

Synthesis of silk fibroin fiber for indoor air particulate removal

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Abstract—The main objective of this research is to synthesize silk fibroin fiber for indoor air particulate removal. Silk cocoons were de-gummed using 0.5 wt % Na_2CO_3 alkaline solutions at 90°C for 60 mins, washed with distilled water, and dried at 80°C for 3 hrs in a vacuum oven. Two sets of experiment were conducted to investigate the impacts of initial particulate matter (PM) concentration and that of air flow rate on the removal efficiency. Rice bran collected from a local rice mill in Ubonratchathani province was used as indoor air contaminant in this work.

The morphology and physical properties of silk fibroin (SF) fiber were measured. The SEM revealed the deposition of PM on the used fiber. The PM removal efficiencies of 72.29 ± 3.03 % and 39.33 ± 1.99 % were obtained of PM_{10} and $\text{PM}_{2.5}$, respectively, when using the initial PM concentration at 0.040 mg/m^3 and 0.020 mg/m^3 of PM_{10} and $\text{PM}_{2.5}$, respectively, with the air flow rate of 5 L/min.

Keywords—Indoor air, Particulate matter, Scanning electron microscope (SEM). Silk fibroin fiber.

I. INTRODUCTION

INDOOR air quality has received immense attention in the early 1990s because of higher level of pollutants in indoor air environments as compared to outdoor air environments [1]. People spend 80-90 % of their time indoors, and indoor environment has important effects on human health and work efficiency [2]. Indoor air pollution should be of particular interest. In 1995, USEPA identified indoor air pollution is one of the top environmental risk. [3]. Indoor air pollutants consist of biological contaminants, chemical contaminants and particulates depend on air pollutant sources [4].

Particle pollution, also called particulate matter or PM, is a mixture of microscopic solids and liquid droplets suspended in air. The constituent particles typically vary in size

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composition and origin [5]. Particles less than 10 μm in diameter are often referred to as “inhalable” in terms of PM_{10} (<10 μm in mean aerodynamic diameter). The “fine particle” is also often referred as $\text{PM}_{2.5}$ (<2.5 μm in diameter) [6]. Particle exposure can lead to a variety of health effects such as headaches, runny nose, cancer, and respiratory diseases [7] depend on long-term or short-term particle exposures [8]. One of the major sources of indoor air particles is rice mills particularly from a rice milling process. Sasinadda et al. [9] found that the PM concentrations in rice mills in Ubonratchathani province, Thailand, were 0.1170 mg/m^3 and 0.0366 mg/m^3 for total dust and respirable dust, respectively.

Traditional technologies for removing indoor air particulates include high-efficiency particulate air filter (HEPA), electronic air cleaners, ion generators etc. Recently, filtration has shown to be a relatively economical and efficient method for improving indoor air quality [10-11]. One of fibrous filters is silk fibroin (SF) fiber from silkworm. *Bombyx mori* silkworm silk fibers, which have a very long history of use as textile materials in China, attracted many researchers in the fundamental science research and application research fields in recent years [12-14]. Silk fiber is natural protein fibers, having two primary components, fibroin and sericin. Silk fibroin is the major component, which accounts for about 70% of novel silk fibers, and sericin is another kind of silk protein, which accounts for about 30% of silk fibers [12].

Recently, SF fiber from silkcocoons (e.g., *Bombyx mori*) has been explored to exploit the properties of this protein as biomaterial [15-17], cosmetics creams, lotions, makeup, powder, bath preparations and pharmaceuticals due to its excellent characters as textile fiber. Moreover, the natural silk fiber is one of the strongest and toughest materials mainly because of the dominance of well orientated β -sheet structures of protein chains [18,19]. The inner filaments of fiber, fibroin, are embedded in an outer rubbery coating made up of sericin. High purity silk fibroin can be obtained easily from degummed silk alkaline solution. Briefly, silk cocoons of *Bombyx mori* were degummed with 0.5 wt% Na_2CO_3 solution and washed with deionized water to remove the sericin [20-22].

The aim of this study is to investigate the ability of silk fibroin as a fiber for filtration of particulate matters in indoor air. The SF fiber was synthesized from cocoons of the *Bombyx mori* silkworm. It was de-gummed with sodium carbonate (Na_2CO_3) solution. Rice bran was selected as a particle pollutant that it was found in indoor air of rice mill process. Thus, in this work SF has been used as a bio-filtration fiber for particulate removal.

II. EXPERIMENTAL

A. Preparation of *Bombyx mori* silk fibroin.

Cocoons of the *Bombyx mori* silkworm were collected from a local farm (Ubonratchatani province, Thailand). They were dried in sunlight and then cut into small pieces of approximately 1 mm × 1 mm dimensions. They were degummed by boiling them in an aqueous solution of 0.5% (w/w) Na₂CO₃ solution at 90 °C for 60 mins to remove all traces of sericin for complete degumming of the shells. The cocoon pieces were subsequently washed thoroughly in distilled water and dried briefly for 3 hrs in a vacuum oven at 80 °C

B. Silk fibroin Fiber Characterization

1. Scanning Electron Microscope (SEM) Analysis

SEM characterization was performed by using a Jeol JSM-5410LV microscope, at an acceleration voltage of 15kV. SF fiber samples for SEM were cryogenically fractured in liquid nitrogen and then mounted onto aluminium specimen stubs by means of double-sided adhesive tape and sputter-coated with a thin gold layer under rarefied Argon atmosphere.

2. BJH Nitrogen Adsorption Technique

Physical properties of SF fiber samples were examined using Autosorb-1(AS1Win Version 1.50). Nitrogen gas was utilized as an adsorbate gas. The sample was degassed by setting the desired temperature at 60 °C. The saturated vapor pressure of the adsorbate (P₀) was 760 mmHg. The BJH method was applied for specific surface area, specific pore volume, and pore size analysis.

3. The Reactor and Measurement

As shown in Fig.1 a glass room with the dimensions of 50 cm × 45 cm × 35 cm was used as a reactor in this study. The temperature and relative humidity were continuously monitored by Hygrometer monitor (Model TECPEL 550). In all sets of experiment, temperature and relative humidity ranged from 25 - 30 °C and 65 - 70 %, respectively. Rice bran from a local rice mill in Ubonratchathani province was used as indoor air contaminant. Four mixing small fans were installed in the room to ensure adequate mixing of rice bran particulate matter in air. Rice bran was added from the top of the room and allowed to reach equilibrium. The initial concentration was controlled to be 0.040 ± 0.005 mg/m³ and 0.020 ± 0.005 mg/m³ for PM₁₀ and PM_{2.5}, respectively. The SF filter was placed inside the filter holder with the diameter of 33 mm. Then, it was connected with the room and an aerosol personal pump (Fig. 1). The PM pollutants in the room were pumped through the SF filter using an aerosol personal pump. The air flow rate was varied from 3, 4 and 5 L/min. The PM concentration was continuously measured for 8 hrs by a Side Pak Personal Aerosol Monitor (Model AM510) with impactor PM_{2.5}, PM₁₀. The interval time was set at 10 sec.

4. The Removal Efficiency of Different Types of Fiber

The commercial fiber mask respiratory protection (3M-8210) was compared the efficient PM removal with two series SF fibers at the same condition.

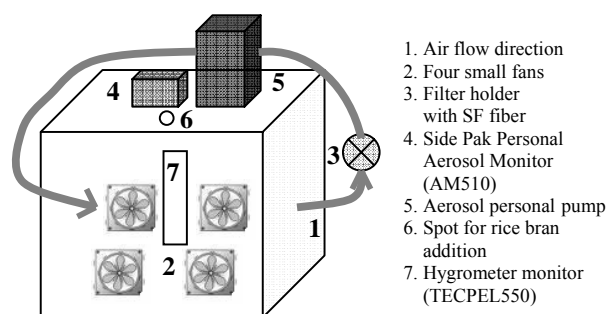


Fig. 1 Schematic diagram of the reactor

III. RESULTS AND DISCUSSIONS

A. Fiber Morphology

Fig. 2 (a) shows the SEM of SF fibers before PM filtration. SEM micrographs revealed the fibrous morphology of the SF fiber. An average diameter of the SF fiber was estimated to be approximately 10 μm. The images of the SF fiber after PM filtration were depicted in Fig.2 (b). SEM images revealed the deposition of fine particle on the SF fiber. Therefore, it could be concluded that PM pollutants were adhered onto the SF fiber. Consequently, the SF fiber may be used as an alternative material for PM filtration. The physical properties of the SF fiber were analyzed using the BJH technique and were reported in Table I. From the results, the SF fiber has the specific surface area and pore volume of 62.325 ± 7.149m²/g and 0.0332 ± 0.004 cc/g, respectively. The pore size of the SF fiber was estimated to be 24.665 ± 0.007 Å and was classified as mesopore.

B. SF Filtration

Two sets of experiment were conducted to observe the filtrations of PM₁₀ and PM_{2.5} using the SF fiber. Initial concentrations of PM₁₀ and PM_{2.5} were maintained at about 0.040 ± 0.005 mg/m³ and 0.020 ± 0.005 mg/m³, respectively. These concentrations were achieved by controlling the amount of rice bran added into the room. As seen in Fig. 3, the initial PM₁₀ concentration reached equilibrium at around 4 hrs. The similar result was observed for initial PM_{2.5} concentration as shown in Fig. 4. Then the treatments of PM were performed using the different air flow rate of 3, 4, and 5 L/min.

The PM₁₀ removal efficiency at the air flow rate of 5, 4, and 3 L/min is showed in Fig. 3. As seen from the figure, the PM₁₀ concentration decreased rapidly during the initial period of treatment. PM₁₀ concentration decreased from 0.039 mg/m³ to 0.011 mg/m³ after the treatment period of 4 hrs. when using the air flow rate of 5 L/min. Also PM₁₀ concentration decreased from 0.038 mg/m³ to 0.017 mg/m³ and from 0.037 mg/m³ to 0.020 mg/m³ when using the air flow rate of 4 L/min and 3 L/min, respectively after the treatment period of 4 hrs. After the 4th hour of treatment, the PM₁₀ concentration tends to reach equilibrium.

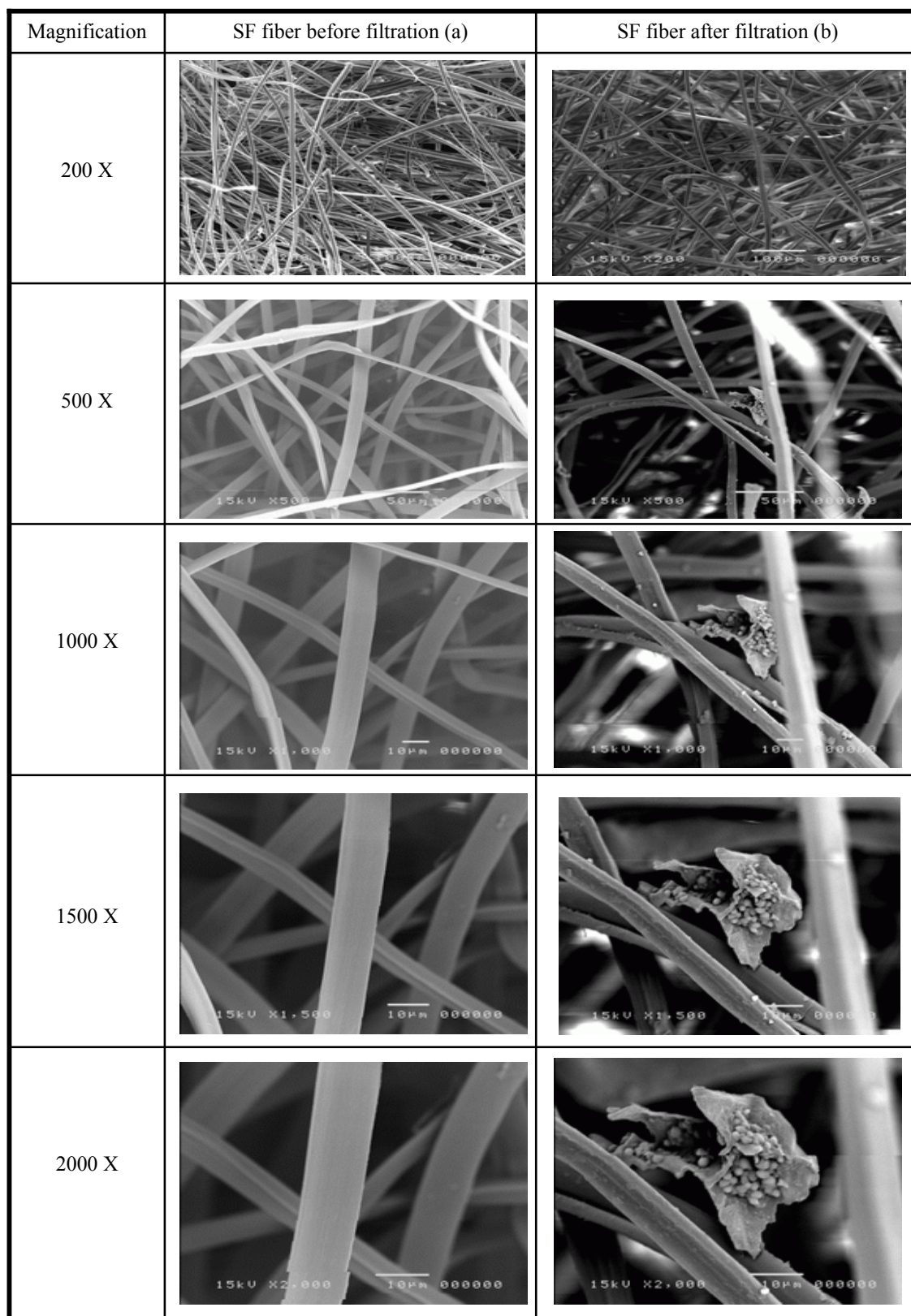


Fig. 2 The morphologies of SF fiber (a.) before filtration and (b.) after filtration

TABLE I
 BJH ANALYSIS OF SF FIBER

Samples	Physical properties		
	Specific surface area (m ² /g)	Specific pore volume (cc/g)	Pore size (Å)
1	67.380	0.036	24.660
2	57.270	0.031	24.670
Average	62.325 ± 7.149	0.033 ± 0.004	24.665 ± 0.007

TABLE II
 PM REMOVAL EFFICIENCIES OF SF FILTRATION

PM removal efficiency (%)	Air flow rate		
	5 L/min	4L/min	3L/min
PM ₁₀	72.29 ± 3.03	54.88 ± 7.46	46.87 ± 7.59
PM _{2.5}	39.33 ± 1.99	33.73 ± 0.76	33.15 ± 6.30

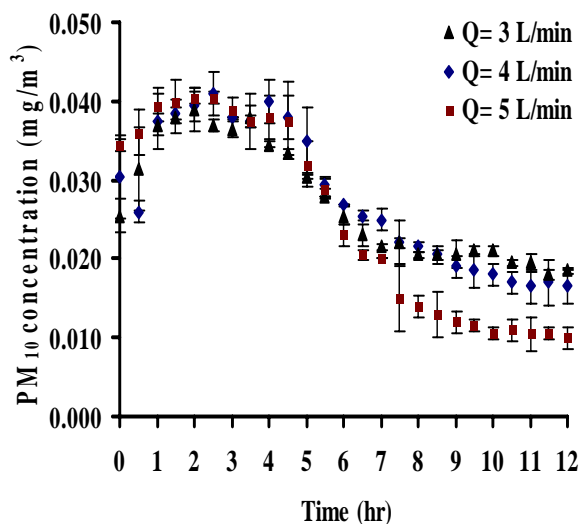


Fig. 3 PM₁₀ concentration before and after treatment

The results also showed that the PM₁₀ removal efficiency increased with the air flow rate. This may be due to the higher the air flow rate, the more particles pumped from the room to the filter. The highest PM₁₀ removal efficiency of

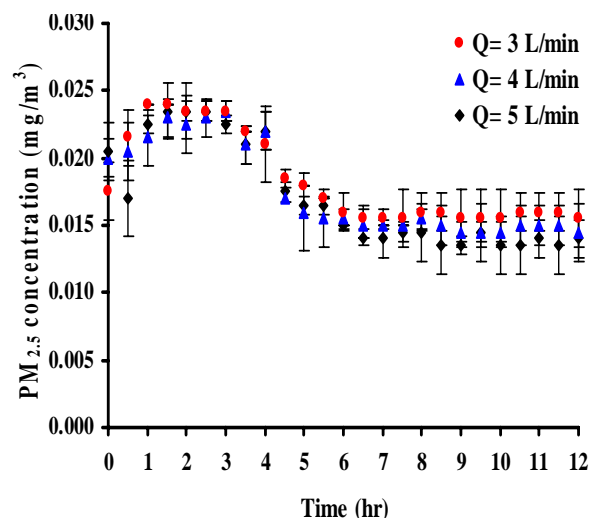


Fig. 4 PM_{2.5} concentration before and after treatment

72.29 ± 3.03% was obtained when using the air flow rate of 5 L/min.

The PM_{2.5} removal efficiency at the air flow rate of 5, 4, and 3 L/min is showed in Fig. 4. As seen from the figure, PM_{2.5} concentration decreased from 0.023 mg/m³ to 0.015 mg/m³ after the treatment period of 4 hrs. when using the air flow rate of 5 L/min. Also PM_{2.5} concentration decreased from 0.022 mg/m³ to 0.015 mg/m³ and from 0.024 mg/m³ to 0.016 mg/m³ when using the air flow rate of 4 L/min and 3 L/min, respectively after the treatment period of 4 hrs. Then PM_{2.5} concentration tends to reach equilibrium for all experiments. Similar to the above, the PM_{2.5} removal efficiency increased with the air flow rate. The highest removal efficiency of 39.33 ± 1.99% was obtained when using the air flow rate of 5 L/min.

TABLE III
 PM REMOVAL EFFICIENCIES OF DIFFERENT TYPES OF FIBER

Types of fiber	PM removal efficiency (%)	
	PM ₁₀	PM _{2.5}
2 series SF fibers	72.95 ± 1.68	62.45 ± 1.06
Commercial fiber (3M-8210)	79.53 ± 0.67	65.03 ± 5.89

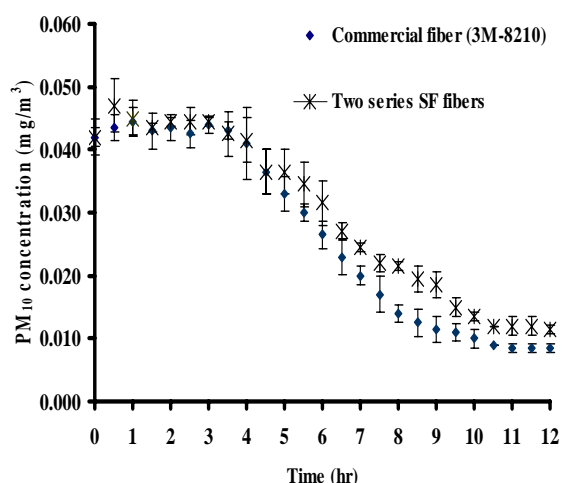


Fig. 5 PM₁₀ concentration before and after treatment at air flow rate of 5 L/min

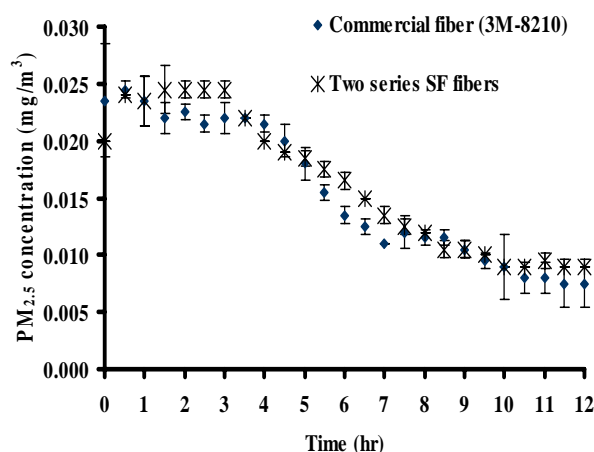


Fig. 6 PM_{2.5} concentration before and after treatment at air flow rate of 5 L/min

TABLE IV
COST COMPARISON OF FIBERS

Types of fiber	Price (Baht/Piece ^a)
SF fiber ^b	0.61
Commercial fiber ^c (3M-8210)	6.50

^a Diameter of each piece is 5.5 cm

^b Total cost for synthesis SF fiber per piece

^c Commercial fiber of mask respiratory protection (3M-8210)

C. The Removal Efficiency of Different Types of Fiber

The comparison of PM removal efficiency between the two series SF and commercial (3M-8210) filters was also included in this study. The initial concentrations of PM₁₀ and PM_{2.5} were maintained at 0.040 ± 0.005 mg/m³ and 0.020 ± 0.005 mg/m³, respectively. The air flow rate of aerosol personal pump at 5 L/min was applied for all experiments. As seen in Fig. 5 and Fig. 6, the PM removal efficiencies of the two series SF and that of the 3M-8210 filters were comparable. In which, the PM₁₀ removal efficiency of the two series SF filter and that of the 3M-8210 filter were 72.95 ± 1.68 % and 79.53 ± 0.67 %, respectively. While, the PM_{2.5} removal efficiencies of 62.45 ± 1.06 % and 65.03 ± 5.89 % were obtained for the two series SF filter and the 3M-8210 filter as shown in Table III.

Cost comparison between two types of fiber is shown in Table IV. The results show that the SF fiber has much less cost than the 3M-8210 fiber. Total cost for synthesis the SF fiber is approximately 0.61 baht/piece, while cost of commercial fiber is 6.50 baht/piece.

IV. CONCLUSION

The SF fiber was readily synthesized using the Na₂CO₃ solution. It was de-gummed in alkaline solution at 90 °C for 60 mins, washed with distilled water, and dried at 80 °C for 3 hrs in a vacuum oven. The physical characteristics of SF fiber were examined by SEM and BJH analysis. The SEM images revealed the deposition of fine particle on the fiber. The BJH analysis shows that most of pore sizes of the SF fiber were mesopores. The removal efficiency of the SF fiber increased with an increasing of air flow rate. The results showed that the highest removal efficiencies of 72.29 ± 3.03 % and 39.33 ± 1.99 % were obtained for PM₁₀ and PM_{2.5}, respectively when using 5 L/min of air flow rate. The SF fiber could be applied as an alternative material for removing particulate matter in air and also it has less cost for synthesis.

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REFERENCES

- [1] A.P. Jones, "Indoor air quality and health," Atmospheric Environment, vol. 33, 1999, pp. 4535 - 4564.
- [2] J. Robinson, W.C. Nelson, "National Human Activity Pattern Survey Data Base," UnitedStates Environmental Protection Agency, Research Triangle Park, NC., 1995.
- [3] USEPA., "Characterizing air emissions from Indoor sources." EPA Report EPA/600/F-95/005, United States Environmental Protection Agency, Washington, DC., 1995.

- [4] J.D. Spengler, J.M. Samet, "A perspective on indoor and outdoor air pollution." In: Samet, J.M. and Spengler, J.D., Editors, (1991). *Indoor Air Pollution: A Health Perspective*, Johns Hopkins University Press, Baltimore, 1991. pp. 1–29.
- [5] Committee of the Environmental and Occupational Health Assembly of the American Thoracic Society, "Health effects of outdoor air pollution." *Am. J. Respir. Crit. Care Med.*, vol.153, 1996, pp. 3–50.
- [6] C.A. Clayton, R.L. Perritt, E.D. Pellizzari, K.W. Thomas, R.W. Withmore, "Particle total exposure assessment methodology (PTEAM) study: distributions of aerosol and elemental concentrations in personal, indoor, and outdoor air samples in a southern California community," *J. Expos. Anal. Environ. Epidemiol.* vol. 3, 1993, pp. 227–250.
- [7] J.L. Devalia, C. Rusznak, J. Wang, O.A. Khair, M.M. Abdelaziz, M.A. Calderón, R.J. Davies, "Air pollutants and respiratory hypersensitivity," *Toxicol. Lett.*, vol. 86, 1996, pp.169–176.
- [8] I. T. T. Higgins, "Effects of sulfur oxides and particulates on Health," *Arch. Environ. Health*, vol 22, 1971, pp 584.
- [9] S. Suwanno., "Health impact assessment from particulate matter and noise on rice mill workers in Ubonratchatani," 2007.
- [10] P. Zhao, J.A. Siegel, R.L. Corsi, "Ozone removal by HVAC filters," *Atmospheric Environment*, vol. 41, 2007, pp. 3151–3160.
- [11] M. Hyttinen, P. Pasanen, P. Kalliokoski, "Reactions of ozone on clean, dusty and sooty supply air filters," *Atmos. Environ.*, vol.40, 2006, pp. 315–325.
- [12] L. Zhou, X. Chen, Z. Z. Shao, P. Zhou, D.P. Knight, F. Vollrath, "Cooper in the silk formation process of *Bombyx mori* silkworm," *Fed Eur Biochem Soc Lett.*, vol. 554, 2003, pp. 337-34.
- [13] R. Valluzzi, S. J. He, S. P. Gido, D. Kaplan, "Bombyx mori silk fibroin liquid crystallinity and crystallization at aqueous fibroin-organic solvent interfaces," *Int J Biol Macromol*, vol. 24, 1999, pp. 227- 236.
- [14] C. Z. Zhou, F. Confalonieri, N. Medina, Y. Zivanovic, C. Esnault, T. Yang, et al., "Fine organization of Bombyx mori fibroin heavy gene," *Nucleic Acids Res.*, vol. 28 (12), 2000, pp. 2413 - 2439.
- [15] G. Y. Li, P. Zhou, Z. Z. Shao, X. Xie, X. Chen, H. H. Wang, et al., "The natural silk spinning process," *Eur J Biochem.*, vol. 268, 2001, pp. 6600-6606.
- [16] X. Wang., X. Zhang, J. Castellot, I. Ira Herman, M. Iafrazi, D. L. Kaplan, "Controlled release from multilayer silk biomaterial coatings to modulate vascular cell responses. *Biomaterials*, vol.29, 2008, pp. 894 - 903.
- [17] V. Karageorgiou, M. Tomkins, R. Fajardo, L. Meinel, B. Snyder, K. Wade, et al., "Porous silk fibroin 3-D scaffolds for delivery of bone morphogenic protein-2 in vitro and in vivo," *J Biomed Mater Res*, vol.78A, 2006, pp. 324- 334.
- [18] Y.Z. Wang, D. J. Blasioli, H. J. Kim, H. S. Kim, D. L. Kaplan, "Cartilage tissue engineering with silks scaffolds and human articular chondrocytes," *Biomaterials*, vol.27, 2006, pp. 4434- 4442.
- [19] G. H. Altman, F. Diaz, C. Jakuba, T. Calabro, R. L. Horan, J. Chen, H. Lu, J. Richmond, D. L. Kaplan, "Silk-based Biomaterials," *Biomaterials*, vol.24, 2003, pp. 401-416.
- [20] Z. Jingxin, Z. Yaopeng, S. Huili, H. Xuechao, "Electrospinning and rheology of regenerated Bombyx mori silk fibroin aqueous solutions: The effects of pH and concentration," *Polymer*, vol.49, 2008, pp. 2880 – 2885.
- [21] C. Chen, C. Cao, X. Ma, Y. Tang, H. Zhu, "Preparation of non-woven mats from all-aqueous silk fibroin solution with electrospinning method," *J. Polymer*, vol.47, 2006, pp. 6322- 6327.
- [22] T. BaoZhong, C. Ping, C. Jian, B. Lun, "Blocking and filtering effect of Bombyx mori silkworm silk fiber filter tips against mainstream smoke of cigarettes," *J. Mater and Design*, 2008, pp.1-6.