Toxic Metals in Some Decorative Cosmetics and Nail Products: Analysis, Evaluation, and Mitigation

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Abstract—**Cosmetic marketing is one of the most profitable and fast increasing markets in Kurdistan Region of Iraq. In recent years, the use of cosmetics has witnessed a rapid increase, especially with the emergence of social media and its impact on this trade. The market is full of different cosmetic brands and nail products. Moderate and low-quality brands of cosmetic samples that available in the local markets were selected to investigate their heavy metals and chemical composition. Samples from face foundation, eye shadow, and nail polish products were taken and examined to evaluate the concentration of metals, that is, Hg, Pb, Cd, As, Mn, Cr, Ni, Co, Fe, Zn, Cu, and Al ions, using X-ray diffraction and X-ray fluorescence techniques. The examination results show high concentrations of Fe and Al metals in the lipstick samples whereas the Hg, Cd, Cr, and Ni were out of detection limit. Moreover, the results show contamination of Hg heavy metal in one of the examined nail polishes brands, whereas the rest of foundation and eye shadow samples show a higher concentration of Al and Fe. Curcumin, as a natural bio-friendly chelate, has been used to deplete metal ions using ultraviolet-visible Spectrophotometer.**

Index Terms—**Cosmetics, Curcumin, Metal ions, Nail polish, X-ray diffraction, X-ray fluorescence**

I. Introduction

Cosmetics are defined according to the U.S. Food and Drug Administration as "articles intended to be rubbed, poured, sprinkled, or sprayed on, introduced into, or otherwise applied to the human body or any part thereof for cleansing, beautifying, promoting attractiveness, or altering the appearance" (Claudia and Giovanni, 2017).

Essentially, cosmetics are classified mainly into leave-on and rinse-off products. Examples of leave-on cosmetics are perfumes, decorative cosmetics, body and face creams, and antiperspirants which are products that are designed for the purpose of spread out on the skin for a quit prolonged time. Meanwhile, the rinse-off cosmetics are products formed to be removed after a short time of stay on the skin or mucous membranes and examples are shampoos, soaps, shower gels, and toothpastes (Claudia and Giovanni, 2017).

Decorative cosmetics handling in addition to pharmaceuticals and many personal care products have been raised especially in the past few years with evolving of social media. These products do not undergo regulations of disinfectants, insect repellents, and dietary supplements; therefore, they need serious consideration due to the pollutants which are continuously discharged into the environment. Large amounts of the decorative cosmetics are used which are related to their environmental impact due to the bioaccumulation ability of these bioactive persistent (Brausch and Rand, 2011, Adepoju-Bello, et al., 2012). Heavy metals assessed in the decorative cosmetics are of substantial heed with different levels as ingredients or contaminants (Al-Dayel, Hefne, and Al-Ajyan, 2011, Ekere, et al., 2014, Golnaz and Parisa 2015; Chen, et al., 2018).

Hazards of the decorative cosmetics to humans are through the ability of the cosmetic molecules to enter the systemic circulation because they can cross the cutaneous barrier when it is applied to the skin or by contact with the mucous membranes or ingestion, for example, lipstick (Wormuth, et al., 2006, Hwang, et al., 2009, Chevillotte, et al., 2014, Ouremi and Ayodele, 2014). Impurities in the cosmetics could be exist as heavy metals (Morra, 2014, Riyadh, 2020). Daily apply of the decorative cosmetics on the skin and nail is enhanced absorption of the heavy metals that pass through hence accumulate in multiple organs and provoke damage of the target organ (Borowska and Brzoska, 2015). Toxic heavy metals are damaged the target organ even with lower level of disclosure and they are recognized as human carcinogens (arsenic, cadmium, chromium, lead, and mercury) (Chauhan, et al., 2010, Borowska and Brzoska, 2015, Muhammed and Hamsa, 2017). Essential heavy metals (manganese, cobalt, and

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nickel, iron, zinc, and copper) are important for human organ function in a low limit, and they turn to toxic and harmful metals when they exceed the permissible limit; however, a light metal as aluminum can cause Alzheimer disease when there is a continuous and high exposure to this metal (Lakshmi, Sudhakar, and Prakash, 2015).

Regulations of the compositions and contents of the cosmetics are varied in different countries. Absorbing cosmetic products through skin and disposing the expired products exposes human life and the environment to the risk of pollution and the diseases resulting from it and this urges to have a data base for the toxicological sources in the cosmetic products (make up and nail polish) that are existed in the local market. As well as finding the eco and bio friendly solution to reduce the risk of the harmful metal and heavy ions if they are existed in high concentration.

II. Experimental

A. Apparatus

An energy dispersive X-ray fluorescence (EDXRF), Rigaku NEX CG with RX9, Mo, Cu, and Al targets was used for quantitative measurements of the metal Hg, Pb, Cd, As, Mn, Cr, Ni, Co, Fe, Zn, Cu, and Al ions. A 200 s and 100 s were the X-ray measuring time for the Al target and other targets, respectively.

The chemical compositions and intensity versus energy is measured from the signal outcome of XRF which is processed to a computer program. X-ray diffraction, Rigaku with a Cu target was applied to the samples to identify the type of material as well as its phase and crystalline properties.

Agilent Cary Eclipse ultraviolet (UV)-visible Spectrophotometer, USA, with a quartz cell of 1.0 cm optimal path length was operated for the spectra measurements of the curcumin-metal ions complexes.

B. Material and reagent

All nitrate salts of the metal ions were of analytical grades. Double distilled water was utilized for the preparation. Curcumin plant was dissolved in absolute ethanol after grinding it as a powder.

C. Preparation of the metal ions and samples

A 1×10^{-4} M concentration solution was prepared for the metal ions in a 100 mL volumetric flask using a doubled distilled water. Curcumin plant was grinded first as a yellow powder and 1×10^{-4} M concentration solution was prepared by dissolving it in absolute ethanol, then filtered using Whatman No. 41 membrane filter paper to remove undissolved fibers of the plant and completed the volume to 100 mL in a volumetric flask. Curcumin-metal ion complex was prepared by mixing 3 mL of curcumin ethanolic solution with 1 mL of each metal ion solution, individually and the volume is completed to 25 mL in a volumetric flask by ethanol.

Decorative cosmetic samples of foundations, eye shadows, lipsticks, and nail polishes were collected from the local market of Kurdistan Region of Iraq. The liquid state sample such as nail polish and lipstick liquid was dried on a microscope slide sheet in an oven of 70°C. The rest of solid samples were applied directly for the analysis. Table I shows the type, brand, and origin country of the decorative cosmetic samples.

III. Results and Discussion

A. XRF analysis

XRF spectroscopy is based on simple relation of the fundamental physics comprising of atom radiation interaction. It is a highly sensitive analytical tool used for the analysis of the metals. The main advantage of XRF is the ability to perform accurate quantitative analysis of a wide range of elements. To determine the contents of metal ions in the cosmetic samples, the levels of heavy, essential, and light metals such as (Hg, Pb, Cd, As, Mn, Cr, Ni, Co, Fe, Zn, Cu, and Al) were evaluated using XRF.

TABLE I
Information of the Collected Decorative Cosmetic Samples

Type	Sample code	Brand name	Color	Country
Lipstick	LP1	3Q beauty	Pink	China
	LP2	Velvet matte	Pink	India
	LP3	Hudamoji	Red	UK
Nail polish	NP4	Mekyach	Black	PRC
	NP5	Flormar	Red	Turkey
	NP12	Asma beauty	Light brown	PRC
	NP13	Gel Polish	Green	UK
	NP17	Rival	Light red	Germany
Foundation	Fd6	NYX	Light gray	USA
	Fd7	Bonjour	Light pink	Canada
	Fd8	Trois coulerurs	Pink	PRC
	Fd9	MAC	Light pink	Canada
	Fd10	Essence	Light pink	Poland
	Fd11	ZARA	Pink	PRC
Eye shadow	ES14	Cien	Light brown	Germany
	ES15	Statement Eye	Purple	UK
	ES16	Malva	Light navy blue	Ukraine
	ES18	MSYAHO	White	China
	ES19	VIVO	Light brown	Taiwan
	ES20	EMERALD	Bronzy	Germany

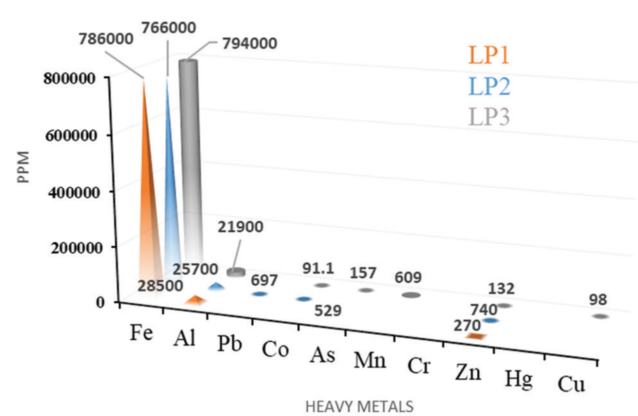

Fig. 1. Concentrations of metals in ppm in the lipstick samples (LP1, LP2, and LP3).

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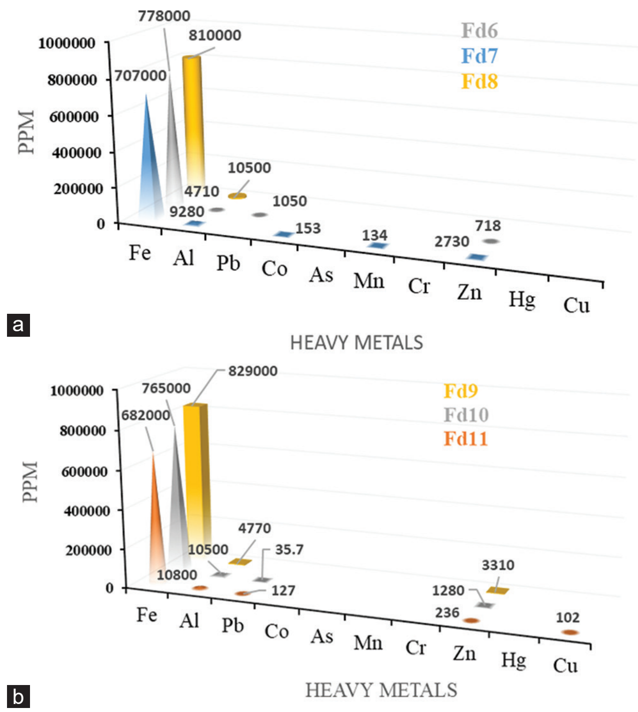

Fig. 2. Concentrations of metals in ppm in the foundation samples (a) Fd6, Fd7, and Fd8, (b) Fd9, Fd10, and Fd11.

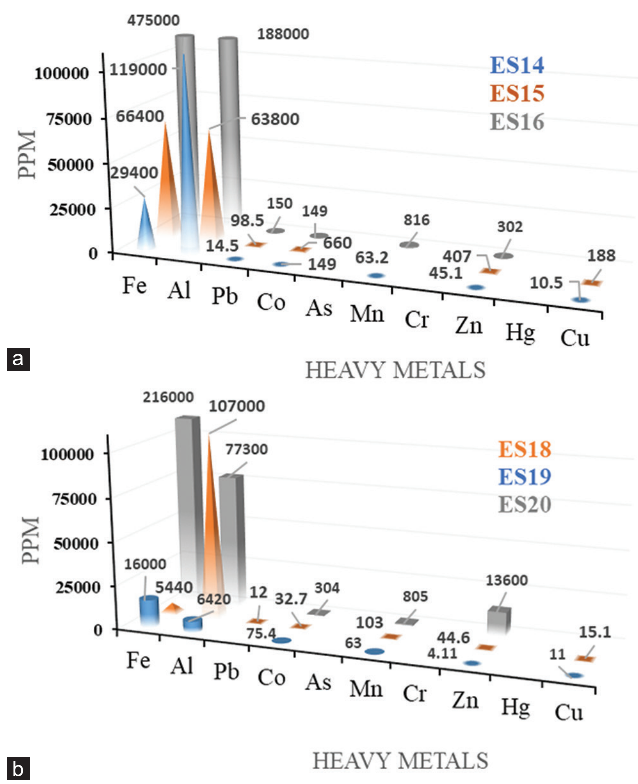

Fig. 3. Concentrations of metals in ppm in the eye shadow samples (a) ES14, ES15, and ES16, (b) ES18, ES19, and ES20.

In different brands of lipsticks (LP1, LP2, and LP3), heavy metals such as Hg, Cd, and Cr are not significant in the selected samples. Fig. 1 shows that LP3 depicted the highest concentration of Fe (794000 ppm), and LP2 displayed the lowest

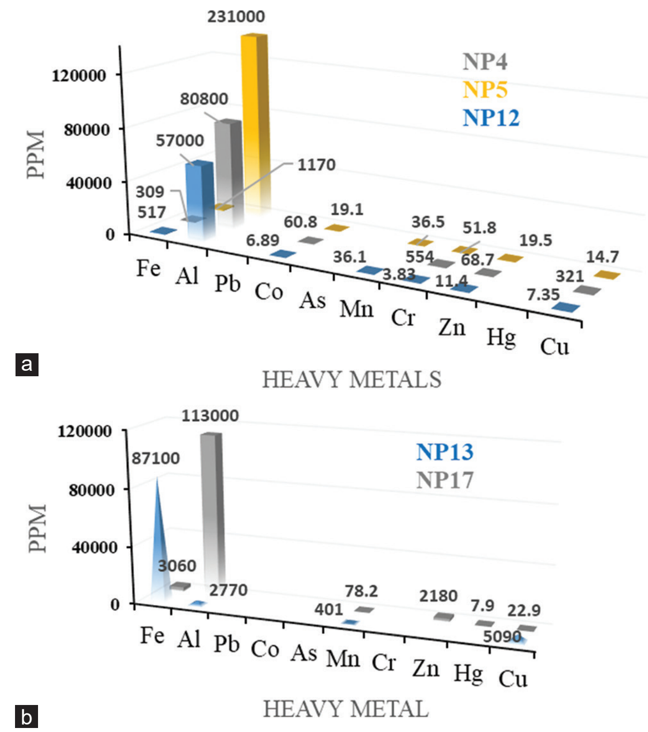

Fig. 4. Concentrations of metals in ppm in the nail polish samples (a) NP4, NP5, and NP12, (b) NP13 and NP17.

TABLE II
Heavy Metals Analysis Date of the Decorative Cosmetic Samples using X-ray Florescence (XRF) Spectrometer

S/M	Fe	Al	Pb	Co	As	Mn	Cr	Zn	Hg	Cu
LP1	786000	28500						270		
LP2	766000	25700	697	529				740		
LP3	794000	21900		91.1	157	609		132		98
NP4	309	80800		60.8			554	68.7		321
NP5	517	57000		6.89		36.1	3.83	11.4		7.35
NP12	1170	231000		19.1		36.5	51.8	19.5		14.7
NP13	87100	2770				401				5090
NP17	3060	113000				78.2		2180	7.9	22.9
Fd6	778000	4710	1050					718		
Fd7	707000	9280		153		134		2730		
Fd8	810000	10500								
Fd9	829000	4770						3310		
Fd10	765000	10500	35.7					1280		
Fd11	682000	10800	127					236		102
ES14	29400	119000	14.5	149		63.2		45.1		10.5
ES15	66400	63800	98.5	660				407		188
ES16	5440	188000	150	149		816		302		
ES18	5440	107000	12	32.7		103		44.6		15.1
ES19	16000	6420		75.4		63		4.11		11
ES20	475000	77300		304		805		13600		

*LP: Lipstick, NP: Nail polish, Fd: Foundation, ES: Eye shadow

concentration (766000 ppm). Concentration of Fe in all lipstick samples is virtually high and contains more than 76% of iron, that is hazards to human health and exceeded the permissible limit according to the WHO. Aluminum is the second high metal ion concentration that reached 28500 ppm in LP1. Toxic heavy metals of Pb and As were assessed only in LP2 and LP3 samples in the concentration of 697 and 157 ppm, respectively.

Foundation samples of (Fd6, Fd7, Fd8, Fd9, Fd10, and Fd11) appraised different results of metal ions as shown in Fig. 2a and b. Among different brands of foundation samples Fe, was the highest concentration (829000 ppm), in Fd9 sample and the lowest concentration (682000 ppm) carried by Fd11 sample. High concentration of aluminum was observed in all samples that out passed the allowable limit. Al concentration range in the foundation samples was between (10800-4710) ppm (Table II). The lone toxic metal ion detected in some foundation samples was Pb as in Fd6 (1050 ppm), Fd11 (127 ppm), and Fd10 (35.7 ppm), however, their value is beyond the 10 ppm limit of Pb which set by the WHO. The rest of the noxious heavy metals Hg, As, and Cr vanished in all foundation samples.

Like foundation samples there was no trace of the poison heavy metals Hg, As, and Cr found in the eye shadow samples (Fig. 3a and b). The metal ions of Fe, Al, Zn, Mn, Co, and Cu were detected in all the investigated cosmetic samples (ES14, ES15, ES16, ES18, ES19, and ES20). Data presented in Table II reveal that the iron concentration in sample ES16 had the highest (475000 ppm) whereas in ES18 and ES14 had the lowest (5440 ppm). In all eye shadow samples the concentration of Al was very high in the range of (188000-6420) ppm in the samples ES16 and ES19, respectively. The presence of the poison metal Pb was detected in the samples ES14, ES15, ES16, and ES18 that reached 150 ppm although Pb level was out of detection limit in the samples ES19 and ES20.

Unlike makeup samples highest concentration of the measurable metal ions was for Al in all nail polish samples as shown in Fig. 4a and b. The highest Al concentrations in the nail polish samples (NP4, NP5, NP12, NP13, and NP17) reached 231000 ppm in NP12 verses the lowest concentration of 2770 ppm in NP13 sample. The main health problem of aluminum toxicity is neurotoxicity effects such as neuronal atrophy in the locus ceruleus, striatum and substantia nigra (Lakshmi, Sudhakar and Prakash, 2015). Fe concentration level ranged from 309 to 87100 ppm. The highest concentration of Cr and Cu 554 ppm and 5090 ppm were detected in NP4 and NP13, respectively. Mercury metal ion was contaminated within one sample NP17 of 7.9 ppm concentration at the same time Pb and As abandoned in all nail polish samples (Table II).

B. X-ray diffraction (XRD) analysis

XRD is one of the powerful techniques applied to the materials analysis and interpretation of inorganic mineralized artifacts such as metal, ceramics, and pigments. It is a non-destructive and

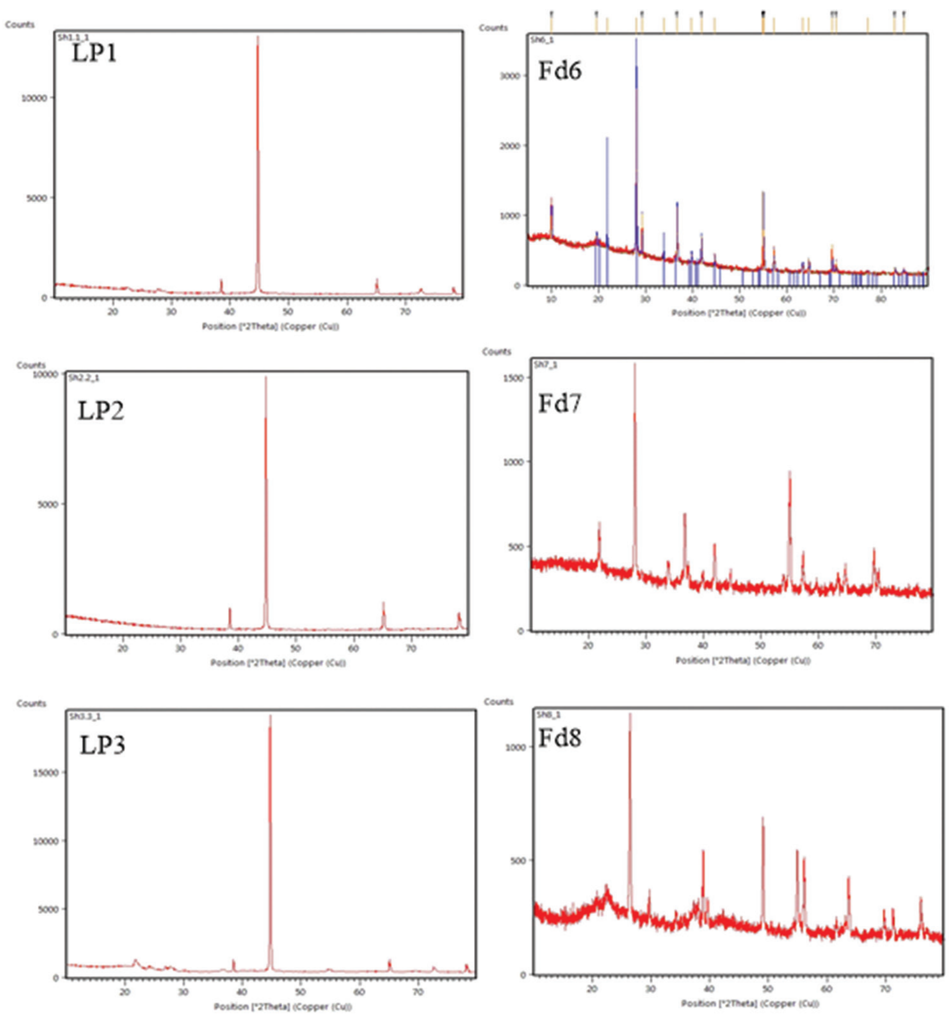

Fig. 5. X-ray diffraction patterns of some cosmetic samples.

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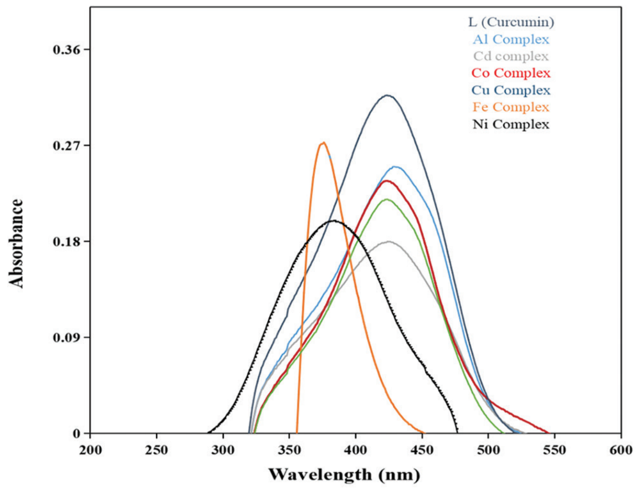

Fig. 6. Comparative ultraviolet-visible spectra of curcumin and its metal complexes.

versatile analytical technique that can rapidly get elaborate phase information and structure of materials. XRD patterns of materials in Fig. 5 shows the characteristic diffraction peaks in the samples LP1, LP2, and PL3 that indicated the major component of the sample were Fe and Al and Fe was almost 80% composed of the chemical composition. The samples Fd7, Fd8, and Fd9 show the same XRD patterns which means that they contain same chemical composition and the majority consist of (Al, 75%), which confirmed by the XRF technique.

C. UV-visible spectra

A vital step to reduce the high concentration of the metal ions during the analysis of cosmetic samples is to have a powerful natural chelating agent as curcumin with its safety assessment even distributed at the high doses in humans (Subhan, et al., 2014). The complexation of curcumin with the most metals has attracted interest over the past year; all the complexes are synthesized by mixing curcumin with metal ions at a molar ratio 3:1 in an ethanolic solution (Subhan, et al., 2014). UV-Visible spectrophotometric technique is the adequate and simplest method to prove the binding and complexation of curcumin with the metal ion.

The electronic spectra of the curcumin were recorded in ethanol and comparative electronic absorption spectra of curcumin with its metal complexes in ethanol are shown in Fig. 6. Curcumin ligand showed that the main absorption band at 420–434 nm, which is indicated to π-π^* transition. The spectrum of the curcumin compared with its complex's spectra where most of the absorption spectra shifted by (2–35 nm) and indicated the participation of the carbonyl group of curcumin in metal complexation. The variation of the absorption peak of curcumin and all complexes depends on the nature of metal (M^+) ion.

IV. Conclusion

High accuracy techniques such as XRF and XRD were used to measure the concentrations of Hg, Pb, Cd, As, Mn, Cr, Ni, Co, Fe, Zn, Cu, and Al in cosmetic samples such as, lipstick, face foundation, eye shadow, and nail polish that were collected from the local market of the region. The essential findings of this work are that concentrations of Fe and Al were found in most of cosmetic samples in higher level than the safe allowable limits. Fortunately, heavy metals of Cd, Hg, and As were not existed in risky level in all samples. Curcumin was used as a natural bidentate ligand to coordinate with various heavy metals, which is a natural and bio-friendly solution to reduce the risk of the high concentrations of the metals.

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Declaration

We declare that this study is not to defame any product or harm the reputation of the product.

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