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Exposure Assessment Model of the Cadmium Ion in Textiles

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Abstract

Textile products due to the industrial design will be left wide variety of chemical substances, when human contact with these chemicals can cause acute injury or chronic cumulative, so the research of exposure assessment of textile products is necessary. Due to cadmium is harmful to human health,we select the cadmium ion as the research object. In this paper, samples from some cities in Shandong were cadmium ion detection, analysis of data and derived their form of distribution. By drawing on the EU recommended harmful chemicals exposure assessment methods, we established a textile heavy metal exposure assessment model, and completed the application and verification. From the result of using this model to assess the amount of cadmium expose to human, we found that could have a bad effect on human body.

***Keywords**: textiles; cadmium; distribution form; exposure model*

1. Introduction

Due to the vast use of chemical substances in textiles[1], harmful residues in textiles may hurt human skin or organs when they achieve a certain amount. Therefore, the potential danger of harmful residues in textiles remains a matter of major concern.

American experts have been done a lot of research on human health exposure assessment[2]. The US EPA is also in a leading position in the field of study and application of exposure assessment on chemicals and hazardous substances in products. It provides the basic principles and methods of exposure hazard assessment for a single kind of chemicals[3] [4] [5]. The formulae is：

（1） $$I = \frac{C \times CR \times EFD}{BW} \times \frac{1}{AT}$$

EU established the skin and respiratory exposure assessment models based on exposure pathways[6]. Two substances, volatile substances and non-volatile chemicals, were generally considered when the pathway was through skin.

In China, the risk assessments of environment, agriculture and food have made certain research. The assessment of exposure to toxic and harmful substances in food mostly borrowed from the United States and European Union principles of food and some dietary exposure assessment methods. In the field of product safety, the value of the concentration of hazardous substances has been limited, but has yet to establish the appropriate exposure assessment models.

This paper is based on the EU's exposure calculation model to establish the exposure assessment model that is applicable to Chinese textile products. According to its Chinese Academy of Inspection and Quarantine long focus on textiles that, on textiles can have 10 kinds of heavy metal residues. They are nickel, zinc, chromium, cobalt, mercury, arsenic, cadmium, antimony, lead, copper. In this paper, cadmium was selected as the research object.

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Section2 analyzed the toxicity of cadmium ions and cited the EU and China laws which provisions on cadmium concentration limits. A feasibility analysis of the reference of European model is conducted in Section3. The exposure model is established and through the analysis of the data detected to modify parameters in Section3. Finally, the model calculates the exposure of cadmium ions.

2. The Hazards and Relevant Provisions of Cadmium Ions in Textiles

According to its Chinese Academy of Inspection and Quarantine long focus on textiles that, the cadmium ion is always existed. Cadmium is an environmental contaminant, highly toxic to humans. This biologically non-essential element accumulates in the body, especially in the kidney, liver, lung and brain and can induce several toxic effects, depending on the concentration and the exposure time.

Each country has enacted regulations to limit the concentration of cadmium. The Council Directive91/338/EC of 18 June 1991 prohibits the use of cadmium as a pigment, dye or stabilizer in plastics and its use as plating on metallic surfaces. It provides that may not be used to stabilize the finished products listed below manufactured from polymers or copolymers of vinyl chloride: Articles of apparel and clothing accessories (including gloves) and impregnated, coated, covered or laminated textile fabrics. In any case, whatever their use or intended final purpose, the placing on the market of the above finished products or components of products manufactured from polymers or copolymers of vinyl chloride, stabilized by substances containing cadmium is prohibited, if their cadmium content (expressed as Cd metal) exceeds 0.01 % by mass of the polymer.

The China Textile Industry Association put forward people's Republic of China National Standard Textiles: Determination of total of total lead and cadmium content (GBT 30157-2013).

In this article, we select cadmium in textiles as the research object and use the proper assessment model to calculate exposure.

3. The Establishment of Exposure Assessment Model of Cadmium Ion

We analyzed the characteristics of China and European content of chemicals in textiles, and then established the chemical exposure calculation model for textiles by drawing the EU's exposure calculation model.

3.1. Feasibility Analysis of Model Reference

The exposure pathways of heavy metals in textiles are similar to the exposure pathways of chemicals which EU exposure calculation model applicable to. The pathways are skin contact, inhalation and oral exposure. What’s more, factors affecting exposure in textiles are basically same as the exposure factors in the EU calculation model.

Whether in China or the European Union, the relationships between exposure and influence factors are the same.

Therefore, exposure to toxic and hazardous substances calculation model in establishing textiles, you can learn the relationship between exposure and influence factors, on which the revised parameter values to establish compliance with toxic and harmful substances in textiles exposure calculation model.

3.2. The Establishment of Exposure Assessment Model of Cadmium Ion

The establishment of exposure assessment modelis to select proper parameters by different exposure pathways.

As exposure means of different harmful substances are different and parameters affecting exposure are also variable, calculation of exposure is certain different. EU has the most mature study on calculation of the exposure of chemicals in textiles and establishes skin exposure model, oral exposure model and respiratory exposure model. In this part, by referring to EU exposure assessment model of chemicals in consumer goods and combining characteristics of domestic textiles to make amendments to the EU assess models in order to establish domestic textile exposure assessment model.

3.2.1. Skin Exposure Model

If exposure of chemicals in textiles through skin is calculated, exposures of two substances are generally considered: that of volatile substances and that of non-volatile chemicals.In this part, two calculation models shall be integrated into one and residual coefficient introduced, value of which is 0~1. If chemical substances are not volatile, value of residual coefficient is 1.

(1) The amount of exposure to hazardous substances

$$A_{der}=\frac{C\times W}{S_0}\times S\times D \qquad (2)$$

C —concentration of harmful substances in textiles, mg/kg;

S_0—total area of textiles, cm^2;

W—qualityof textiles, kg;

S—contact area with skin,cm^2;

D—residual coefficient of toxic substances after volatilized in textiles, $0<D\leq 1$.

(2) Absorptionamount of chemical substances by human body

$$I_{der}=c_{der}\times f_{der}\times t \qquad (3)$$

Where,

f_{der} — mass percentage of hazardous substance transferred to the human bodyper unit time;

c_{der}—concentration of hazardous substances exposing to skin, μg/kg;

T—contact time for once.

(3) exposuredose of the human body through skin

$$Ex_{der}=\frac{I_{der}\times n}{bw} \qquad (4)$$

Where,

Ex_{der}—exposure of the human body through skin to toxic and hazardous substances;

t—contact time for once;

n—daily contact frequency.

3.2.2. Oral Exposure Model

Exposure through the mouth is mainly intended for infants and young children, so the toxicity of hazardous substances through oral exposure is more intense. If exposure of hazardous substances through the mouth is calculated, two situations will also be considered: one is that they get in touch with the mouth directly in normal use of the textiles and the other is that they don't get in touch with the mouth directly in normal use of the textiles. However, textiles don't contact mouth generally directly, so the latter situation will be discussed in this part.

(1) Amount of hazardous substances in textiles which people contact with

$$A_{oral}=C_{oral}\times\frac{S}{S_0}\times W\times D \qquad (5)$$

where, C_{oral}—intake concentration of products, kg/m^3。

(2) Intake amount of hazardous substances in textiles through the mouth by a person

$$I_{oral} = C_{oral} \times f_{oral} \quad (6)$$

where, f_{oral}—mass percentage of hazardous substance transferred to the human body through the mouth in each exposure time

(3) Exposure of human body through the mouth

(7) $$Ex_{oral} = \frac{I_{oral} \times n}{bw}$$

The meaning of other parameters is the same as those in skin exposure model.

3.2.3. Inhalation Exposure Model:

Hazardous substances in textiles are volatile so that they can enter human body through the respiratory tract, which mainly consists of formaldehyde.

(1) Concentration of chemicals exposing to human body by breathing

(8) $$C_{inh} = \frac{C \times W \times f_v}{V}$$

Where, f_v—volatilization coefficients of chemicals; V—space around human body,m^3.

(2) In take amount of hazardous substances of human body

（9） $$I_{inh} = C_{inh} \times \frac{Q_{inh}}{24} \times t$$

Where,Q_{inh}—daily respiratory rate of human body；

t—residence time in the environment with chemicals。

(3) Exposure of human body

（10） $$Ex_{inh} = \frac{I_{inh} \times n}{bw}$$

Where, bw—weight of contacted crowd

The meaning of additional parameters where is the same as skin exposure parameters.

4. The Correction of Main Parameters

Determining the model parameters concentration values is to estimate the mean concentration based on the tested concentration and then using it to calculate the exposure dose.

To establish the exposure assessment is based on a large number of detection samples.

The sample data of cadmium ions collected from the textiles parts of the city, Shandong, China. The concentration of cadmium ions was obtained as shown in Table 1.

Table 1. Samples Tested Results

$Cd^{+}/(\mu g \bullet kg^{-1})$				
0.38	0.66	0.01	0.52	0.40
0.30	0.60	0.10	0.42	0.50
0.42	0.64	0.01	0.40	0.48
0.48	0.68	0.14	0.44	0.52
0.56	0.60	0.08	0.38	0.44
0.46	0.62	0.36	0.40	0.50
0.58	0.32	0.18	0.38	0.46
0.60	0.28	0.22	0.34	0.52
0.60	0.18	0.48	0.48	0.50
0.78	0.06	0.38	0.42	0.50
0.78	0.26	0.44	0.48	0.01
0.56	0.20	0.36	0.42	0.01
0.80	0.18	0.38	0.46	0.01
0.54	0.10	0.44	0.34	0.01
0.56	0.01	0.38	0.44	0.01

This paper selects UCL value as concentration values of human exposure to chemical substances [7].

Data distribution is generally normal, lognormal distribution or other [8][9][10], so the value of the calculation UCL, generally starts with the normal distribution test, if not, then the distribution of the other tests. If you can't determine the distribution of morphological data, you can use a non-parametric method of its calculation. Shown in fig1 is the flowchart to calculate UCL value.

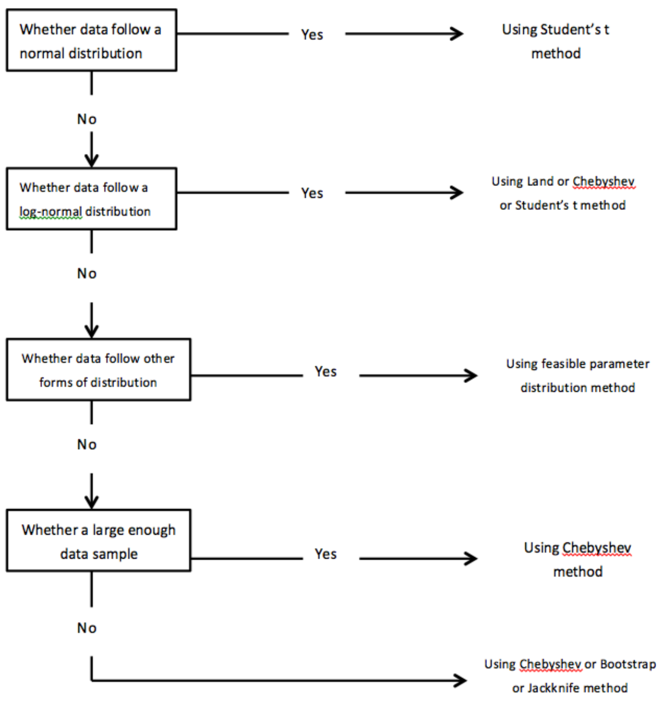

Figure 1. Flowchart Tocalculate UCL Value

Determining the model parameters concentration values is to estimate the averageconcentration based on the tested concentration and then using it to calculate the exposure dose.

Q-Q probability plots in SAPP software can be used to inspect if the sample observationcoincides the population from a specified probability distribution. Q-Q probability distribution detection figures and detection deviation figures of the three kinds of distribution forms were obtained by verifying distribution of inspected cadmium ion concentration, as shown in Figure2~Figure 4.

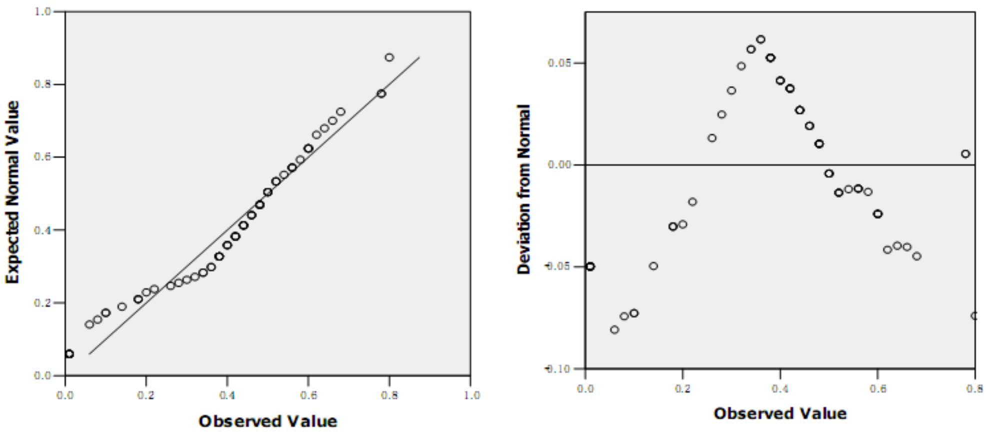

Figure 2. Q-Q Verification and Deviation of the Normal Distribution of Cadmium Ion Concentration

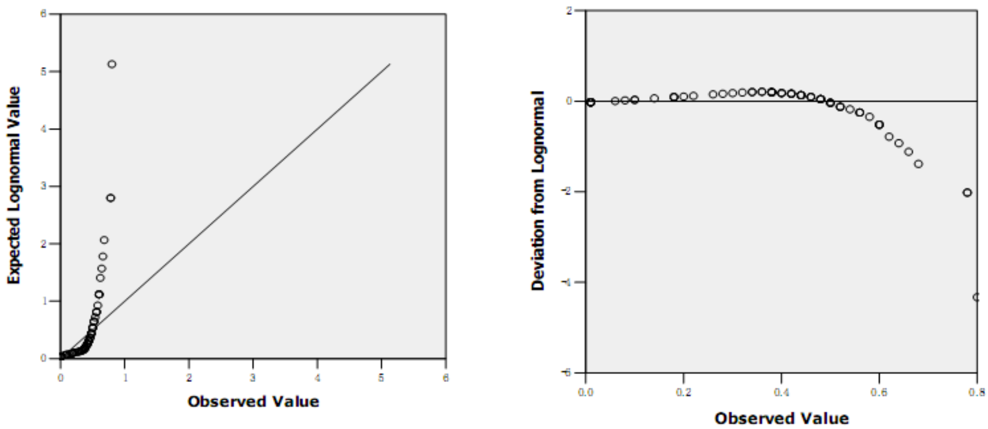

Figure 3. Q-Q Verification and Deviation of the Cadmium Ion Lognormal Distribution

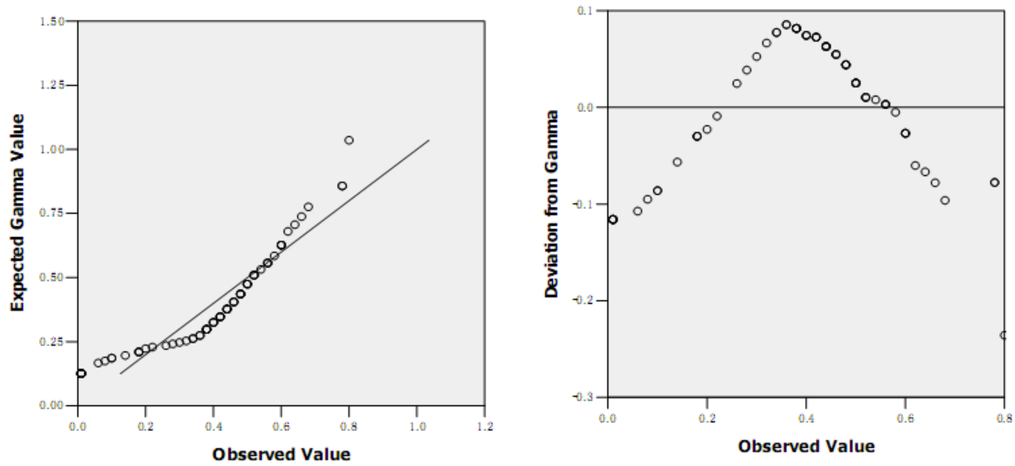

Figure 4. The Concentration of Cadmium Ion Gamma Distribution Verification and Deviation of the Q-Q

Seen from Figure 2~Figure 4, detection deviation of cadmium ion concentration in domestic textiles based on these three distributions are large.Due to the limitations of the sample, it is impossible to sample around the country, so use Bootstrap method to get the distribution of total samples. The basic idea applied in Bootstrap method is to put samples back to the sample group and conduct duplicate sampling [11] [12], that is, put samples back to the sample group after each sampling is finished and only the information about test samples given is relied on.

Bootstrap resampling theory assumes: numerical distribution ofBootstrap resampling samplecomplies with sample overall form[13][14]; mean and standard deviation of numerical distribution of the sampleare in accordance with its population. Therefore, mean and standard deviation of Bootstrap resampling sample in line with normal distribution can be used as robust estimates of limited single sampling.

Bootstrapping standard errors of Bootstrap is a statisticcharacterizing distribution standard error of the sample and defined as follows:

$$SE_{boot,\bar{x}} = \sqrt{\frac{1}{B-1}\sum\left(\bar{x}^{*} - \frac{1}{B}\sum\bar{x}^{*}\right)^{2}} \quad (11)$$

Where, $\bar{X}^{*}$ represents the average of single Bootstrapping resampling,B times of Bootstrap resampling.

Conduct analog sampling 1000 timesfor detection concentration of cadmium ion with Bootstrap method. The histogram of the data obtained is as shown in Figure 5. Then apply Q-Q probability plots of SPSS to test and verify the distribution of the data obtained and the result of the verification can be seen in Figure 5.

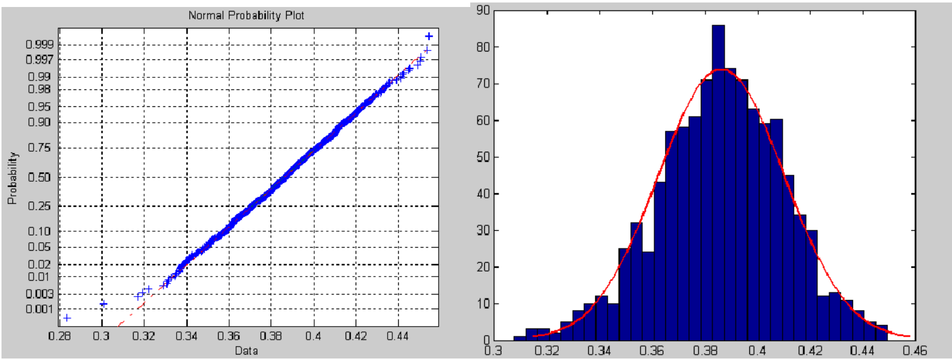

Figure 5. Cadmium Ion Concentration Bootstrap Parameter Estimation and Simulation of the Sampling Results to the Distribution of Morphological Verification

Seen from Figure 5, overall distribution of cadmium ion concentration obtained from analog sampling obeys normal distribution well. Aftersimulation, the mean of population sample obtained is 0.375 and Bootstrap standard error is 0.024. Seen from Figure 4 and Bootstrapping standard error, it is reasonable and effective to use mean and standard deviation of samples that derives from analog sampling ofcadmium ion concentration withBootstrap method as values of limited single sample.

5. Calculation of the Amount of Exposure

It has been verified in the preceding part that sampling results of cadmium ion concentration obtained from Bootstrap analog sampling obeys normal distribution well. The mean of population sample obtained is 0.375 and Bootstrap standard error is 0.024. 95% of confidences upper limit, that is, UCL value is used as the density of chemical substances that human body contacts.

Given thatthe mean and standard error of population sample and assuming a=0.05, obtained UCL value of cadmium ion in domestic textiles is 0.385μg/kg.

Most of textiles used in the test are women shirts. According to the measurement, total area of textiles is 9000cm2 and quality is 0.15kg. UCL value of concentration of cadmium ion in domestic textiles,0.385mg/kg, is used as detectable concentration of textiles and contact area between textiles and human body accounts for half of the total surface area of human body.

It has been calculated according to statistics that the formula of body surface area of adult females in China is $Sb = 0.0073 \times H + 0.0127 \times W - 0.2106$, in which, H stands for the height with cm as measure unit, W represents weight with kg as measure unit and the unit of body surface area is m2. Average height of adult female is 158.6cm and formula of adult weight is $W = (H-100) \times 0.9$, so average weight of females is 52.74kg and average body surface area1.62m2, thus surface area of women shirts which contacts human body being 0.81m2.

Considering exposure of cadmium ionposes the greatest hazard, and given that mass percentage of cadmium ion transferred to the human body through skin was 1, contact time per time 8h, contact frequency once per day and residual coefficient 1.

As cadmium ion is mainly exposed through skin, the exposure dose of cadmium ion in domestic textiles is 3.25 × 10-4μg/（kg・d） calculated by skin exposure model. According to provisions of U.S. Environmental Protection Agency (EPA), human body will not be hurt if the amount of cadmium ion a person contacts during the whole life is lower than 0.005ppm. However, exposure of cadmium ion in domestic textiles to human body has exceeded. It can be seen that exposure of cadmium ion in domestic textiles to human body has been large, which may have a bad effect on human body.

6. Conclusions

The objective of this work aims at establishing a new exposure assessment model of the cadmium ion in textiles. A step-by-step procedure is established in order to ensure the consistent implementation of the proposed methodology. To this end, the case studies completed so far, produced encouraging results in establishing suitable exposure to hazardous substances in textiles calculation model.

The aim is to diminish risk by decreasing the concentration of heavy metals in textiles in order to protect the safety of persons. A first step towards validation of the proposed methodology has been taken by examining the results of the present case study. A further step would be to examine other possible hazards and use the assessment model to calculate the risk quantity of exposure. The proposed model needs to be further implemented, tested and adjusted to a variety of situations in products.

The proposed method is based on a new challenging theoretical background that can support the assessment and improvements of Products Health & Safety conditions.

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