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Assessment of heavy metal concentration in wastewater of silk dyeing in Kalasin, Thailand

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ABSTRACT

Mudmee silk is a well-known product of Ban Non-Chard village, Kalasin, Thailand. Untreated wastewater from dyeing process and washing dyed silk yarns is generally discharged into the environment. This study aimed to assess the heavy metals (Cd, Cr, and Pb) in effluents produced by dyeing silk yarns in three colors. The 39 effluent samples from different houses were collected and classified by color, i.e., black, red, and yellow. An atomic absorption spectrometer was used to determine the heavy metal concentrations. The results were evaluated in accordance with the wastewater standards of the World Health Organization (WHO). The mean concentration values of heavy metals in wastewater samples were found to occur in the order Cr > Pb > Cd. The results showed that the black dye effluents had significantly higher concentrations of Cr than other colors dye effluents. All samples of red, black, and yellow effluents had pH values within the permissible limits, excepting three samples of black effluents. The metals Cd, Cr, and Pb were found in most red, black, and yellow effluent samples, and most concentrations exceeded the WHO standard.

Keywords: heavy metal; concentration; effluent; wastewater; dyeing; silk yarn

1. INTRODUCTION

Rapid urbanization and industrialization in developing countries have caused water quality degradation (Qin et al., 2014). The industrial sector requires a high volume of water and also discharges a high volume of wastewater. The textile and dyeing industry are the fastest growing industries in Thailand, providing a high volume of exports. The manufacturing process also requires high volumes of water and toxic chemicals for producing and dyeing textiles, which causes increasing environmental pollution (El-Rahim et al., 2008). The synthetic chemicals used in the printing and dyeing processes contain various contaminants, mainly heavy metals (Sorsa et al., 2015). The wastewater from these processes is a major environmental issue, especially the discharge of untreated effluent. The untreated effluent causes water pollution by increasing concentrations of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solid (TDS), chloride, sulfate, heavy metals, etc. Moreover, the dye color in the wastewater effluent reduces the transparency and aeration of the water surface, which seriously affects the efficiency of photosynthesis, consequently significantly reducing the level of dissolved oxygen (DO) in water (Hussain et al., 2019).

Large quantities of effluents contaminated by toxic metal components are discharged into water bodies, soils, and groundwater, causing water pollution. Chiamsathit et al., (2020) found that concentrations of heavy metals such as Fe and Mn in the groundwater supply during the monsoon season were above the desirable limit. Polluted water and soil are used for agriculture, and crops produced in polluted environments will affect the food chain (Akter et al., 2010). The consumption of toxic components causes serious effects on human health and other species in the environment (Mishra and Soni, 2016). Siyanbola et al., (2011) noted that the continuous discharge of wastewater and higher concentration of toxic metals cause bioaccumulation of metals in fauna and flora. Heavy metals in the effluent are non-biodegradable so they accumulate in primary human organs, causing health hazards. Harmful metals such as lead, copper, zinc, chromium are found in the metal complex dyes and chromium salts used in dyeing as oxidizers (Jaishree and Khan, 2014). It was found that about 10–15% of dye components were lost from the dyeing process into the effluent (Husain, 2006). Therefore, heavy metals in effluent must be removed to meet the water quality standard before discharge into water bodies. Recently, water treatment technologies to eliminate heavy metals and to improve effluent quality have been studied, such as adsorption, ion exchange, membrane separation (Johari et al., 2016; Abdel-Raouf and Abdul-Raheim, 2017; Varghese et al., 2018). However, monitoring of heavy metals in effluent and in water bodies is required to evaluate treatment efficiency and to prevent their accumulation in the environment. Therefore, many researchers have analyzed the concentrations of heavy metals in textile effluents, particularly lead (Pb), chromium (Cr), cadmium (Cd), copper (Cu), and nickel (Ni), which are widely used for color pigments in textile dyes (Akter et al., 2010; Bhardwaj et al., 2014; Bishnoi and Roy, 2017).

Synthetic dyes have been widely used in rural Thailand for products such as reeds and krajood, cotton and silk fabric. Some researchers have studied the production of community enterprise groups in Thailand and analyzed the heavy metal contamination in the wastewater of synthetic dyeing processes such as reed production (Thongthummachat et al., 2011), krajood production (Kuntacha, 1999), and handwoven fabric production. Many community enterprise groups produce traditional handwoven silk and cotton fabric in all regions in Thailand. The production of traditional woven fabric has been developed by the One Tumbon One Product (OTOP) program. The finest Thai silk fabric is made in Kalasin province, known as Praewa Thai silk fabric and often called the "queen of Thai silk." Praewa Thai silk is a famous OTOP product in Kalasin, Thailand. Praewa silk is an old traditional handwoven handicraft using tie-dyed mudmee designs. A special type of handwoven fabric known as "Mudmee silk" is a very famous OTOP product in Ban Non-Chard village, Somdet district, Kalasin province, Thailand. This community is primarily engaged in tie-dyeing and hand weaving of silk yarns as a small scale industry. The well-known mudmee silk is regularly produced at the weaver's house using the wisdom and tradition of elders. It is made from high-quality silk yarns which are tied together and dyed repeatedly. Most weavers produce mudmee silks by dyeing the silk yarns, using synthetic dyes, which became popular because of their consistency and intensity as well as the wide range of colors available. Moreover, synthetic dyes are inexpensive and easy to use. However, wastewater from the synthetic dyeing process is harmful and has serious effects on the environment and human beings. The weavers have directly discharged the untreated wastewater from the dyeing process and from washing dyed silk yarns into the surrounding area where they live and grow vegetables and trees. It is therefore essential to study the contamination of heavy metals in untreated wastewater due to this industry. The main aim of this study was to assess the contents of the trace metals Cd, Cr, and Pb in untreated wastewater samples from the dyeing process for black, red, and yellow silks, and to evaluate the wastewater for adherence to water quality standards.

2. MATERIALS AND METHODS

2.1 Materials

Untreated effluent water discharged from the silk yarn dyeing process was collected by separately sampling wastewaters contaminated with black, red, and yellow dyes from the houses of weavers in Ban Non-Chard village.

2.2 Study area

Ban Non-Chard village is situated in the Nong Wang sub-district, Somdet district, nearly 20 km away from the main city of Kalasin, at latitude 16°38' N and longitude 103°41' E. The maps shown in Figures 1 and 2 were created using the QGIS3.6.3 program. Groundwater is only one of a number of water sources in this area. Agriculture provides the major income of the villagers. The chief crops are paddy, cassava, and sugarcane. There are 128 households with a total population of 568. There are 42 members of the community enterprise group producing traditional handwoven silk. The process for dyeing silk yarns uses 5–6 small bags (20 g per bag) of synthetic dyes mixed with 2 small bags (20 g per bag) of wetting agents. The most common dyes used are black, red, and yellow. This type of dyeing produces about 10 L of wastewater through the water-based process of color fixation, which may cause pollution of soil, plants, groundwater, and drainage systems. Therefore, the dyeing and washing of dyed silk yarns produce effluents which are of concern to the community.

2.3 Sample collection and storage

The effluent samples were collected from different households of the Ban Non-Chard community enterprise group from September 2019 to December 2019, in order to measure their heavy metal concentration. There were 39 wastewater samples consisting of three colors, collected according to the frequency of color use for the silk dyeing process. There were 15 samples of red, 15 samples of black, and 9 samples of yellow wastewater, which were collected in 1 L clean polyethylene bottles. The collected samples were acidified by adding 2 mL of concentrated nitric acid (HNO_3) to produce a pH < 2 to prevent microbial degradation (American Public Health Association, 2017). The samples were transported to the laboratory on the same day and preserved in a refrigerator at 4°C to prevent changes in volume due to evaporation. Hydrogen ion concentration (pH) was measured at the site using a digital pH meter (HQ40D, HACH, Colorado, United States), while the Cd, Cr, and Pb trace metal contents were measured in the laboratory.

Figure 1. A map of Ban Non-Chard village, Kalasin, Thailand

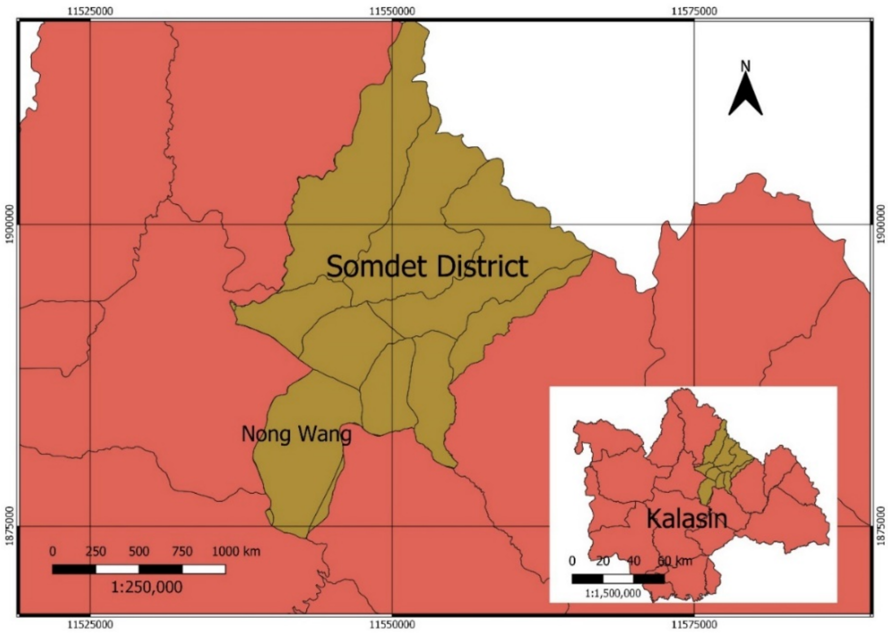

Figure 2. A map of Nong Wang sub-district, Somdet district, Kalasin, Thailand

2.4 Analysis of heavy metals

Samples of untreated wastewater were analyzed following the standard methods for the examination of water and wastewater (American Public Health Association, 2017). One hundred milliliters of the sample was put into a 300-mL glass conical flask and 5 mL of HNO_3 was added. The digestion was then performed by evaporating the sample on a hot plate to approximately 5-10 mL. The sample was then removed from the hot plate and left to cool down at room temperature, and deionized water was added to adjust the final volume to 100 mL. Finally, the prepared samples were analyzed for heavy metal concentrations of Cd, Cr, and Pb with an atomic absorption spectrophotometer (PinAAcle 900F, PerkinElmer, Massachusetts, United States). To assess the measured value of pH and heavy metals, the mean, minimum, maximum, and standard deviation (SD) were calculated using Microsoft Excel (Version 2016). The heavy metal concentration was analyzed using the Kruskal-Wallis test (STATA version 15.1) to determine the significance of difference among three groups of effluent color (red, black, and yellow) with alpha set at 0.05. The guideline value as specified by the World Health Organization (WHO) and the Thai Ministry of Natural Resources and Environment (MONRE) for effluent discharge standards were used to evaluate the results, as shown in Table 1. The WHO is an organization responsible for directing and coordinating international public health works within the United

Nations system. MONRE is a cabinet ministry in the government of Thailand responsible for the management of natural resources and environmental protection.

Table 1. Effluent discharge standards

Parameters	MONRE	WHO
pH	5.5–9	5–9
Heavy metals		
Cd (ppm)	0.03	0.01
Cr (ppm)	0.25	0.05
Pb (ppm)	0.2	0.05

Note: MONRE = Thai Ministry of Natural Resources and Environment (Pollution Control Department, 2016) WHO = World Health Organization (World Health Organization, 2013)

3. RESULTS AND DISCUSSION

The wastewater parameters measured in this study are pH and concentration of Cd, Cr, and Pb. Heavy metals are generally used for the production of color pigments in textile dyes. The 39 effluent samples were collected from different houses in Ban Non-Chard village and were classified by color for analysis. The results of the red, black, and yellow effluent analyses are reported and summarized in Table 2. MONRE has identified an effluent standard in order to control the heavy metal concentration of effluent from medium- and large-scale industries; however, these standards were not applied to the households or the community enterprise group. Therefore, the MONRE and WHO effluent discharge standards were considered as guidelines for comparative study in this research. The red effluent results presented in Table 2 clearly showed that all 15 samples had a pH between 6.02 and 7.35. The pH of nine yellow effluent samples in Table 2 was found to be between 5.91 and 6.57, in the slightly acidic range. However, the pH of 15 black effluent samples fell between 6.22 and 9.87, in the neutral to slightly alkaline range. The pH values of three black effluent samples were higher than the permissible limit of 9, as per the MONRE standard. However, the mean pH values of red, black, and yellow effluents were within the permissible limit.

All 39 effluent samples were analyzed for the concentration of heavy metals. The results in Figure 3 showed that the concentration of heavy metals was detectable in all samples, excepting only three red effluent samples that had concentration below the detection limit. The heavy metal concentration assessed for samples of red, black, and yellow effluents is presented in Figure 3, 4, and 5, respectively. The mean concentration of heavy metals in the effluents of red, black, and yellow samples were clearly found to occur in the order Cr > Pb > Cd, as shown in Table 2. The results showed that the Cd, Cr, and Pb concentrations in black effluents were higher than those in red and yellow effluents. These results indicated that black dye contained high heavy metal concentration and created greater effect on the environment.

The concentration of Cd determined in the red, black, and yellow effluents varied between non-detectable and 0.021 ppm, 0.001 and 0.026 ppm, and 0.001 and 0.012 ppm, respectively. The average concentration of Cd in the red, black, and yellow effluents was 0.009±0.002 ppm, 0.014±0.002 ppm, and 0.008±0.001ppm, respectively. The results showed that there was no significant difference among the Cd concentration in the various colors (p = 0.054). The Cd concentration in all 39 samples did not exceed the permissible limit of MONRE (0.03 mg/L). However, 53% of red samples, 73% of black samples, and 11% of yellow samples had concentration slightly greater than the WHO recommended limit of 0.01 ppm (World Health Organization, 2003). Non-detection of Cd in this study does not mean that no Cd was presented in the samples; These samples may have Cd concentration below the instrument (AAS) detection limit. This might be due to the composition of materials and the amount of water used in the dyeing process during the study period. Cd is a very toxic and carcinogenic metal in humans, accumulating in the human body through inhalation and ingestion and negatively affecting several organs, causing lung, liver, and kidney damage, as well as irritation of the respiratory system (Abdel-Raouf and Abdul-Raheim, 2017). However, the effluents of the mudmee dyeing process contained lower concentration of Cd than the dyeing and printing wastewater of other textile industries, which ranged between 3.45 to 26.24 ppm (Mishra and Soni, 2016).

Table 2. Average pH and concentration of heavy metals in the effluent samples (mean±SD)

Parameters	Red	Black	Yellow
pH	6.66±0.08	7.43±0.34	6.32±0.08
Cd (ppm)	0.009±0.002	0.014±0.002	0.008±0.001
Cr (ppm)	0.069±0.007	1.469±0.241	0.062±0.005
Pb (ppm)	0.047±0.009	0.065±0.008	0.056±0.005

The average concentration of Cr in the red, black, and yellow effluents was 0.069±0.007 ppm, 1.469±0.241 ppm, and 0.062±0.005 ppm, respectively. The maximum concentration of Cr recorded in the black effluent samples (2.628 ppm) was much higher than those recorded in the red effluent samples (0.116 ppm) and the yellow effluent samples (0.083 ppm). The results showed that 80% of Cr concentration in black effluent samples exceeded the MONRE permissible limit and 100% of samples exceeded the WHO permissible limit. It was found that 100% of red effluent samples had Cr concentration below the MONRE effluent standard while 67% of red samples had Cr concentration greater than the WHO recommended limit. It was also found that 100% of yellow effluent samples had Cr concentration below the MONRE effluent standard, while 89% of yellow samples had Cr concentration greater than the WHO recommended limit. The Cr concentration in the black samples was found to be significantly higher than those of red and yellow effluent samples and also greater than the acceptable levels of the MONRE and WHO standards in most analyzed samples. The results showed that there were significant differences between the Cr concentration of the black effluent samples and those of the other colors (p<0.05 for red and black and p<0.05 for yellow and black), but there was no significant difference between red and yellow (p=0.596). Therefore, the black dye effluents containing higher values of Cr are more likely to be harmful to the environment and have a potential risk for human, livestock, and vegetable products in the study area. Similar studies assessing the dyeing and printing wastewater of Balotara textile industries reported that Cr concentration values varied between 1.2 and 6.6 ppm, which are higher than the permissible limit (Mishra and

Soni, 2016). Cr accumulates in the human body by inhalation, ingestion, and absorption through the skin, negatively affecting several organs and causing lung damage and irritation of the respiratory system (Abdel-Raouf and Abdul-Raheim, 2017).

The Pb concentration determined in the red, black, and yellow effluents varied between 0.005 and 0.101 ppm, 0.028 and 0.122 ppm, and 0.032 and 0.072 ppm, respectively. The average concentration of Pb in the red, black, and yellow effluents were 0.047±0.009 ppm, 0.065±0.008 ppm, and 0.056±0.005 ppm, respectively. The results showed that there was no significant difference among the Pb concentration in the various colors (p=0.242). The Pb concentration value in all studied samples were below the MONRE permissible limit (0.2 ppm). However, 40% of red effluent samples, 60% of black effluent samples, and 78% of yellow effluent samples had Pb concentration slightly above the WHO acceptable level (0.05 ppm). However, the Pb concentration in effluents of the mudmee dyeing process were lower than Pb concentration in effluents of the handloom cottage dyeing and printing industries, which ranged between 0.289 to 0.702 ppm (Akter et al., 2010).

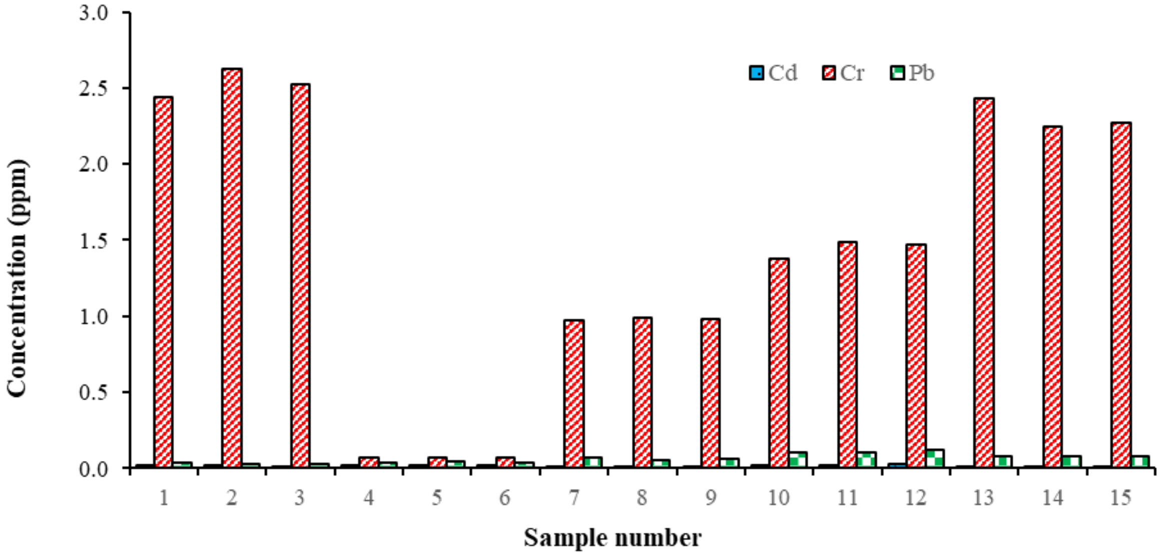

Figure 3. Mean concentration (ppm) of heavy metals in the red samples

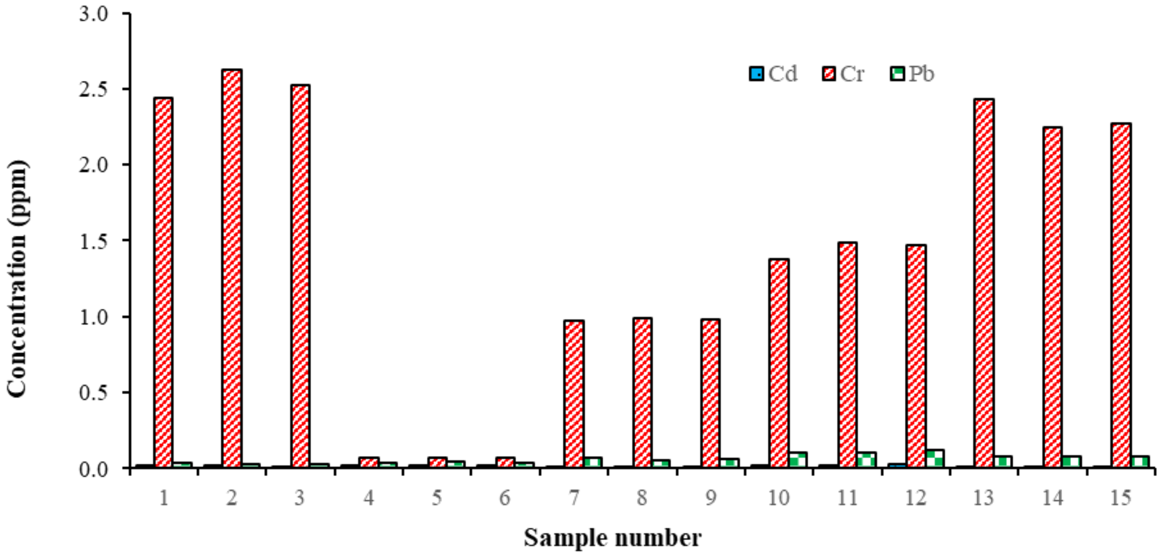

Figure 4. Mean concentration (ppm) of heavy metals in the black samples

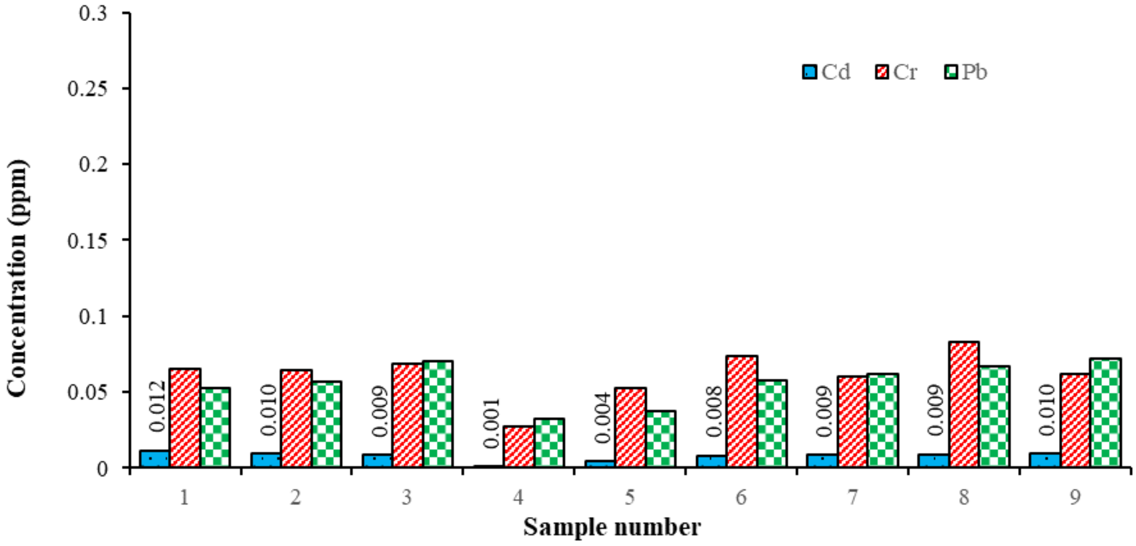

Figure 5. Mean concentration (ppm) of heavy metals in the yellow samples

4. CONCLUSION

This study analyzed the effluents produced by the process of dyeing silk yarns by a community enterprise group making traditional handwoven silk. The effluents were analyzed for three heavy metal trace elements in samples of three dye colors. The results of this study found that the black dye effluents had higher concentration of heavy metals than other dye colors studied. The results clearly showed that the concentration of Cr was a problem based on 15 samples of the untreated effluent, because its concentration exceeded the permissible limit of the MONRE wastewater standard values, while other trace elements, i.e., Cd and Pb, had concentration within the MONRE permissible limit. However, the concentration of Cd and Pb in the effluents were higher than the WHO acceptable level in most samples. Three samples had pH values higher than the permissible limit of 9. The MONRE wastewater standard does not apply to community enterprise groups, but it has been used as a guideline in this study. This study showed that effluent from the dyeing process was polluted and thus increased the potential environmental hazards. Therefore, proper treatment of wastewater is recommended before its discharge to the surrounding area and drainage system.

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