J. of Korean Oil Chemists' Soc.,
Vol. 33, No. 1. March, 2016. 195~203
ISSN 1225-9098 (Print)
ISSN 2288-1069 (Online)
http://dx.doi.org/10.12925/jkocs.2016.33.1.195

Determination of Heavy metals on the non-woven in wet wipes using ICP-MS

Sung-Min Choi* · Jin-Kun Song** · Sang-Jin Kim**,***,†

*PCAM Korea, 12, Techno 11-ro, Yuseong-gu, Daejeon 34036, Korea
**Chemolee Lab Corporation, 3820 Conflans Rd, Irving, TX 75061, USA
***Department of Cosmetic Science, Daejeon Health Sciences College, 21, Chungjeong-ro, Dong-gu, Daejeon 34504, Korea
(Received February 16, 2016; Revised March 18, 2016; Accepted April 1, 2016)

Abstract : Heavy metals have been analyzed on the non-woven from the 24 kinds of wet wipes and 8 kinds of mask packs. The following materials used in the non-woven according to each product are: rayon+polyester for the 12 wet wipe products, rayon+PET for the 5 wet wipe products, and rayon, cotton, rayon+polyester+cotton, pulp+polypropylene for the rest of the wet wipe products. No further information on the materials was found on the 3 wet wipes and 8 mask packs. However, polyester may be applied for the non-woven in wet wipes, because PET is part of the polyester group. The heavy metals analysis in the 24 kinds of wet wipes and 8 kinds of mask packs revealed the following: arsenic was found from 47.14±1.13 to 71.75±1.64 ㎍/L on the 3 products, the amount of nickel in the 2 products were 261.26±5.14 and 1,242.63±43.71 ㎍/L, 53.69±1.45 and 103.52±2.02 ㎍/L on the 2 mask packs. It was also revealed that lead was detected from 7.23±0.32 to 55.67±1.46 ㎍/L on the 6 wet wipes, antimony was ranged from 187.86±5.24 to 19,558.35±3,537.30 ㎍/L on the 12 wet wipes, and 5.25±0.25 and 8,936±55.22 ㎍/L on the 2 mask packs. No cadmium, mercury, or thallium were detected from all the products. A high concentration of antimony might come from antimony trioxide, which was used as a catalyst when manufacturing the polyester. Therefore, it is strongly recommended that a non-woven used for cosmetic purposes should not use heavy metals as a catalyst when manufacturing, and it's important to clarify which materials are used in non-woven.

Keywords : Wet wipes, mask pack, non-woven, heavy metals, ICP-MS

1. Introduction

The MFDS (Ministry of Food and Drug Safety) recently announced that the cosmetics has been covered and broadened its area of application from skin and hair to teeth and oral mucosa, based on the definition of cosmetic issued by the Cosmetic Act. As a result, toothpaste, oral care products, and wet wipe for baby and restaurant use are regulated as cosmetics [1]. "Cosmetics" are defined as goods used by applying, rubbing and spraying or in similarly applying to the human body in

†Corresponding author
(E-mail: kimsj@hit.ac.kr)

order to increase attractiveness by cleanse or beautify the body, brighten the appearance, and maintain or improve the health of skin and hair. All of which have insignificant effects on the human body as defined in subparagraph 1 of Article 2 of the Cosmetic Act [2]. Companies that manufacture the wet wipes used for the human body are required to institute and practice quality control, safety regulation, indication of which raw materials are used, and advertisement according to the Cosmetic Act [3]. The wet wipe is a moisturized non-woven used for cleaning the human body [4] and consists of liquid and solid phases. The major role of the liquid phase is to clean and supply moisture to the human body, especially for infants; preserve the product, supply the fragrance according to the customer's needs, and improve product quality. The major ingredient of the liquid phase would be one or more of the followings: plant extracts, including aloe, chamomile, peppermint, jojoba, eucalyptus, olive, lavender, lime, green tea, tea tree oil, and propylene glycol, butylene glycol, hexylene glycol, citric acid, tocopherol, sodium benzoate, panthenol, shea butter, glyceryl caprylate, lecithin, dimethicone, cyclopentasiloxane, and etc,.

The NIFDS (National Institute of Food and Drug Safety Evaluation) collected 120 wet wipes from the market, and evaluated risk assessment on 28 components. Toxic contaminants, such as ethanol, dimethylol dimethyl hydantoin, ethylene oxide, coconut diethanolamide, propyl paraben, methylisothiazolinone, chloromethylisothiazo-linone, 1,2-benzisothiazolin-3-one, poly hexamethylene biguanide hydrochloride, 1-butoxy-2-propanol, sodium lauryl ether sulphate, trimethylammonium chloride, and alcohol ethoxylate, were detected. However, the amount found was not considered toxic or hazard. The amount of alcohol ethoxylate was as low as 1/500 of the regulation limit and lower than 1/100 of the regulation limit on the rest of 19 contaminants [5]. Also, the KATS (Korean Agency for Technology and Standards) investigated the 51 wet wipes containing cetrimonium, which is used as germicide and preservatives, and found that the amount of cetrimonium bromide in the wet wipes were ranging from 0.0055% (55 mg/kg) to 0.0604% (604 mg/kg), which is much less than the regulation limit of 0.1% (1,000 mg/kg) [6].

Wet wipes are made of materials such as polyester, polypropylene, cotton, wood pulp, or rayon fibers, and then formed into sheets. They may be packaged individually, or in small or bulk packaging. The characteristic of non-woven has been developed recently. This development includes hydrogel, of which non-woven coated with gel [7], micro fiber which minimize the dynamic friction coefficient [8], and bio-cellulose, of which non-woven is 3-dimensional net shape structure [9-11]. A non-woven is not considered a raw material but, a subsidiary material. Therefore, it should be tested, inspected, and verified under the enforcement regulations of the Cosmetic Act [3]. Rayon, polyester, PET, or cotton is used for non-woven materials. The rayon is made from purified cellulose, mainly from wood pulp, which is chemically converted into a soluble compound. Polyester is one of the polymers, which is made of more than 2 alcohols and carboxylic acids using polycondensation. Polyethylene terephthalate (PET), which is the polymerization of ethylene glycol and terephthalic acid, and poly butylene terephthalate (PBT), which is the polymerization of butanediol and terephthalic acid, are the kinds of polyester. The use of a catalyst when manufacturing PET is inevitable in the industrial or academic area. Metallic oxides, such as Sb, Ti, Ge, Fe, Zn, Co, Pb, Mn, Nb, or their organic compounds are added during the process of PET manufacturing in order to increase the speed of polymerization [12]. However, it is regulated in most countries to use metallic

oxides or their organic compounds due to their harmful side effects. There is a tendency to use something other than metallic catalysts. The use of wet wipes has increased and the market of wet wipes is expected to reach 18.3 million dollars in the year of 2019 [13]. Infant wet wipes are expected to grow 5.4% CAGR (Compound Annual Growth Rate) during 2014 and 2019 [14], and will be expected to grow more in the near future.

The wet wipe market is expected to grow continuously. There has been an increased advancement on the liquid phase of the wet wipe, but not much progress has been made on the safety and toxicity on the non-woven. The purpose of this research is to show how much heavy metals exist in the non-woven wet wipe and guide safer and more environmental friendly ways to manufacture the non-woven.

2. Materials and Methods

2.1. Materials

Thirty two non-wovens, including 21 kinds of wet wipes purchased in the country and 3 kinds of wet wipes purchased from the USA, 4 kinds of national brand mask packs and 4 kinds of international brand mask packs, have been analyzed for the heavy metals. The materials used for the non-woven are rayon+ polyester on the 12 products, rayon+PET on the 5 products, and rayon, cotton, rayon+ polyester+cotton, pulp+polypropylene on each kind, and no further information was available on the 3 wet wipe products and the mask packs.

2.2. Sample Preparation

The method of microwave digestion was used with the application of Milestone start D (Milestone Inc., Shelton, CT 06484, USA). Approximately 0.2 g of sample was added into a PTFE vessel containing 7 mL of 70% HNO_3 (Sigma-Aldrich, St. Louis, MO 63103, USA) and 1mL of 50% HF (Sigma-Aldrich, St. Louis, MO 63103, USA), then performed a microwave digestion. The microwave digestion procedure is shown in the Table 1. The samples were then transferred and diluted with 25 mL of ASTM type 1 water.

2.3 Instrumentation

A NexION 300X ICP-MS (Perkin Elmer, Shelton, CT 06484, USA) was utilized for the measurement of antimony, arsenic, cadmium, lead, mercury, nickel and thallium. The Table 2 showed the test conditions of the ICP-MS. A Milestone DMA 80 Mercury Analyzer (Milestone Inc., Shelton, CT 06484, USA) was applied for the mercury analysis. The mercury analysis did not require any sample preparation. The Table 3 presented the mercury analysis conditions.

2.4. Standard Solutions and Reagents

Multi-element, internal standard, standard stock solutions were purchased from Agilent Technologies (Santa Clara, CA 95051, USA), 70% nitric and 50% hydrochloric acid were purchased from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO 63103, USA), and D.I water was produced by using a Milli-Q system (Millipore, Bedford, MA).

Table 1. Microwave Digestion Program

Step	Temperature (℃)	Power (W)	Ramp (min)	Dwell (min)
1	120	1,000	8	·
2	120	1,000	·	2
3	180	1,000	8	·
4	180	1,000	·	10

Table 2. ICP-MS Instrument Conditions

Parameter	Setting
RF power (W)	1,350
Coolant flow (L/min)	16
Nebulizer flow (L/min)	0.99
Auxiliary flow (L/min)	1.2
Spray chamber	PFA
Nebulizer	Teflon nebulizer
Torch	Quartz torch
Injector	Alumina injector

Table 3. Mercury Analyzer Instrument Conditions

Parameter	Setting
Max, Start temperature	300℃
Purge time	60 sec
Decomposition temperature	750℃
Decomposition time	210 sec
Amalgamator heating time	12 sec
Signal recording time	30 sec
Wavelength	253.65 nm

2.5 Calibration Curve

The four calibration standards, including 0, 10, 50, and 100 ㎍/L, were utilized for the measurement of antimony, arsenic, cadmium, lead, nickel and thallium, and lower range sets of calibration standards, including 0, 2.5, 5, and 10 ㎍/L, were applied for the mercury analysis. Four point external calibrations with standards were used to quantify the elements in the digestate. The value of each R^2 was ranging from 0.9992-0.9999, which showed the very close relationship between concentration and peak area. Each calibration standard graph was presented in the Fig 1.

2.6. LOD and LOQ

LOD (Limit of Detection) is defined as $3\times SD_0$, where SD_0 is the value of the standard deviation as the concentration of the analysis approaches to zero. The value of SD_0 can be obtained by extrapolation from a plot of standard deviation versus concentration where three concentrations are analyzed. On the other hand, LOQ (Limit of Quantification) is defined as $10\times SD_0$. The LOQ on arsenic, mercury and nickel is 007, 0.08, and 0.33 ㎍/L, respectively, and the rest of them are 0.03 ㎍/L. The LOD and LOQ were shown in the Table 4.

Table 4. LOD and LOQ of Heavy Metal Elements (unit; ㎍/L)

Elements	LOD	LOQ	Instruments
As^{75}	0.02	0.07	ICP-MS
Cd^{111}	0.01	0.03	
Ni^{60}	0.11	0.33	
Pb^{208}	0.01	0.03	
Sb^{121}	0.01	0.03	
Tl^{205}	0.01	0.03	
Hg	0.025	0.80	Mercury Analyzer

3. Results and Discussions

The heavy metals analysis on the non-woven from 24 kinds of wet wipes and 8 kinds of mask packs showed that arsenic was ranging from 47.1±1.13 to 71.75±1.64 ㎍/L on the 3 wet wipe products, nickel was 261.26±5.14 and 1,242.63±43.71 ㎍/L on the 2 wet wipe products, 53.69±1.45 and 103.52±2.02 ㎍/L on the 2 mask pack products, lead was ranging from 7.23±0.32 through 55.67±1.46 ㎍/L on the 6 wet wipe products, antimony was ranging from 187.86±5.24 to 19,558±3,537.30 ㎍/L on the 12 wet wipe products, and 5.25±0.25 to 8,936±55.22 ㎍/L on the 2 mask pack products. No heavy metals, such as cadmium, mercury, or thallium were found from the all products. Test results on the wet wipes and mask packs were presented in the Table 5, and 6, respectively.

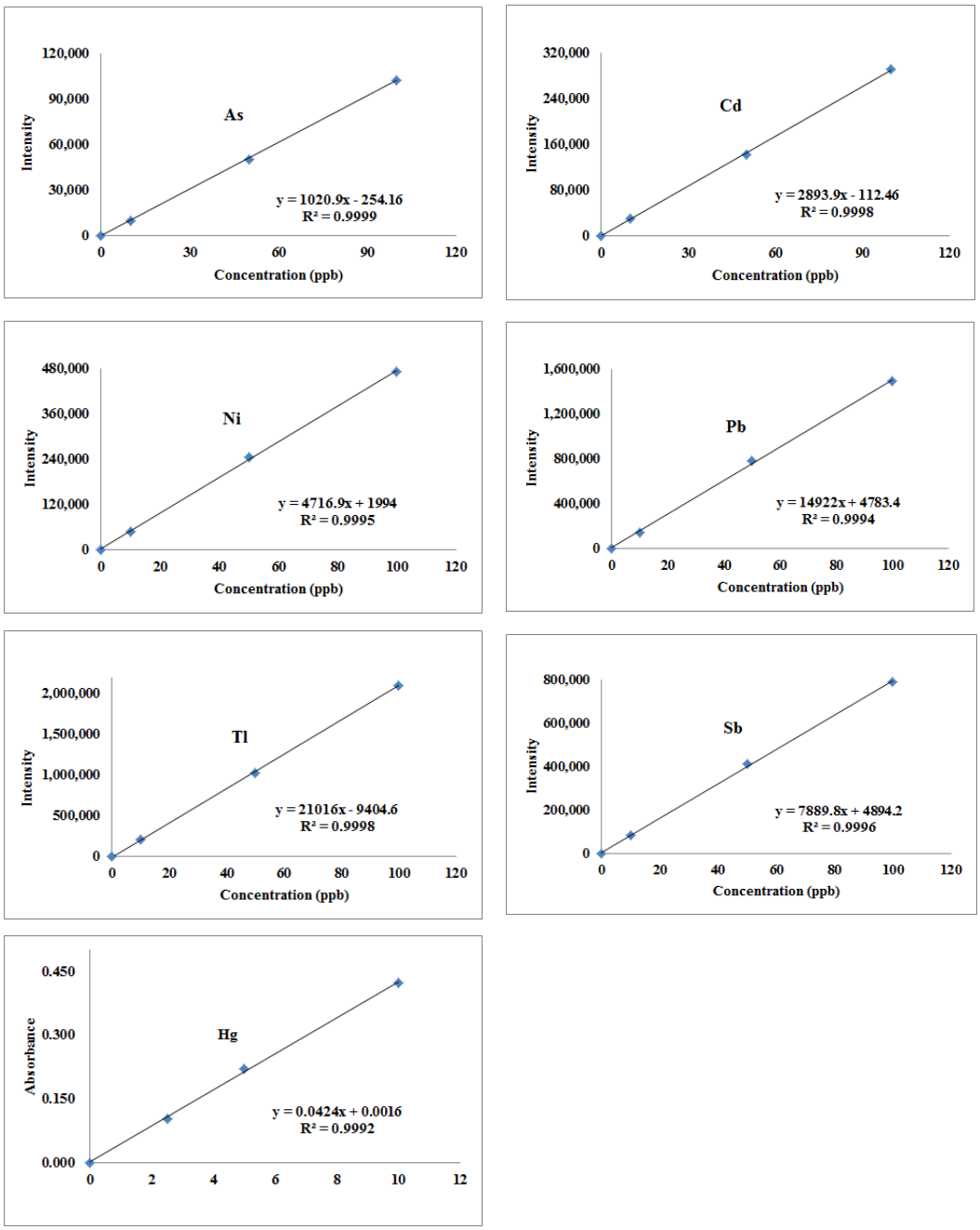

Fig 1. Calibration standard graph of As, Cd, Ni, pb, Sb, Tl, and Hg.

Table 5. Heavy metal analysis on the non-woven from wet wipes (unit; μg/L)

Sample Name	As	Cd	Hg	Ni	Pb	Sb	Tl	Non-woven fabric	Use
BE	-	-	-	-	-	298.93±11.86	-	Rayon+Polyester	Infant
BO	-	-	-	-	-	10,428.77±231.28	-	Rayon+Polyester	Infant
BU	-	-	-	-	-	-	-	Rayon+Polyester	Infant
DR	-	-	-	-	11.08±0.51	8,208.00±53.20	-	Rayon+Polyester	Infant
EC	-	-	-	-	36.77±0.93	281.34±11.71	-	Rayon+Polyester	Infant
GU	-	-	-	-	-	-	-	Rayon+Polyester	Infant
MA	-	-	-	-	-	187.86±5.24	-	Rayon+Polyester	Infant
TO	-	-	-	-	-	-	-	Rayon+Polyester	Infant
CR	-	-	-	-	-	-	-	Rayon+Polyester	General
FR	-	-	-	-	-	352.17±12.78	-	Rayon+Polyester	General
JA	-	-	-	-	-	3,867.05±51.89	-	Rayon+Polyester	General
SE	-	-	-	-	-	-	-	Rayon+Polyester	General
BA	-	-	-	-	17.97±0.43	8,904.71±20.43	-	Rayon+PET	Infant
OG	-	-	-	-	-	-	-	Rayon+PET	Infant
GO	-	-	-	-	-	-	-	Rayon+PET	General
KR	-	-	-	-	-	12,669.97±445.46	-	Rayon+PET	General
PE	-	-	-	-	-	-	-	Rayon+PET	General
MO	-	-	-	261.26±5.14	55.67±1.46	11,692.77±610.26	-	Rayon+Polyester+Cotton	Infant
ML	-	-	-	-	-	19,558.35±3,537.3	-	Rayon	Infant
HA	-	-	-	-	-	-	-	Pulp+Polypropylene	Infant
PU*	71.75±1.64	-	-	-	-	-	-	Cotton	Unknown
PA*	47.14±1.13	-	-	1,242.63±43.71	25.00±1.42	3,655.52±53.45	-	Cloth Like	Unknown
SC*	49.87±1.48	-	-	-	7.23±0.32	-	-	Unknown	Unknown
DE	-	-	-	-	-	-	-	Unknown	Infant

- ; Non detected, * ; Made in USA, The values are means±standard deviation (n=3).

Table 6. Heavy metal analysis on the non-woven from mask packs (unit; μg/L)

Sample name	Sampling position	As	Cd	Hg	Ni	Pb	Sb	Tl	Non-woven fabric
AL	Non-woven & Liquid	-	-	-	-	-	7.24±1.87	-	Unknown
	Liquid	-	-	-	-	-	-	-	
	Non-woven	-	-	-	-	-	-	-	
ES	Non-woven & Liquid	-	-	-	-	-	-	-	Unknown
	Liquid	-	-	-	-	-	-	-	
	Non-woven	-	-	-	-	-	-	-	
FA	Non-woven & Liquid	-	-	-	-	-	5.25±0.25	-	Unknown
	Liquid	-	-	-	-	-	-	-	
	Non-woven	-	-	-	-	-	-	-	
GA	Non-woven & Liquid	-	-	-	103.52±2.02	-	8,935.52±55.22	-	Unknown
	Liquid	-	-	-	-	-	38.95±1.86	-	
	Non-woven	-	-	-	-	-	8,895.28±42.86	-	
GE	Non-woven & Liquid	-	-	-	-	-	9.76±1.29	-	Unknown
	Liquid	-	-	-	-	-	-	-	
	Non-woven	-	-	-	-	-	-	-	
IT	Non-woven & Liquid	-	-	-	53.69±1.45	-	-	-	Unknown
	Liquid	-	-	-	-	-	-	-	
	Non-woven	-	-	-	-	-	-	-	
SO	Non-woven & Liquid	-	-	-	-	-	-	-	Unknown
	Liquid	-	-	-	-	-	-	-	
	Non-woven	-	-	-	-	-	-	-	
SU	Non-woven & Liquid	-	-	-	-	-	-	-	Unknown
	Liquid	-	-	-	-	-	-	-	
	Non-woven	-	-	-	-	-	-	-	

- ; Non detected, The values are means±standard deviation (n=3).

4. Conclusion

Wet wipe is categorized as a cosmetic under the regulation of the 2014-230 from the Ministry of Food and Drug Safety. The risk assessment was tested and proved safety on wet wipes by the National Institute of Food and Drug Safety Evaluation and the Korean Agency for Technology and Standards. Twenty four kinds of wet wipes and eight kinds of mask packs were collected and found that the following materials are used in the non-woven: rayon+polyester for the 12 wet wipe products, rayon+PET for the 5 wet wipe products, and rayon, cotton, rayon+polyester+cotton, pulp+polypropylene for the rest of the wet wipe product. No further information was available on the materials used for the 3 wet wipes and 8 mask packs. Polyester may be applied for the non-woven in wet wipe, because PET is part of the polyester group.

The LOQ on antimony, cadmium, lead, and thallium was 0.03 ㎍/L, and arsenic was 0.07 ㎍/L, and nickel was 0.33 ㎍/L, and mercury was 0.80 ㎍/L. The heavy metal analysis in 24 kinds of wet wipes and 8 kinds of mask packs revealed the following: arsenic was ranged from 47.14±1.13 to 71.75±1.64 ㎍/L on the 3 products, the amount of nickel in the 2 products was 261.26±5.14 and 1,242.63±43.71 ㎍/L, 53.69±1.45 and 103.52±2.02 ㎍/L on the 2 mask packs. It was also revealed that lead was ranged from 7.23±0.32 to 55.67±1.46 ㎍/L on the 6 wet wipes, antimony was ranged from 187.86±5.24 to 19,558.35±3,537.30 ㎍/L on the 12 wet wipes, and 5.25±0.25 and 8,936±55.22 ㎍/L on the 2 mask packs. No cadmium, mercury, or thallium were detected from all the products. Relatively high concentration of antimony from the non-woven may come from the process. A catalyst, such as antimony trioxide or antimony glycolate, was added into the process when manufactured polyester, which is the material of non-woven. The toxicity of antimony trioxide was reported: it caused pneumoconiosis, or fibroma on the reproductive toxicity and acute oral toxicity [15]. It is regulated by the Toxic Chemical Control Act [16], IARC group 2B (International Agency for Research on Cancer group 2B: possibly carcinogenic to humans) by US EPA (United States Environmental Protection Agency) and ACGIH A2 (The American Conference of Governmental Industrial Hygienists: Suspected human carcinogen) [17].

In summary,

1. Even though the amount found from non-woven was not considered toxic or hazard, it is still recommended to control the non-woven material that is used in wet wipes or mask packs.
2. It is recommended to clarify which materials are used in non-woven in wet wipes or mask packs.
3. It is suggested to use a heavy metal free catalyst during the process of non-woven manufacture.

Acknowledgement

This paper was supported by Daejeon Health Sciences College in 2015.

References

1. Enforcement regulations of the Cosmetic Act, Pre-announcement of legislation No 2014-230, Minister of Food and Drug Safety. (2014.8.19.).
2. Cosmetic Act, Partially amended from legislation No 13117, (2015.1.28.).
3. Enforcement regulations of the Cosmetic Act, Article 12(7), Partially amended by prime minister decree No 1182,

(2015.7.29.).
4. Self-regulatory safety confirmation annex 49, Wet wipe (Wet tissue), Notification No. 2012-170 of Korean Agency for Technology and Standards, (2012.4.17.).
5. J. H. Wang, Comprehensive risk assessment report of household chemical products Part 1. Risk assessment of wet wipes, National Institute of Food and Drug Safety Evaluation, ISBN 11-1471057-000117-01, (2015.4).
6. Korean Agency for Technology and Standards, Result of actual condition survey on the wet tissue - Cetrimonium group cosmetics are detected within the safety limit, Press release of Ministry of Trade, Industry and Energy, (2014.12.1.).
7. A. Sannino, C. Demitri, and M. Madaghiele, Biodegradable cellulose-based hydrogels: Design and applications, *Materials*, **2**(2), 353-373(2009).
8. J. W. Lee, D. S. So, and H. S. Su, Nanofibers : Preparations and applications, *KIC News*, **13**(1), 32-50(2010).
9. M. Catel-Ferreira, H. Tnani, C. Hellio, P. Cosette, and L. Lebrun, Antiviral effects of polyphenols: Development of bio-based cleaning wipes and filters, *J. Virol. Methods*, **212**, 1-7(2015).
10. ezcostec, Manufacturing method of cosmetic biocellulose sheet and cosmetic biocellulose sheet by using therof, Korea patent 10-1385501(2014.04.09.).
11. KAERI, Microbial fermentation of cellulose porous filters and manufacturing method thereof, Korea patent 10-1583058 (2015.12.30.).
12. KRICT, SKchemicals, Development of clean process technology for preparing PET, Ministry of Environment, (2003. 7.21.).
13. Smithers Apex Market Intelligence, The future of nonwoven wipes to 2019, Smithers Apex, (2014.12).
14. TechNavio, Global baby wipes market 2015-2019, Infiniti Research Ltd., (2015. 2.25).
15. M. K. Noh, Result report of actual condition survey on the use and distribution of chemical materials (Antimony), Korea Occupational Safety and Health Agency, (2010.4.).
16. Antimony trioxide : Toxic material, Notification No. 2005-21 of the National Institute of Environmental Research (Amendment Notification), (2005.6.28.).
17. EPA Document # 740-Z1-4001, Antimony trioxide, United States Environmental Protection Agency, (2014.8).