt, arsenic and zinc using Atomic Absorption Spectroscopy MY19479002 for 30 minute which reflects the average amount of time before consumption after purchase.

RESULTS AND DISCUSSION

Table 1 : Heavy Metal Content of the Wrapping Sheet Sample.

The heavy metal content of the papers analyzed are presented in table 1.

Samples Heavy Metals	Newspaper	Printed paper	Ink pen paper	Foil paper	Plain paper	Permissible limit (ppm)
Chromium	2.763±0.001^{c}	1.677±0.001^{b}	1.578±0.001^{a}	7.736±0.001^{e}	1.677±0.001^{b}	0.250
Zinc	1.189±0.002^{d}	0.749±0.001^{b}	0.591±0.001^{a}	1.243±0.001^{e}	0.923±0.001^{c}	5.000
Mercury	1.205±0.001^{a}	1.825±0.001^{c}	1.801±0.001^{b}	4.508±0.001^{e}	1.857±0.001^{d}	0.003
Iron	6.945±0.001^{b}	7.810±0.001^{c}	8.229±0.001^{d}	16.260±0.004^{e}	4.657±0.001^{a}	40.000
Copper	0.580±0.001^{e}	0.067±0.001^{b}	0.018±0.001^{a}	0.209±0.001^{d}	0.074±0.001^{e}	4.000
Lead	0.891±0.001^{d}	0.293±0.001^{a}	0.341±0.001^{b}	1.103±0.001^{e}	0.353±0.001^{c}	0.010
Manganese	0.228±0.001^{b}	0.249±0.001^{c}	0.193±0.001^{a}	0.493±0.001^{e}	0.264±0.001^{d}	1.800
Nickel	0.215±0.001^{a}	0.243±0.001^{b}	0.215±0.001^{a}	1.062±0.001^{d}	0.274±0.001^{c}	0.140
Arsenic	0.01±0.0001^{a}	0.05±0.0011^{d}	0.03±0.0004^{b}	0.03±0.0002^{b}	0.04±0.0004^{c}	0.002
Cobalt	0.04±0.0010^{b}	0.02±0.0019^{a}	0.02±0.0002^{a}	0.02±0.0024^{a}	0.04±0.0005^{b}	0.02

Values are mean of triplicate determination ± standard deviation. **Values in the same row bearing the same superscript are not significantly different (p≥0.05)BDL = Below Detection Level**

The wrapping sheet samples were analysed for the presence of 10 heavy metals which are generally present as residues of the recycling process and due to their presence in the paper and pulp industry, so as to determine their suitability to be used as packaging materials which come in direct contact with foodstuffs.

The heavy metal content of 5 locally procured packaging materials is as presented in Table 1 bove. The level of heavy metals varied in the range of; Cr (1.578 – 7.736 ppm), Zn (0.591 - 1.189 ppm), Hg (1.205 - 4.508 ppm), Pb (0.293 - 1.103 ppm), Fe (4.657 - 16.060 ppm), Cu (0.018 - 0.580 ppm), Mn (0.193 - 0.493 ppm), As (0.010 – 0.050), Co (0.020 – 0.050) and Ni (0.215 - 1.062 ppm). The permitted concentration as suggested by the European Union is Mn- 1.80 ppm, Co-0.02 ppm, Cr- 0.25 ppm, Cu – 4.0 ppm, Fe-40.0 ppm, Ni - 0.14 ppm, Hg – 0.003 ppm, Zn – 5.00 ppm, As – 0.002 ppm and Pb - 0.010 ppm(Cederberg *et al*., 2015). The highest concentration of Cr, Fe, Hg, Fe, Pb, Mn and Ni were observed in foil paper. Newspaper had higher concentration of copper and cobalt while printed paper had higher concentration of arsenic. All samples contain Cr, Ni, Pb and As in more than the permitted concentration, Zn, Mn, Fe and Cu were observed to be within the permissible limit, while Co had some samples above the permissible limit as suggested by the European Union. Lead and Chromium mainly come from printing inks (Xue *et al*., 2010). Chromium (vi) could have a severe impact on living organisms owing to its having both carcinogenic and mutagenic properties (Skrzydlewska *et al*., 2003; Kim *et al*., 2008). Lead toxicity could damage the central nervous system and has negative impacts on various body organs in humans. Infants are especially prone to lead toxicity because of the greater retention of lead in their brains and bones. Even a subacute consumption of lead could result in mental retardation, convulsions, and encephalopathy in children (Skrzydlewska *et al*., 2003; Robertson, 2006).

Table 2: Heavy Metal Content of the Food Samples (ppm)

The heavy metal content of the food sample (bean cake) is presented in table 2.

Heavy Metals	Temp.	Newspaper	Printed paper	Ink pen paper	Foil paper	Plain paper
Nickel	Room temp.	0.01±0.0049^{a}	0.01±0.0003^{a}	0.01±0.0013^{a}	0.01±0.0004^{a}	0.02±0.0001^{a}
	45^{o} C	0.03±0.0003^{a}	0.01±0.0005^{a}	0.01±0.0012^{a}	0.01±0.0009^{a}	0.02±0.0009^{ab}
	65^{o} C	BDL	0.02±0.0003^{c}	BDL	0.01±0.0011^{b}	0.01±0.0007^{b}
	85^{o} C	0.01±0.0005^{a}	0.01±0.0001^{a}	0.01±0.0007^{a}	0.01±0.0001^{a}	0.01±0.0002^{a}
Arsenic	Room temp.	BDL	BDL	BDL	BDL	BDL
	45^{o} C	BDL	BDL	BDL	BDL	BDL
	65^{o} C	BDL	BDL	BDL	BDL	BDL
	85^{o} C	BDL	BDL	BDL	BDL	BDL
Cobalt	Room temp.	BDL	BDL	BDL	BDL	BDL
	45^{o} C	BDL	BDL	BDL	BDL	BDL
	65^{o} C	BDL	BDL	BDL	BDL	BDL
	85^{o} C	BDL	BDL	BDL	BDL	BDL
Lead	Room temp.	BDL	0.01±0.0022^{b}	BDL	BDL	BDL
	45^{o} C	0.02±0.0011^{b}	BDL	0.01±0.0015^{c}	BDL	BDL
	65^{o} C	0.02±0.0029^{b}	BDL	0.02±0.0016^{b}	BDL	BDL
	85^{o} C	0.01±0.0017^{b}	BDL	0.03±0.0014^{c}	BDL	BDL
Chromium	Room temp.	0.03±0.0001^{a}	0.05±0.0007^{b}	0.03±0.0001^{a}	0.03±0.0004^{a}	0.03±0.0003^{a}
	45^{o} C	0.05±0.0002^{d}	0.04±0.0002^{c}	0.03±0.0003^{b}	0.02±0.0001^{a}	0.04±0.0003^{c}
	65^{o} C	0.04±0.0003^{a}	0.03±0.0003^{b}	0.03±0.0003^{b}	0.02±0.0003^{a}	0.03±0.0003^{b}
	85^{o} C	0.03±0.0002^{b}	0.03±0.0001^{b}	0.02±0.0001^{a}	0.04±0.0003^{c}	0.03±0.0002^{b}

BDL= Below Detection Level Values are mean of triplicate determination ± standard deviation. Control for all metals were below detection level

The heavy metal content of the food sample (bean cake) not wrapped in any of the packaging materials, for all the metals analysed were all below detection level (BDL). The heavy metal content of the food sample (bean cake) wrapped in the packaging material at varying temperatures; room temperatures 45^{o}C, 65^{o}C and 85^{o}C is as presented in Table 2 above. The level of heavy metals varied in the range of; Ni (BDL – 0.02 ppm), As (BDL), Co (BDL), Pb (BDL – 0.03 ppm) and Cr (0.02 – 0.05 ppm). This result indicates that heavy metal migration was observed for Ni, Pb and Cr, though at very low concentrations. It was observed that temperature had no effect on the concentration of the metals of heavy metals migrating. The permitted concentration as approved by the WHO/FAO is Ni – 0.02 ppm, As – (0.1- 0.2 ppm), Co – 0.01 ppm, Pb – 0.01 ppm and Cr – 0.05.

Higher concentration of nickel was observed in food wrapped in newspaper above the threshold value, chromium occurred in higher concentration in food wrapped in newspaper and printed paper, lead was found in higher amount in food wrapped in ink pen paper above the maximum permissible limit, while arsenic was present above the permissible limit of the WHO/FAO in plain paper. This result agrees with Park et al., 2018 and Ali et al., 2013 where the migrating metals from the food packaging materials to food were observed to be below maximum legal concentrations except for arsenic and lead which were above the threshold values.

Metals such as lead (Pb), arsenic (As), chromium (Cr), zinc (Zn) etc are used in paper recycling, this process involves the use of paper additives to improve the papers surface, colour and printing properties (Ginebreda *et al.,* 2012).

Certain green ink contains Pb, Cr, and soluble Cu metals. Reds may contain Pb, yellows contain Zn, and blues contain Co and Cu. Whites contains Pb and Zn, while blacks contain Pb (EPA 2009; Ministry of Health 2013).

Chromated Copper Arsenate (CCA) is used as a wood preservative. Arsenic enters the paper and pulp industry if such woods are used as raw materials. Exposure to arsenic results in cutaneous, developmental, hematologic, reproductive, and vascular effects (Hughes, 2006). Lead as a heavy metal has been reported to be highly toxic and their presence in foods is not to be accepted even in trace quantities (Ogunkunle *et al*., 2014). It causes damage to the kidneys, and various systems like, the cardiovascular, immune, hematopoietic, central nervous and reproductive system (Sood and Sharma, 2019).

The transition metals copper and cobalt are involved in the electrochemical oxidation of paper and pulp mill wastewater. The health effects include a complex clinical syndrome, which mainly includes endocrine, neurological and cardiovascular deficits (Sood and Sharma, 2019). Severe lung damage has been recorded following acute exposure to nickel carbonyl. Another reported health effect is; allergic skin reactions (Ezeocha et al., 2021). Exposure to nickel can also cause increased risk of laryngeal cancer, kidney cancer and cancer of the prostrate. Nickel is present in the form of catalysts and pigments. Nickel is an important human toxicant, as it has the ability to cause carcinoma (Ezeocha et al., 2021).

Zinc is an essential trace element found in almost all foods and portable water; it is found in forms of salts or organic complexes. Zinc has the least toxicity effects among other minerals and its deficiency in a diet can cause health problems (Ezeocha *et al*., 2021).

The presence of Mn, Cu and Fe ions in the paper and paperboard food packagings catalyses the initiation of autoxidation of unsaturated fatty acids leading to the formation of odorous volatile compounds like aldehydes, ketones, and alcohols which brings an unpleasant feeling in the customer and may lead to rejection of food whether the food has been spoiled or not (Sood and Sharma, 2019).

CONCLUSION

The packaging products used in this study pose health risks with respect to maximum metal concentrations of Ni, Cr, As, Co and Pb. The migration of these metals to food may be of concern because of the toxicity of heavy metals on biological systems as they do not undergo biodegradation, so they get accumulated in humans causing many diseases and disorders even when present in very low concentrations leading to health implications and sudden deaths. Based on the migration ability of these heavy metals from the packaging papers to the food products, the best packaging paper is foil paper with very low concentration of metals migrating compared to other papers.

Given the facts arising from this study, it is recommended that: Newspaper, printed paper and ink pen papers are not fit and ideal for wrapping food products, Foil paper may be better wrappers and routine or even daily controls with official methods should be made available.

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