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A REVIEW ON HEAVY METALS CONTENTS IN HIDE, SKIN AND PROCESSED LEATHERS

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Abstract: *Heavy metals are metals with high atomic weight which can be deposited in soil, water, plants and animals. It is generally known that mammal tissues are good bioindicators of trace elements, including heavy metals. Heavy metal analysis serves to identify and quantify the elements that are a potential hazard to the consumer after varying levels of contact. Usage area of leather is increasingly expanding in these days and it has also become a material requested and demanded by effect of fashion. Leather must protect its appearance and physical stability and also be problem-free in ecological terms and harmless to human health. There is a lack of data concerning the content of toxic elements in raw hide and skin of animals. Mainly information concerning metals content, including toxic ones, in processed leathers may be found in the literature. The aim of the present study was to review and compare the content of some heavy metals in raw hide, skin and the processed leathers in order to evaluate their accumulation and transition to the end-up product.*

Keywords: *Heavy metal, Hide, Bioindicator, Tanning, Leather*

1. INTRODUCTION

Heavy metals are metals with high atomic weight which can be deposited in soil, water, plants and animals. It is generally known that mammal tissues are good bioindicators of trace elements, including heavy metals. Hides and skins are generally one of the most valuable by-products from animals. The uses of animal skin and hide include food, cosmetics, medicine, pharmaceutical and photography industries. Gelatin extracted from animal skins and hides can be used for food. Approximately 6.5% of the total production of gelatin is used in the pharmaceutical industry. Collagen from hides and skins has a wide variety of applications, from food to medical. Collagen can be used as an emulsifier or filler in meat products or to make collagen sausage. It is used in cosmetic surgery and burn surgery [1]. The tanning industry enables the skin and hide to be recovered and made into special and fashionable material as leather. All kinds of leathers have to pass through three main stages viz. preparatory processes, tanning and finishing processes. Items harmful to environment and human health such as heavy metals may form within the leather due to chemicals added and methods used during leather processing steps to cause leather have desired characteristics [2]. Regulatory requirements are important for reasons of all product safety and quality.

Heavy metal analysis serves to identify and quantify the elements that are a potential hazard to the consumer after varying levels of contact. Interest in the heavy metal content of ecological textile has been increasing recently. It is likely that investigations concerning ecological textile will expand

in the future and will include leather goods as well [3]. It is important to have adequate information about the composition of trace elements in leather, because some of the elements could prove toxic to man at certain concentrations [4]. There is a lack of data concerning the content of toxic elements in raw hide and skin of animals. Mainly information concerning metals content, including toxic ones, in processed leathers may be found in the literature [3, 4, 5, 6]. But heavy metals may have been transferred to the leather through the metabolic activities of the animal while it was alive [5].

In this research, a review and comparison of the content of some heavy metals in raw hide, skin and the processed leathers in order to assess their accumulation and possible transition to the end-up products were performed.

2. HEAVY METAL CONTENS IN RAW SKIN AND HIDES

Environmental pollution highly influences the bioaccumulation of chemical elements in animals and plants [7]. Skin is an invasive matrix and its use in biomonitoring studies can be questioned because of ethical reasons [8]. There is lack of a data concerning the chemical composition, including the levels of toxic elements, in animal raw skin or hide and their possible relationship with the chemical composition of the processed leather.

Statistically significant differences for some heavy metals between wild and farm animals were detected in skins of foxes [8]. Farm and wild foxes differed significantly in terms of the content of Pb, Cr and Ni, and highly significantly with Zn and Cu content in skin (Table 1). The level of Pb was higher in wild animals, while that of Cu, Cr, Zn and Ni was higher in farm foxes. The latter group was probably fed with feed enriched with microelement supplements. Higher levels of Pb in wild animals can be justified with environmental exposure. Over a 2-fold higher content of Zn in skin of farm foxes as compared to wild ones is remarkable.

Table 1: *Heavy metal contents in fox skins (mg kg^{-1})*

Foxes	Cr	Cu	Ni	Pb	Zn	Ref
Wild	1.405	7.680	0.447	1.445	151.500	[8]
Farm	2.338	10.847	0.803	0.827	403.833	
Farm Silver (mean values)	0.422	10.846	0.970	0.826	403.833	[9]
Farm Arctic (mean values)	0.285	16.383	0.515	0.696	299.000	

In their latter study, authors have investigated the influence of two farms locations on the concentration of some heavy metals in skin of arctic and silver foxes [9]. Generally, considerably higher content of heavy metals was found in skins of these foxes, but Cr content was found lower than in the previous study even for the same silver farm fox (Table 1). Although there were differencies in the contents of heavy metals in skins of the arctic and silver foxes, the elements were placed in the sequence as Zn>Cu>Pb>Ni>Cr. Despite of the most prefered bioindicators as the tissues and organs of animals, the usefulness of skin of foxes in bioindication and ecotoxicological studies has been started by the mentioned studies [8, 9].

As it is known in African countries skins and hides of some animals like goat and cattle are used as food after dehairing or singeing with different methods. Researchers investigated the effect of singeing methods on heavy metals contents in goat skins [10]. The data regarding the contents of some metals in un-singed and un-cooked goat skins are given in Table 2. The heavy metal concentrations observed in the un-cooked samples were lower for some metals than results obtained for un-singed goat skins [11]. However, they confirmed the possible means of contamination of skin

samples with heavy metal prior to analysis by the metal content of the tyre scraps used [12]. Researchers reported that singeing is not the only means by which animals could pick up heavy metal residues, but also, the soil, feed and drinking water are potential avenues from which the heavy metal residues could be picked up by the animals [13]. This explained why there were heavy metal residues in the skins of the unsinged carcasses. The levels of Mn, Cu, Ni and Cd in fresh, un-singed goats hide were respectively 0.64 ± 0.12, 1.06 ± 0.12, 1.74 ± 0.24 and 1.89 ± 0.27 mg/kg (Table 2). The animals could potentially have picked heavy metals from the environment during grazing, drinking water from polluted drains and streams, scavenging in open waste dumps for fodder and exposure to atmospheric depositions particularly from automobile fumes [12].

Table 2: *Heavy metal contents in goat skins (mg kg^{-1})*

Process	Fe	Mn	Cu	Zn	Pb	Cd	Ni	Ref
Un-singed	NA	0.64±0.12	1.06±0.12	NA	NA	1.89±0.27	1.74±0.24	[10]
Un-singed	9.67	ND	10.24	19.01	0.04	ND	NA	[11]
Un-cooked	5.78±0.17	0.27±0.07	0.25±0.00	2.35±0.03	0.12±0.02	ND	0.016±0.01	[12]

ND - not detectable; NA - not available

The substantial levels of heavy metals revealed by analysis of the cattle hides are given in Table 3. Magnesium, Cu, Ni, Cd, Mg and Zn in un-singed cattle hide in Ghana were, respectively 1.43 ± 0.12, 2.47 ± 0.26, 2.63 ± 0.12, 1.12 ± 0.48, 41.30 ± 2.49 and 17.71 ± 3.48 mg/kg [10]. The hides of cattle slaughtered in Nigeria accumulated varying levels of heavy metals and the mean concentrations of Cd, Cu, Fe, Ni and Pb in un-singed hides were 1.93±0.39, 10.45±1.19, 9.88±1.11, 1.95±0.12 and 5.65±0.70 mg/kg, respectively [14]. The mean concentration of Cu and Cd were higher while Ni had lower value than those of the first study (Table 3).

The high concentration of heavy metals recorded in the unsinged hides may be attributed to the presence of heavy metals in the local environment which the animal could easily have come in contact with through scavenging in open waste or refuse dumps, free range grazing, drinking water from polluted streams and drains and exposure to atmospheric depositions especially from automobile fumes and open burning of solid waste [10]. These metals could also have come from various sources like vehicle emissions, tyre and engine wears, and agricultural chemicals, urban and industrial wastes [15]. Authors reported high levels of lead and cadmium in polluted soils could serve as a source of heavy metals in animals grazing in such area [16].

Table 3: *Heavy metal contents in raw cattle hides (mg kg^{-1})*

Process	Cu	Zn	Cd	Pb	Fe	Cr	Ni	Ref
Un-singed	2.47±0.26	17.71±3.48	1.12±0.48	NA	NA	NA	2.63±0.12	[10]
Un-singed	10.45±1.19	NA	1.93±0.39	5.65±0.70	9.88±1.11	NA	1.95±0.12	[14]

NA - not available

3. HEAVY METAL CONTENS IN THE PROCESSED LEATHERS

Although the heavy metals may have been transferred to the leather through the metabolic activities of the animal while it was alive, large quantity of some of them in the natural leathers may originate from the metal based chemicals used in the many steps of leather manufacture, heavy metals in the water used in processing, or contamination from mechanical processes [6].

European Commission completely prohibited Pb, Cd, Cr (VI), As, Hg content and their compounds in textile and leather products. Limit values were imposed for other heavy metals as well [17]. Therefore, a more awareness and controlled manufacturing process has become mandatory for leather industries.

Table 4 shows the analysis results for As, Br, Co, Fe, Rb, Sb and Zn in leather samples from Kano, Nigeria. When 12 samples were analysed, As was determined in 2 of them, while Sb was determined in 1 of the samples. It was stated that arsenic was used to protect cattle from parasites and it is possible that this could be a source of arsenic in hides [4]. The presence of antimony may be due to the metal salts in the dyes and fixing agents for dyes used in leather production [3].

Table 4: *Trace metal contents in leathers from tanneries of Kano, Nigeria (mg kg^{-1})*

	Places taken	As	Br	Co	Fe	Rb	Sb	Zn
Processed leather	Craft market	-	4.4	0.33	242	-	-	10.9
	Local tannery	1.16	0.7	0.93	4000	-	0.2	41.7
	Collected	-	3.7	0.6	5333	8.9	-	39.6

Most of studies concerning heavy metal contents, including toxic ones, in the processed leathers were performed in Turkey (Table 5). Aslan (2009) observed eleven chemical elements in tanned leathers with the amounts dependent on tanning technique. Chromium, aluminium and zirconium showed the highest levels, while Hg, As, Sb, Cd and Ni the lowest. It was observed that tanned animal hides contain from 0 to 36,000 ppm of Cr depending on tanning technique [2]. Basaran et al. (2006) obtained the highest amount of Cr, and a considerably lower level of Zn and Cu [5]. The heavy metal detected in natural upholstery leathers in the greatest quantity was chrome. Small amounts of aluminum, cobalt, copper, nickel and zinc were also determined [6]. An amounts of heavy metals revealed by exposure of the furniture leathers to sweat during use have been identified and compared to limit values presented for leather products [18].

Table 5: *Heavy metal contents in different types of the processed leathers (ppm)*

Metals	Gloving leather	Bootee leather	Garment leather	Upper leather	Insole leather	Upholstery leather	Furniture leather	Leather solid waste
Cd	0.29	1.28	0.39	0.55	0.34	-	0.52	0.41
Co	1.13	-*	1.40	1.65	7.99	2.94	31.74	-
Cr	22 105	29 614	19201	17.728	-	168.42	16 549	36 000
Cu	83.46	-	9.46	35.37	51.60	6.57	53.74	18.11
Zn	33.45	-	28.06	31.66	27.35	11.93	-	27.70
Pb	11.42	1.21	14.42	4.19	11.16	-	2.13	5.15
Ni	3.97	-	3.27	2.26	2.25	0.11	1.89	2.59
Sb	-	1.45	-	-	-	-	-	2.71
As	-	0.63	-	-	-	-	-	0.13
Ba	-	0.91	-	-	-	-	-	-
Se	-	1.63	-	-	-	-	-	-
Hg	-	0.51	-	-	-	-	-	0.01
Al	-	-	-	-	-	602.33	-	581.99
Zr	-	-	-	-	-	-	-	180.37

*- not available

Authors reported that the high concentration of heavy metals in the processed leathers may be attributed to the industrial chemicals used during the leather manufacture. For example, the presence of cobalt in some of the leather samples may be attributed to dyes that are used for leather finishing, since leather dyes may contain cobalt metal complex [4]. Presence of cobalt may also be originated from bioaccumulation while animal was alive or from the machines used during the processing of the leathers [6]. The amounts of cadmium determined can varied according to the color of leathers, and be resulted from pigments used in the leather production process [5]. The high amount of chrome is the result of the fact that tanning is mostly done with chrome sulfate salts. Manufactured goods tanned with chrome contain at least 2.5% Cr_2O_3 [19]. Calculated by the atomic weights of chrome and oxygen, this amounts to approximately 17 100 ppm chrome. The high chrome content may be a result of colorants and contamination during mechanical processes as well [20, 21]. The copper detected in processed leathers may be caused by contamination during the production of leathers and metal complex dyes used in dyeing [5, 20]. The presence of Zn and Al may have been caused by contamination, inorganic pigments, or the water used in leather manufacture [6]. Besides Zn may have originated from the metabolic activities of the animal while it was alive as it was seen in the above studies [8-12, 14], and aluminum is used during the tanning and retanning of the natural leathers [2]. Lead and mercury determined in natural leather samples may derive from the environment of the animal or the slaughterhouse [22]. Ni detected in leathers might be caused by dyestuffs used in leather production process or stainless steel based machines and tools [6].

4. CONCLUSIONS

Toxic metals are accumulated in plants, and animals fed with these plants will tend to accumulate toxic metals themselves. The effects of their accumulation must be taken into account when considering the increased expectation of life quality. Although contamination of animal feed by toxic metals cannot be entirely avoided given the prevalence of these pollutants in the environment, there is a clear need for such contamination to be minimized, with the aim of reducing both direct effects on animal health and indirect effects on human health. In addition, the heavy metal restrictions in consumer products have had a significant impact on industrial developments. It is extremely important that all the by products from hides and skins contain only a low quantity of harmful substances or, if possible none at all.

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