A new approach for risk assessment of aggregate dermal exposure to banned azo dyes in textiles

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Xuezhang Chen[a,*], Qixi Deng[a], Shubao Lin[a], Chao Du[b], Shengqiao Zhao[a], Yongjie Hu[b], Zhongguo Yang[a], Yanhui Lyu[b], Jianjian Han[b]

[a] Guangdong Institute of Standardization, 563 Nantian Road, Haizhu District, Guangzhou, 510220, China
[b] Guangdong Testing Institute of Product Quality Supervision, No.10 Science Avenue, Huangpu District, Guangzhou, 510663, China

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ABSTRACT

A semi-quantitative risk assessment of banned azo dyes in textiles was performed to assess the health risk when consumers have direct dermal contact with these products. A novel model, which includes three exposure scenarios, was proposed to estimate the absorption of leachable azo dyes from twenty textiles samples. The effective daily uptakes of benzidine from sample 1 and sample 19 in chronic exposure model were 0.318 ng/kg-day and 0.011 ng/kg-day, respectively. Compared to virtually safe dose (VSD), the corresponding cancer risks were 7.42×10^{-5} (Sample 1) and 2.56×10^{-6} (Sample 19). As noted by nomograph assessment, the health risk induced by long-term exposure of banned azo dyes from textiles was at the range of "very low" to "low". In short-term exposure cases, the risks were acceptable though the amount of detected aromatic amines was relatively high in particular samples. The amount of exposure and the risk level might be overestimated as a series of assumptions were made under extreme conditions.

1. Introduction

Azo dyes are a group of organic compounds which contain azo bonds. They are widely used in textile industry and almost 70% of synthetic dyes contain azo group (Golka et al., 2004). As stated by Qian et al. (2013), 7%–8% of azo dyes are prohibited by governmental regulations as they can release carcinogenic aromatic amines, such as benzidine and 3,3′-dimethylbenzidine. In recent years, the probability of occurrence of textiles with excessive banned azo colorants in the market has dropped around 90%. Mao and Yang (2007) reported that the content of banned azo colorants in 13.6% of textiles inspected by governmental labs were found to exceed the limit in 2004. According to a questionnaire survey from 12 governmental labs in 2016, this number has fallen to 0.96% and only one third of these defective products would contact with skin directly. However, the public concern on health risk of azo colorants in textiles remains at a high level since they are potential carcinogenic substances. Whenever certain textile products are reported to contain banned azo dyes, it usually generates a wide media attention. Therefore, people would easily fall into panic and this might result in potential risk of social problems.

In the past years, several studies were conducted on human exposure to azo dye precursors. It has been proven that chronic exposure to aromatic amines would lead to bladder cancer (Bi et al., 1992;

Carreon et al., 2010; Sorahan, 2008; You et al., 1990). Additionally, Zeilmaker et al. (1999) concluded that the dermal exposure to certain amount of aromatic amines from textiles may lead to cancer risk. Since 1990s, the usage of azo dyes in textile coloration has been strictly regulated by the German government. Later on, a number of countries introduced similar regulations. At present, azo dyes which are able to release specific aromatic amines are prohibited in most countries of the world.

Despite the fact that a number of risk assessments have been conducted on azo colorants in textiles, the majority of them focused on the extractable amines in liquid phase. In reality, not only from sweat or saliva could dyes be extracted, but also the direct rubbing between clothes and skin would bring dyes to the skin surface. Additionally, most of these assessments were performed more than 10 years ago and the dye industry has changed a lot. It is necessary to apply a new approach to assess the risk of this type of compound in textiles.

In the present study, a semi-quantitative risk assessment is conducted. Compared to previous studies, a novel model towards consumer exposure is designed to determine the absorption of leachable azo dyes from textiles. The risk of exposing to carcinogenic amines is assessed by considering toxicity data from certain toxicity databases. Finally, a nomograph tool is used to assess the risk level.

2. Material and methods

2.1. Samples and materials

Twenty textiles obtained from Guangdong Testing Institute of Product Quality Supervision (GQI) were tested. All samples were found to contain leachable aromatic amines that exceeded the OEKO-TEX standard, which was 20 mg/kg (OEKO-TEX, 2017), according to previous inspections. L-histidine monohydrochloride monohydrate (CAS No. 5934-29-2, Chemical grade) was purchased from Shanghai Textile Industry Institute of Technical Supervision. Sodium dithionite (CAS No. 7775-14-6, Analytical grade) was purchased from Tianjin Fuchen Chemical Reagents Factory. All other chemicals (Analytical grade) were purchased from Guangzhou Chemical Reagent Factory. Shimadzu G-CMS-QP2010plus was used for the characterization.

2.2. Preparation of artificial sweat

A modified preparation process of artificial sweat was used (ISO 105-E04:2013). 0.5 g of L-histidine monohydrochloride monohydrate, 5 g of sodium chloride and 5 g of disodium hydrogen orthophosphate dodecahydrate (CAS No. 10039-32-4) were dissolved in distilled water. The solution was made up to 1 L with distilled water. It was then adjusted to pH 6.8 with 0.1 mol/L sodium hydroxide solution.

2.3. Exposure scenario

2.3.1. Principles

In this paper, the leaching of azo dyes was experimentally determined by a dermal exposure model. The extractable azo dyes was conservatively assumed to be 100% converted to aromatic amines. The interaction between skin and textiles in daily life could be classified into three types. The first type is the dry contact, which is described by dry rubbing scenario in 2.3.2. It represents the contact between clothes and skin without sweat effect. The interaction between clothes and skin with sweat is defined as wet contact. It could be subdivided into two types, one is wet rubbing (2.3.3) and the other is wet extraction (2.3.4). white cloths were used as simulated skin in this experiment.

2.3.2. Dry rubbing scenario

A modified rubbing process was applied (ISO 105-X12-2001). First, a piece of cotton rubbing cloth (50 mm × 50 mm) was mounted on a rubbing finger. Then the rubbing finger would rub to and fro in a straight line 50 times, along a (104 ± 3) mm track onto the sample (50 mm × 140 mm). Then a new piece of rubbing cloth was used in the process and a total of 10 pieces of cloth were used for one sample. Dry rubbing test was regarded as an accelerated resistance test of the color of the samples. After a 500-time rubbing, the surface condition of a sample was regarded to be equal to surface condition when it was worn out. Later, those 10 pieces of cloth were immersed in citrate buffer solution at 70 °C for 30 min (EN 14362-1:2012). Sodium dithionite solution was added to reduce azo dyes. Then the aromatic amines were extracted with ether. Finally, the amount of aromatic amines was determined by GC-MS.

2.3.3. Wet rubbing scenario

The cotton rubbing cloths were first immersed in artificial sweat. Then followed the same process in 2.3.2.

2.3.4. Sweat bath scenario

A modified extraction method was used according to the procedures provided by Oomen et al. (2003). 5 g of sample was immersed in 30 mL of artificial sweat at 37 °C for 16 h. The azo dyes were further reduced by sodium dithionite and extracted with ether, followed by GC-MS for the quantitative analysis. For a piece of cloth, only the inner surface would directly contact with skin. Hence, it was assumed that only one third of leachable amine could reach the skin and be absorbed, while the left was retained on the fabric.

2.4. Color fastness to perspiration

Each sample was immersed in artificial sweat for 30 min (ISO 105-E04:2013). Then it was placed in an oven at 37 °C for 4 h. Later, the change of each sample in color was measured.

3. Theory

3.1. Mechanism

The absorption mechanism of aromatic amines could be divided into several steps. Firstly, free amines and azo dyes migrated from textiles onto skin surface (U.S. EPA, 2011). Secondly, free aromatic amines penetrated through the skin, while azo dyes might be reduced to amines by skin microorganisms or by specific enzymes (Stingley et al., 2010). Then they were absorbed by the skin. Or azo dyes might be absorbed through the skin directly and then degraded by reductive enzymes in the human body.

In the proposed exposure model, two dressing situations are considered. Firstly, during most of the daily time, no liquid is considered to be involved in the contact between fabric and skin, which is called dry rubbing scenario. Secondly, during vigorous exercise, the exposure scenario is simplified as the combination of wet rubbing scenario and sweat bath scenario. The vigorous exercise is assumed to occur once a week and each exercise lasts for 2 h. In ideal case, the shirt is considered to be completely wet with sweat during the whole period. In this study, two exposure models are proposed by the combination of different scenarios discussed above.

3.2. Acute exposure model

Acute exposure investigates the maximum possible uptake of carcinogenic amines in a short period. The proposed injury scenario is that an adult wears a T-shirt with regulated azo dyes for a 2-hour intense exercise. Therefore, a combination of wet rubbing scenario and sweat bath scenario is considered in this model. The model is expressed by the following equations, detailed explanations of symbols are shown in Table 1.

$$E_w = A \div T \div W_2 \tag{1}$$

$$E_s = A \div W_2 \times M \tag{2}$$

$$A = D \times W_1 \times P \times F_s \times F_a \tag{3}$$

$$E_{total} = E_w + E_s \tag{4}$$

3.3. Chronic exposure model

Chronic exposure investigates long-term percutaneous exposure to the azo dyes in clothes. The proposed injury scenario is that an adult could wear two pieces of T-shirt for three years consecutively. It is assumed that after three-years' wearing, both of the two shirts are worn out. As a result, the leachable azo dyes could be absorbed by human body as much as possible. Therefore, a combination of dry rubbing scenario, wet rubbing scenario and sweat bath scenario are considered in the model.

$$E_w = A \div T' \div W_2 \tag{5}$$

$$E_s = A \div T'' \div W_2 \times N \tag{6}$$

$$E_{total} = E_d + E_w + E_s \tag{7}$$

The detailed explanations of symbols are shown in Table 1.