HEALTH RISK ASSESSMENT OF LINEAR ALKYLBENZENE SULFONATE AMONG SNOW WASH WORKERS

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ABSTRACT

The increase in car volume on the road together with existing number of cars would definitely boost with the snow wash industry, leading to increase in snow wash service. The purpose of this study was to determine the concentration of Linear Alkylbenzene Sulfonate (LAS) among snow wash workers and to determine the health risk of LAS through bioaccumulation of the chemicals in detergents used by the snow wash workers. In a survey to determine concentration of LAS, 15 respondents who works at snow wash services were interviewed on demographic information such as age, working experience, duration of works, and number of car washed per day and usage of PPE (glove), and nail samples were collected from all 10 fingers with a stainless nail cutter. The determination of LAS was performed with High Performance Liquid Chromatography (HPLC) method. Carcinogenic and non carcinogenic risks were calculated using calculation of carcinogenic indicator. The mean levels of LAS concentration among snow wash workers were 44.063 ppm. The carcinogenic risk and non carcinogenic risk of LAS were in acceptable range which were 3.660×10^{-6} and 4.658×10^{-4} which does not possess any significant risk to the workers in snow wash services. It was concluded that the snow wash workers were not get risk from the LAS chemical. There is a need for further study of LAS levels in biological samples as there have been few reports concerning LAS levels in biological samples.

ABSTRAK

Peningkatan jumlah kereta di jalan raya bersama-sama dengan jumlah yang sedia ada pasti akan meningkatkan industri mencuci kereta , yang membawa kepada peningkatan dalam perkhidmatan mencuci kereta . Tujuan kajian ini adalah untuk menentukan kepekatan *Linear Alkylbenzene Sulfonate* (LAS) dalam kalangan pekerja pencuci kereta dan untuk menentukan risiko kesihatan LAS melalui bio-pengumpulan bahan kimia dalam bahan pencuci yang digunakan oleh pekerja pencuci kereta. Dalam penyiasatan untuk menentukan kepekatan LAS, 15 responden yang bekerja di perkhidmatan mencuci kereta telah ditanya mengenai maklumat demografi mereka seperti umur, pengalaman bekerja, tempoh bekerja , jumlah kereta dicuci setiap hari dan penggunaan PPE (sarung tangan) , dan sampel kuku dikumpulkan daripada semua 10 jari dengan menggunakan pemotong kuku tahan karat. Penentuan LAS telah dilakukan dengan kaedah HPLC, di mana data tidak risiko karsinogenik dan karsinogenik telah dikira menggunakan kaedah standard. Tahap min kepekatan LAS dalam kalangan pekerja pencuci kereta ialah 44,063 ppm. Risiko karsinogen dan risiko bukan karsinogen LAS berada dalam julat yang boleh diterima iaitu 3.660×10^{-6} dan 4.658×10^{-4} yang tidak memiliki apa-apa risiko yang besar kepada pekerja-pekerja dalam perkhidmatan mencuci kereta. Ia telah membuat kesimpulan bahawa pekerja pencuci kereta tidak mendapat risiko daripada kimia LAS itu. Terdapat keperluan untuk kajian LAS dalam sampel biologi kerana hanya terdapat beberapa laporan mengenai tahap LAS dalam sampel biologi

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LIST OF ABBREVIATIONS

ABS	Branch Alkylbenzene Sulfonate
AE	Alkylethoxylates
AES	Alkyl Ethoxy Sulphates
APE	Alkylphenol Ethoxylates
AS	Alkylsulphates
CESIO	European Committee on Organic Surfactants and their Intermediates
HERA	Human and Environmental Risk Assessment on ingredients of Household Cleaning Products
HPLC	High Performance Liquid Chromatography
LAS	Linear Alkylbenzene Sulfonate
LOAEL	Lower Observed Adverse Effect Level
NOAEL	No Observed Adverse Effect Level
QAC	Quaternary Ammonium Compounds
SPE	Solid Phase Extraction
US EPA	US Environmental Protection Agency
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

This chapter provided the general ideas on the subjects that were studied included background of study, problem statement, research question, research objective, scope, significant of study, conceptual framework and expected result.

1.1 BACKGROUND OF STUDY

A surfactant is briefly defined as a material that can greatly reduce the surface tension of water when used in very low concentrations. It is a form a unique class of chemical compounds. They generally consist of a polar head group (either charged or uncharged), which is well solvated in water, and a nonpolar hydrocarbon tail, which is not easily dissolved in water. Hence, surfactants combine hydrophobic and hydrophilic properties in one molecule. They have the ability to radically alter surface and interfacial properties and to self-associate themselves into aggregates called micelles. These properties allow to apply surfactants in wet ability modification, detergency, and the displacement of liquid phases through porous media on one hand, and to stabilize dispersions (including foams, froths and emulsions) on the other. Linear alkylbenzene sulphonates (LAS), branch alkylbenzene sulphonates (BABS), alkyl ethoxy sulphates (AES), alkylsulphates (AS), alkylphenol ethoxylates (APE), alkylethoxylates (AE), and quaternary ammonium compounds (QAC) are the commonly used commercial surfactants (CESIO statistics, 2009).

Linear Alkylbenzene Sulfonate (LAS) is an anionic surfactant. It was introduced in 1964 as the readily biodegradable replacement for highly branched alkylbenzene sulfonates (ABS). Commercially available products are very complex mixtures containing homologues with alkyl chains ranging from 10 to 14 carbon units (C10-14 LAS). Furthermore, since the phenyl group may be attached to any internal carbon atom of the alkyl chain, each homologue contains 5-7 positional isomers.

LAS is one of the major anionic surfactants used in laundry and cleaning products. LAS are commonly used in many household detergents, including laundry powders, liquids, and tablets. It lowers the surface tension of water, enabling soils and stains to loosen and release from fabrics and surfaces. LAS provide excellent removal from fabrics of oily soils and of particulates like clay. LAS have excellent foaming characteristics important to the consumer acceptance of detergents.

According to the latest statistic of car industry in Malaysia (total population: 28 million people), the total vehicles sales volume in the first half 2012 (between January and June) is 331,221 units and is forecasted to hit a new record of a total of 615,000 units at the end of 2012 compared to 605,156 units and 600,123 units in 2010 and 2011, respectively.. The increase in car volume on the road together with existing number of cars would definitely boost with the car wash industry, leading to increase in car wash service, particularly in high population of residential area located in urban areas. Thus, the use of detergents in order to run the snow wash service will increase. This will lead to the bioaccumulation of anionic surfactants such as linear alkyl benzene sulphonate in the snow wash worker's body also will be increase. (W.J. Lau, 2013)

Furthermore, anionic and cationic surfactants have potential to damage human skin; SLS is a powerful irritant and increased the trans epidemeral water loss in human volunteers in vivo (R.A. Tupker, J. Pinnagoda, J.P. Nater, 1990) and both anionic and cationic surfactants swell the stratum corneum and interact with intercellular keratin.

Fingernails and toenails are keratinous matrices with the potential capability to accumulate substances and metabolites. Nails are often used for forensic purposes, e.g, in cases or arsenic intoxication (Luca Morini, 2012), and for determination of occupational/environmental exposure to lead, cadmium, copper, and other metals or drugs of abuse (Luca Morini, 2012)

In comparison to other biological samples, there are many advantages in utilizing nails as biomarker of exposure, especially because specimen collection is noninvasive and the nails can be easily sampled, stored, transported and handled. The non-invasive sampling would facilitate research concerning children and large population. Moreover, once compounds are incorportated into keratin of nails, the levels remain isolated from other metabolic activities in the body with no flunctuation due to changing body metabolic activities. Thus, nails could reflect long-term exposure. Besides, nails take several months to grow out and are used for the measure of past exposure. Human nails have been extensively employed as a biomarker of toxic element exposure and nutritional mineral status (Wei Liu, 2011)

The purpose of the present study is to determine concentration of LAS through snow wash worker's nails and also to determine the health risk of LAS through bioaccumulation of the chemicals in detergents used by the snow wash workers.

1.2 PROBLEM STATEMENT

LAS bioaccumulation has become an increasing human health concern as emerging evidence suggests reproductive toxicity, skin irritation, and eye irritation, and some LAS are considered to be likely human carcinogens. Moreover, occupational exposures to LAS may occur during formulation of various products, but no data are available on the effects in humans of chronic exposure to these compound.

The snow wash services are not excluded in using detergents as their main materials of their service. Thus, it is not aquavalent if the workers at the snow wash services are also exposed to the fate of LAS. Moreover, anionic materials such as LAS tend to permeate relatively poorly through human stratum corneum upon short time period exposure (for example when mimicking occupation exposure) but permeation increases with application time.

Thus, it is essential to determine the health risk assessment of LAS among the snow wash workers in order to know if they are get affected seriously by this surfactants or not.

1.3 RESEARCH QUESTION

There are two research questions to be considered in this study which were:

1.3.1 What is the concentration of LAS in snow wash worker's nails?

1.3.2 What is the health risk of LAS through bioaccumulation of the chemicals in detergents used by the snow wash workers?

1.4 RESEARCH OBJECTIVE

In order to ensure the research is in right direction, two research objectives were being established as follows:

1.4.1 To determine concentration of LAS in snow wash worker's nails.

1.4.2 To determine the health risk of LAS through bioaccumulation of the chemicals in detergents used by the snow wash workers.

1.5. RESEARCH HYPOTHESIS

The hypotheses of the research were:

1.5.1 The concentration of LAS is low among snow wash workers.

1.5.2 The health risk of LAS is not significant towards snow wash workers.

1.6. SCOPE OF STUDY

The scope for this study was focused on laboratory experimental design to evaluate human health risk assessment on LAS bioaccumulation through nail of snow wash workers. Fingernails were obtained from 15 snow wash workers, 15-50 years old, during September-October, 2014. The purpose of this study was to determine the concentration of LAS that accumulates in snow wash worker's body.

The samples analyzed through the laboratory experiment via High Performance Liquid Chromatography (HLPC) under optimum instrumental collections.

From the data collected the health risk of LAS through bioaccumulation of the chemicals in detergents used by the snow wash workers can be measured.

1.7. SIGNIFICANCE OF STUDY

This study made a broad understanding of bioaccumulation of LAS may cause many adversely affect to human and ecosystem. It is important to determine the accumulation of this surfactant in order to know the fate of these surfactants towards the human's body. Furthermore, the determination of LAS in nail samples has not been reported. Thus the determination of concentration of LAS among snow wash workers by using nail samples was the purpose of this study.

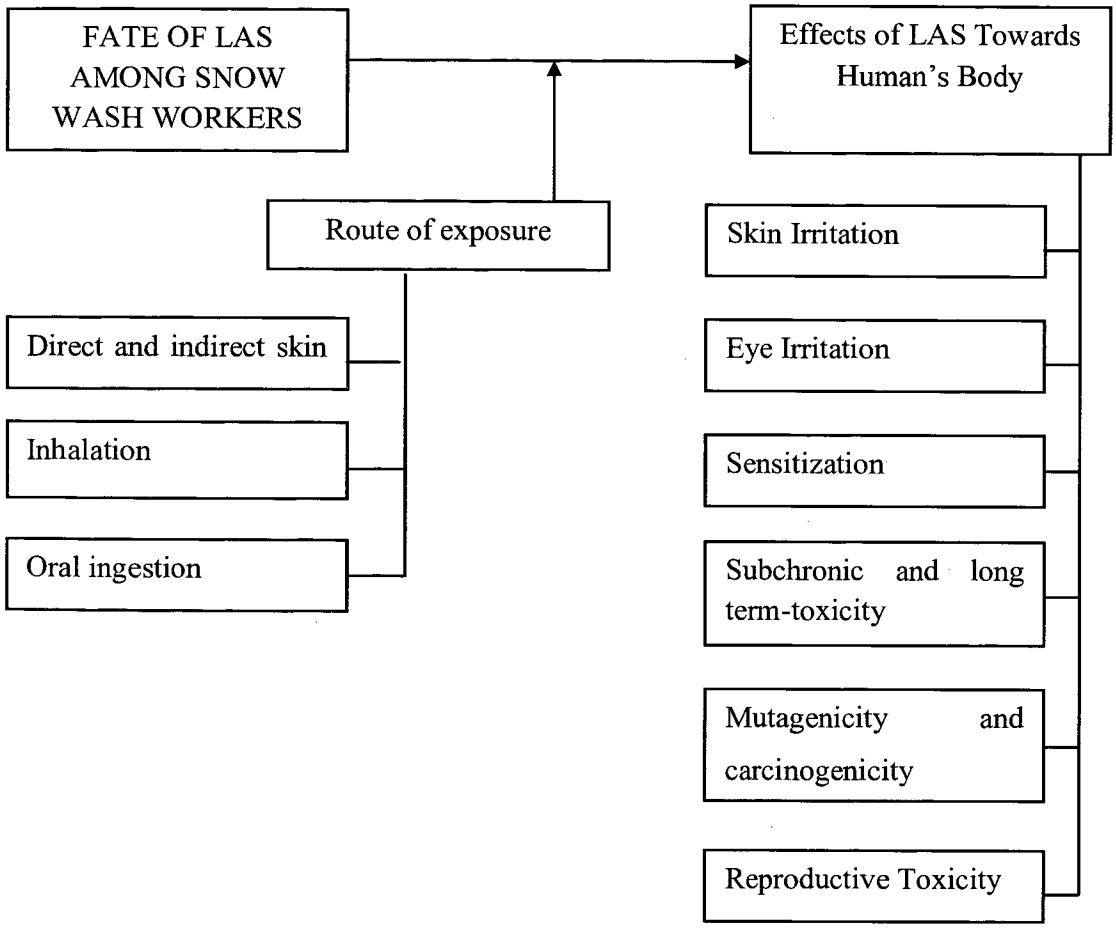
Apart from that, this study also may give awareness to the snow wash services by showing them the affects of these surfactants to them.

Besides, in the academic area, this study can be the references for the further study of the health risk assessment of LAS. Apart from that, there are not many studies on health risk assessment of LAS towards human's body. Thus, this study was a preliminary study in order to determine LAS in biological samples such as fingernails.Therefore, this study can be one of the references for those that want to further the study about this surfactants and its fate among the detergents user.

1.8 CONCEPTUAL FRAMEWORK

Figure 1.1 illustrates the conceptual framework of this study related to route of exposure to LAS and effects of LAS towards human's body. Route of exposure to LAS are direct and indirect skin, inhalation and oral ingestion. The effects of LAS towards human's body are skin irritation, eye irritation, sensitization, subchronic and long term toxicity, mutagenicity and carcinogenicity and also reproductive toxicity.

Figure 1.1: Conceptual framework of study



1.9 OPERATIONAL DEFINITION

1.9.1 Direct and indirect skin

The snow wash workers being exposed to the LAS through the bioaccumulation of the surfactant in the skin as they are usually using their hands in doing their jobs.

1.9.2 Mutagenicity and carcinogenicity

The probability effects of LAS towards snow wash workers.

1.10 STUDY LIMITATION

The determination of LAS in nail samples has not been reported. Moreover, there have been few reports concerning LAS levels in biological samples. To obtain the more reliable and accurate data, future researchers are encouraged to use the combination of bio-indicators such as hair and blood sample in one particular research to determine the LAS exposure among the snow wash workers. In term of choosing fingernails as the bio-indicators compared to blood, this is due to the nails were more exposed to the detergents as the snow wash workers used their bare hands to wash the cars without using glove. In fact, the blood analysis will be more accurate and effective in order to trace all the elements that exist due to the occupational exposure to the surfactants. However, drawing blood from the workers requiring their medical consent and it only can be done by the presence of competent person such as medical assistant or medical doctor to carry out the procedure.

1.11 SUMMARY

This study aims to determine the concentrations of LAS among snow wash workers and to determine the health risk of LAS through bioaccumulation of the chemicals in detergents used by the snow wash workers. This is because occupational exposures to LAS may occur during formulation of various products, but no data available on the effects in humans of chronic exposure to this compound. Furthermore, the determination of LAS in nails has not been reported. Thus the determination of concentration of LAS among snow wash workers by using nail samples was the purpose of this study.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

The purpose of this chapter is to provide a review of past research efforts related to surfactants, health risk assessment, fate or LAS towards human and environmental fate of LAS. A review of other relevant research studies is also provided.

2.2 SNOW WASH INDUSTRIES

Since 1939, professional car wash businesses offer consumers an easy, time-saving, and practical way to wash dirt and grime from their automobiles. Cleaning an automobile basically consists of the actual removal of oil and dirt, and then treatment to provide protection. Degreasing solvents and cleaning agents remove traffic grime and particulate matter on automobiles, then the subsequent application of wax polishes and protects coatings. The operation of professional car wash facilities, both traditional and modern, generally falls under the following categories: hand car wash, self-service, in-bay automatics, tunnel washes, chemical car wash, and steam car wash facilities.

In the conveyor-operated car wash, the car moves by means of a conveyor through a tunnel and is washed by either friction or frictionless system. The frictionless system uses high-pressure nozzles to spray the car with cleaning solutions, whereas in the friction system, a series of brushes wash the car when moving through the system. In the in-bay automatic process, the car remains stationary while a machine moves back and forth as it washes over the vehicle. In self-service stations, the customer is responsible for washing the car using a low-pressure brush or hoses with nozzles that dispense either water or the cleaning solution at controllable amounts and pressures. In both conveyor and in-bay automatic systems, workers are needed to physically spray some chemicals on the car. The ideal car wash cleaning solution removes road dust, rust stain, dirt, films from brakes, and grime from the automobile with minimal effort. (Homer C. Genuino, 2012).

2.3 ENVIRONMENTAL POLLUTION

A study by Huybrechts *et al.*, (2002) states that cars that are washed in the street can pollute streams, rivers, bays and estuaries. The soaps, oil and grimes that run off the car into the gutters, go into the storm water system. Storm water unlike the water that enters the sewers does not undergo treatment before it is discharged into waterways. Any pollutants in storm water end up in our lakes, rivers, harbors and oceans, and are considered non-point source pollution (EPA, 1994).

A study by Hamada and Miyazald (2004) states that wastewater from car washing stations contains a number of impurities such as sand and dust, free oil, grease, oil/water emulsion, carbon, asphalt, salts, surfactants and organic matter, which is discharged directly into municipal sewage treatment plant. (Zulfiqar Ahmad Bhatti, 2011).

A study by Verge et al. (2000) shows that LASs (LAS) are the most commonly used synthetic anionic surfactants, with an estimated global consumption of 2.8 million tonnes in 1998. As a result, they are one of the most frequently found xenobiotics in urban wastewaters; they occur in high concentrations in STW effluents, and

consequently in their receiving waters. Holt *et al.*, (2003) predictions indicate that concentrations of LAS in STW influents may be as high as 16 mg/L. This means that, whilst they are highly degradable, with more than 95% removed during the treatment process, concentrations in effluents can still be in hundreds of μg/L. For example, concentrations of up to 444μg/L have been detected in densely populated areas, although they are more commonly found in the range of tens of μg/L. Further accumulation of LAS in river waters is unlikely, since they are easily degraded in aerobic conditions, although they may potentially occur in higher concentrations in anaerobic sediments (Catherine A. Harris, 2009).

2.4 SURFACTANTS

Most detergents contain larger amounts of anionic surfactants than nonionic surfactants. Detergents are the parts of a large group of chemical compounds, collectively referred to as 'surface active agents or surfactants', which all have the property, to some degree, of reducing surface and interfacial tensions, i.e., they are emulsifying agents. In other words, the detergents are classified as emulsifying and cleaning agents who frequently possess the antibacterial properties; through the term detergent has become a common household name for a chemical cleansing agent. Soaps (anionic detergents) have been used s detergents for many years to emulsify the grease and to loosen the keratin, dirt, and similar debris (Jain Varsha, 2011) .

Soap is no longer as important in many parts of the world as it was before the existence of mass-produced synthetic surfactants. Although soap powders for washing once contained as much as 40% soap as their sole surfactant, powder detergents have since the 1950s been formulated with mixtures of far more effective surfactants in considerably smaller proportion. A further reason for the decreasing use of soap in laundry detergents is its sensitivity to water hardness, manifested through inactivation due to formation of lime soap, which tends to accumulate on fabrics and washing machine parts. Such accumulation reduces the absorbency of fabrics and their permeability to air, and eventually through "aging" causes laundry to become discolored and to develop malodors. The primary function that remains for soap currently is as a foam regulator in laundry detergents in Europe. Nonetheless, soap has remained

worldwide the largest surfactant by volume. It is still the surfactant of choice in many countries with low gross national product. (Smulders, 2002)

Surfactants form a unique class of chemical compounds. They generally consist of a polar head group (either charged or uncharged), which is well solvated in water, and a nonpolar hydrocarbon tail, which is not easily dissolved in water. Hence, surfactants combine hydrophobic and hydrophilic properties in one molecule. They have the ability to radically alter surface and interfacial properties and to self-associate themselves into aggregates called micelles. These properties allow to apply surfactants in wettability modification, detergency, and the displacement of liquid phases through porous media on one hand, and to stabilize dispersions (including foams, froths and emulsions) on the other. Synthetic surfactants are economically important chemicals. They are widely used in household cleaning detergents, personal care products, textiles, paints, polymers, pesticide formulations, pharmaceuticals, mining, oil recovery and pulp and paper industries.

Surfactants (surface-active agents) are a diverse group of chemicals consisting of a polar, water-soluble head group and a nonpolar hydrocarbon tail group, which is not soluble in water (HRENOVIĆ, 2010). Surfactants are best known for their solubility and cleaning properties which secured them a place among detergents and other cleaning products. Massive quantities of surfactants are being use in households and industry every day, and most ended up dispersed in different environmental compartments (soil, water, sediment). More than 4.2 million tones of detergent products and 1.2 million tones of softener products were used annually in Western Europe ten years ago In the same period the world production of synthetic surfactants was 7.2 million tonnes. In 2006, worldwide production of surfactants rose to 12.5 million tonnes, and in 2007 over 3 million tonnes were produced in Western Europe alone. (HRENOVIĆ, 2010)

Surfactants are split into groups depending upon the nature of their hydrophilic head groups: anionic, cationic, non-ionic, amphoteric. As with all systems of classification there are grey areas and some may transcend the boundaries. For example, amine ethoxylates are generally non-inonic if the lipophile is a long chain and cationic if it is a short chain. Also, amphotheric surfactants can change to behave as cationics depending upon pH.