Water quality of effluent treatment systems from local batik industries

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Abstract. Most of the batik premises are still dominated by small and medium enterprises (SMEs). Nonetheless, a conventional wastewater treatment unit is very expensive to be owned by them. Therefore, many local batik premises discharge their untreated effluents directly to the river, which can be potentially toxic and pose a great threat to the environment. The government has started initiative collaboration with educational institutes to develop an affordable treatment system for batik effluents. For that reason, this study was carried out within three batik premises that were equipped with the treatment systems to evaluate their efficiencies. Each treatment system had a different approach in treating batik effluents: (1) Treatment system A started the treatment with screening (sand filtration), aeration, neutralisation (sulphuric acid), coagulation process, and activated carbon filtration; (2) Treatment system B used a similar treatment method as system A except that no coagulant was applied; and (3) Treatment system C starts with screening, neutralisation (sulphuric acid), two tanks of activated carbon filtration before going through the photodegradation process. Physical parameters such as pH, temperature, dissolved oxygen (DO), salinity, conductivity, total suspended solids (TSS), chemical oxygen demand (COD), and colour were measured before and after treatment to determine the effectiveness. The results showed that treatment system C had the highest COD reduction of 91%, followed by treatment systems A and B. Treatment system C also achieved 86% of decolourisation, followed by treatment system A with 82%. Almost all the parameters measured from this study met the Environmental Quality Act (EQA) 1974 (Industrial Effluents) Regulations after the treatment process. The finding from this study should help with the development of any future recommendation and improvement of the treatment system for batik effluent discharges.

1. Introduction
The Malaysian Investment Development Authority (MIDA) stated that in 2016 the textile product industry was the tenth largest exporter from the total of Malaysia’s exports of manufactured goods [1]. These facts and figures showed that the textile industry is one of the major economical contributors in Malaysia, including the batik industry, which is one of the long-established local textile industries in Malaysia. Many researchers agreed that the production of batik in Kelantan and Terengganu can be traced up to the early 1900s [2, 3]. Most of the batik premises are still dominated by small and medium enterprises (SMEs) and these manufacturers usually operate on a small scale by building their industrial units at their backyard and alongside the river [4]. Generally, batik manufacturers still use traditional methods for producing batik and cannot afford to own a conventional wastewater treatment system; thus they resort to releasing untreated toxic effluents straight into bodies of water.
The textile industry including the batik industry consumes large amounts of water during the production, and consequently produces high volumes of wastewater effluent. In the process of batik making, the uses of various dyes and pigments for dyeing, paraffin wax for batik drawing, sodium silicate, sodium bicarbonate, sodium carbonate (soda ash), and sodium hydroxide (caustic soda) as dye-fixing agents may contribute to the increasing amount of toxicants in the discharge [5]. A study on batik effluent characteristics concluded that the discharges have high chemical oxygen demand (COD) values, which consequently lead to the depletion of dissolved oxygen in the receiving drainage. This creates an anaerobic condition that can distress biological activity [6]. Visually, batik wastewater has colour, mostly due to the addition of dyes. The existence of organic materials in water could increase turbidity; thus preventing light penetration and oxygen diffusion to the water. The presence of excess inorganic materials and heavy metals in the water can also have detrimental effects to aquatic organisms [7]. Fortunately, based on previous findings, the average concentrations of each heavy metal measured in the batik effluents was below the standard limit [6]. According to a study on the effects of batik wastewater towards water quality in Kali Wangan River, Indonesia, the effluents did not greatly affect the river, nor caused its water quality to decrease [9]. This was due to the relatively stable river water discharge during both rainy and dry seasons. Nonetheless, several studies on batik effluent showed a similar trend on high COD and pH levels, which eventually had a huge effect on the effluent colouration [9,10,11]. Individually, small businesses have less impact towards the environment; but cumulatively, they contribute significantly towards environmental degradations. In fact, their total negative impacts towards the environment are too high, surpassing big organisations [13].

According to a study on the environmental awareness of batik entrepreneurs in Kelantan, the results indicated that most entrepreneurs had a lack of knowledge about the relationship between batik industry and the environment and also insufficient information about the green batik concept [13]. The initiatives to control untreated batik production effluents and educate batik entrepreneurs only begun in 2010, after the Malaysian Department of Environment (DOE) issued the Green Industry Practice Guidelines for batik manufacturing premises. The guidelines are intended to provide exposure and guidance to batik entrepreneurs on the green industry practices in batik premises, in order to control and reduce wastewater production, cost of energy consumption, and environmental hazards at an early stage [13]. Subsequently, in 2011, Malaysian Handicraft Development Corporation, or Perbadanan Kemajuan Kraftangan Malaysia, initiated an effort to develop a batik effluent treatment system that can be afforded by batik SMEs. Then, in 2015, the Ministry of Higher Education Malaysia launched the Public-Private Research Network (PPRN) that aims to improve the productivity of SMEs through the adaptation of appropriate technology with the participation of academics to carry out research based on demand. As a result, the PPRN initiative eventually managed to attract many researchers from higher education institutions to get involved in solving the batik effluent treatment problems.

Various studies have been carried out in treating batik effluents, whereby most of the studies focused on improving the COD and pH levels of the effluents and removing colour compounds from wastewater discharge. As studied by Rashidi et al., a pre-treatment using a baffle tank had more than 88% removal efficiency of waxes and resin [14]. Photocatalysis was utilised effectively as the decolourisation technique in batik effluents by using zinc oxide (ZnO) and P(3HB)-TiO2 nanocomposite films [15, 16]. Another treatment method associated with batik effluent is activated carbon. This economical treatment showed a great result in reducing COD and removing reactive dyes from the effluents [17, 18].

This paper focuses on the complete units of effluent treatment system that have been applied on the batik premises. The objectives were to evaluate the water parameters of the effluents before and after the treatment and then to compare the effectiveness of these systems in reducing COD, total suspended solids (TSS), and colour. The findings from this study should help with the development of any future recommendation and improvement of the treatment systems.
2. Methods

2.1. Sampling sites
Samplings of batik effluent discharges were undertaken at three locations of batik premises: two locations in Kelantan (Kota Bharu and Tumpat) and one in Selangor. There are a total of 128 batik entrepreneurs registered (manufacture and sales) in Kelantan. Among all the 128 entrepreneurs, only three premises had already installed the batik effluent treatment system. In Selangor, there are two batik premises that have been equipped with the effluent treatment system, but both premises use the same type of treatment system. Therefore, in this study, the convenient sampling technique was used in selecting three types of batik effluent treatment systems for water sampling. Treatment systems A (Gombak, Selangor), B (Kota Bharu, Kelantan), and C (Tumpat, Kelantan) were developed by different institutions with three similar goals: (i) to ensure that the waste of batik sewage released into the environment complies with the regulations in the Environmental Quality Act 1974; (ii) to introduce a low cost and affordable system for SMEs entrepreneurs; and (iii) to have a treatment system with an uncomplicated maintenance process. The specific mechanisms and flow of treatment systems A, B, and C are shown in Figures 1, 2, and 3, respectively.

2.2. Water sampling and analysis
The sampling process of batik wastewater started at the batik premise located in Selangor on 22nd February 2018. Meanwhile, for the other two sampling sites located in Kelantan, it was done on 21st and 23rd March 2018, respectively. The effluent samples before and after treatment were manually collected and stored in polyethylene bottles and kept at 4°C in accordance with the standard method. The physicochemical characteristics of the wastewater were studied, i.e. pH, temperature, dissolved oxygen (DO), salinity, conductivity, COD, TSS, and colour (wavelength absorbance). The in situ parameters of pH and temperature were measured using YSI 60 Portable pH and Temperature Meter. YSI 30 Salinity/Conductivity/Temperature Meter was used for salinity and conductivity readings, while the DO levels of the samples were taken by using YSI 52 Dissolved Oxygen Meter. The preserved effluent samples were analysed for COD, TSS, and colour within a week after sampling. The COD value was measured using HACH DR 2800 Spectrophotometer (Method 8000).

The values of COD or TSS before and after treatment were further analysed to find the removal efficiency of the parameters. The COD or TSS removal efficiency is calculated as follows:

$$\text{Percentage removal efficiency (\%)} = \left(1 - \frac{\text{Measurement after treatment}}{\text{Measurement before treatment}}\right) \times 100 \quad (1)$$

Then, the colour of each effluent sample was analysed to determine the colour removal efficiency of each treatment system. The decolourisation efficiency of effluent samples was verified by using a single wavelength absorbance test. Due to the fact that the samples of batik effluent were a mixture of various dyes, a dominant dye colouration of the effluents was selected as a wavelength representative of the samples. The types of dominant dye used in effluent samples taken from treatment systems A, B, and C were Cibacron Dark Blue W-R, Remazol Turquoise Blue, and Remazol Red F-3B, respectively. The characteristics of each dye are shown in Table 1. The colour removal efficiency of the dyes is defined by the following formula:

$$\text{Colour removal (\%)} = \left(\frac{\text{Abs}_{\text{before}} - \text{Abs}_{\text{after}}}{\text{Abs}_{\text{before}}}\right) \times 100 \quad (2)$$
Table 1. Characteristics of dyes.

| Dyes                             | Colour Index | $\lambda_{\text{max}}$ (nm) | Molecular weight (g/mol) |
|----------------------------------|--------------|------------------------------|--------------------------|
| Cibacron Dark Blue W-R (Reactive Black 5) | 20505        | 600                          | 991.82                   |
| Remazol Turquoise Blue (Reactive Blue 15) | 74459        | 674                          | 1347.13                  |
| Remazol Red F-3B (Reactive Red 180) | 181055       | 540                          | 933.76                   |

3. Results and Discussion
The data obtained from all the treatment systems were analysed and compared with the Environmental Quality Act 1974 (Sewage and Industrial Effluents) Regulations 1979 (Table 2). From the seven parameters that were analysed, only two parameters, namely COD and pH level, were higher than the industrial effluents’ standard limit.

The pH level for the samples before treatment from all of the systems were 11.19, 10.45, and 11.35, respectively. The samples had a high alkalinity level due to the many uses of alkaline compounds,
such as sodium silicate, sodium bicarbonate, and sodium carbonate, as a dye-fixing agent. For the neutralisation process, all treatment systems employed a similar method by adding sulphuric acid to reduce the pH level of the effluents. The final pH readings of all the treated samples were within the standard limit, except for treatment system B with a reading of 0.53, which was higher than the effluent standard. The average DO level from the three samples before the treatment process was 2.77 mg/L, which was very low and insufficient to support aquatic life. In water treatment, the DO level is important for native microorganisms to efficiently break down any organic or chemical compound in the water. For treatment systems A and B, the aeration tank improved the DO level to 6.04 and 5.4 mg/L, respectively. For treatment system C, no aeration process was involved but the stirring mechanism during the photodegradation process helped to improve the DO level to 6.5 mg/L.

### Table 2. Effluent quality before and after treatment.

| Treatment system | Treatment system | Treatment system | EQA (1974) Standard B |
|------------------|------------------|------------------|-----------------------|
|                  | A                | B                | C                     |                        |
| pH               | Before 11±0.29 | After 8±0.02     | Before 10±0.12 | After 9±0.5 | Before 11±0.17 | After 8±0.06 | 5.5-9.0 |
| temperature(°C) | 30±0.14         | 29±0.04          | 28±0.24        | 29±0.35     | 30±0.13         | 29±0.08     | 40       |
| DO (mg/L)        | 2±0.17          | 6±0.09           | 2±0.23         | 5±0.18      | 2±0.14          | 6±0.05      | *        |
| Salinity (ppt)   | 3±0.04          | 4±0.1            | 3±0.15         | 2.9±0.0     | 3±0.03          | 2±0.16      | *        |
| Conductivity     | 8±0.01          | 8±0.02           | 6±0.05         | 5±0.03      | 5±0.06          | 4±0.08      | *        |
| TSS (mg/L)       | 0.090           | 0.124            | 0.038          | 0.033       | 0.063           | 0.035       | 100      |
| COD (mg/L)       | 1390            | 131.5            | 647            | 403         | 1479            | 142         | 250      |

* Not stated in EQA (Industrial Effluent Regulation)

Conductivity is the ability of water to conduct an electric current, which is mostly influenced by dissolving electrolyte ions in the water. Significant increases in conductivity may be an indicator that polluting discharges have entered the water. For that reason, the conductivity level of sample A after the treatment process increased from 8.01 to 8.21 µS/cm due to the use of polyaluminium chloride as the coagulant. The data on TSS showed that the treatment systems managed to reduce the volume of TSS after the treatment process, except for treatment system A. The value of COD was significantly reduced after the effluent treatment; nevertheless, the final COD value of treatment system B still did not comply with the effluent discharge standard.

Table 3 shows the COD and TSS removal efficiency (%) for each treated sample from the treatment systems. The highest efficiency among the samples was treatment system C with COD reduction of 91%. The treatment used was a combination of activated carbon and photodegradation processes. Activated carbon contains well-developed internal pore structures that act as unique adsorption properties for removing organic compounds, heavy metals, and some inorganic pollutants [19]. This result is in agreement with another study on activated carbon, which was found to reduce the COD concentrations of effluents to a considerable extent [20]. Besides, the treatment system used P(3HB)-TiO$_2$ nanocomposite films as photocatalyst in the photodegradation treatment, which had also been proven to achieve high COD removal with exposure to solar irradiation [16].

### Table 3. COD and TSS removal percentages after three different treatment processes.

| Treatment System | Treatment used          | COD removal (%) | TSS removal (%) |
|------------------|-------------------------|----------------|-----------------|
| A                | aeration+ coagulant + activated carbon | 90 | -38 |
| B                | aeration + activated carbon | 38 | 13 |
| C                | activated carbon + photodegradation | 91 | 44 |
Treatment system A also achieved high COD removal with 90% efficiency with aeration, coagulant, and activated carbon treatment. COD is a measure of water capacity to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals; thus, with a consistent supply of oxygen gases to the water (aeration process), it will improve the COD level of the water. Meanwhile, the addition of polyaluminium chloride as a coagulant agent can help in removing small particles of natural organic matter via sedimentation, which can help reduce the oxidation process of organic matter in the water. Although, treatment system A had a high percentage reduction of COD, yet the result displayed some increase in the volume of total suspended solid. TSS increased about 38% due to the use of polyaluminium chloride coagulant, which could leave relatively high aluminium residuals in finished water, especially in cold temperature or low pH [21]. The optimal pH for aluminium-based coagulation is in the range of 5.0–6.5. The water sample from treatment system A had already exceeded the pH range with a reading of 8.45. The treatment system also had no proper settlement tank; therefore, most of the aluminium residuals still existed in the mixture and contributed towards the increase in TSS. Treatment system B exhibited the lowest removal efficiency of COD with only 38% reduction. The low removal efficiency of COD was due to the fact that the activated carbon might have reached the optimal adsorption capacity and could not adsorb any contaminants properly. Proper maintenance should be conducted to improve the treatment.

Reactive dye is the most common type of dye used in batik production due to its nature that allows it to be applied in very low temperature (25°C–50°C), which is suitable for making painted and stamped batik. Nonetheless, reactive dyes have the poorest degree of fixation on fibre, i.e. only 5% of the colourants are absorbed and the remaining 95% will be disposed of as waste [23]. For the colour reduction analysis, three types of reactive dyes were identified as dominant colourants for each respective sample: Reactive Black 5 in sample treatment A, Reactive Blue 15 in sample treatment B, and Reactive Red 180 in sample treatment C. These dyes were selected as the wavelength representative of each effluent sample to find the decolourisation percentage of treatment systems A, B, and C. The decolourisation results are shown in Table 4 and Figure 4. Treatment system C had the highest decolourisation efficiency of 86% because the treatment consisted of activated carbon and photodegradation process, in which both of the processes had the ability to degrade coloured compounds. The effectiveness of using activated carbon in the decolourisation process could also be seen in treatment system A’s result with 82% colour reduction. Meanwhile, the low decolourisation percentage of treatment system B was due to the lack of maintenance service of the treatment system.

| Dye                  | λ_{max} (nm) | Absorbance (abs) Before | Absorbance (abs) After | Decolourisation % |
|----------------------|-------------|-------------------------|------------------------|-------------------|
| Reactive black 5     | 600         | 0.247                   | 0.045                  | 82                |
| Reactive blue 15     | 674         | 0.384                   | 0.311                  | 19                |
| Reactive red 180     | 540         | 0.233                   | 0.032                  | 86                |

**Figure 4.** Colour comparison of effluents before and after treatment.
The correlation analysis was carried out between COD and other parameters. The correlation analysis showed that COD was positively correlated with temperature and pH, and was negatively correlated with DO and total dissolved solids. The temperature of the batik wastewater was acceptable since it was under the standard limit. High temperature will reduce the solubility of gases in water, which is ultimately expressed as high COD. In contrast, extremely low temperature will adversely affect the efficiency of sedimentation in the effluent [23].

4. Conclusion and recommendations
Treatment systems A and C recommended to improve the batik effluent characteristics and complied with Environmental Quality Act 1974 (Industrial Effluents) Regulations 2009 before discharge. Three parameters that showed significant improvement from the three treatment systems are pH, COD, and effluent colour. Batik effluent treatment C displayed the highest efficiency in treating the effluents, followed by treatment systems A and B. Activated carbon is low-cost, renewable, easily available, and can be made from plant-based materials. TiO_2 is another feasible photocatalyst as it is chemically stable, inexpensive, and commercially available. Therefore, these two are the perfect combination in treating batik effluent. Since the volume of TSS is very low and does not exceed the effluent standard, any use of coagulant agent is unnecessary because it does not help any suspended solid precipitation. In some way, the use of coagulant increases the TSS volume with high coagulant residuals in the finished water. If the use of coagulant is necessary in treating the effluent, the treatment system should include one settlement tank so that any particle of suspended solid can settle down properly at the bottom of the tank before being removed. The application of sand filtration should only be applied at the early stage of the treatment as a wax and resin screening process; otherwise, sand filtration towards the end of the treatment system is futile due to the very low volume of TSS. Therefore, a further study needs to be performed in searching for a more efficient and affordable treatment of batik effluents to help even more batik SMEs to move towards green batik production.

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References
[1] Lembaga Pembangunan Pelaburan Malaysia 2016 Laporan Prestasi Pelaburan Malaysia (Lembaga Pembangunan Pelaburan Malaysia: Malaysia)
[2] Rahman I A, Akhir N S, Memon A H, Nagapan S. 2014 Risk level of factors contributing to waste generation in construction phase. InInCIEC 2014 (Singapore:Springer) pp. 199-209
[3] Ahmed N Y 2015 Sumbangan Che Su dan keluarga kepada pembangunan perusahaan batik di Kelantan (Doctoral dissertation, University Malaysia Kelantan)
[4] Subki N S Rohasliney H A 2011 ICCEBS'2011 Bangkok Dec 2011 Dec.
[5] Department of Standards Malaysia 2007 Malaysian Standard. (Malaysia:Department of Standards)
[6] Noor Syuhadah S Muslim N M Rohasliney H 2015 International Journal of Chemical, Environmental & Biological Sciences 3(1) 7-9
[7] Connell D W Miller G J 1984 Chemistry and ecotoxicology of pollution (John Wiley & Sons)
[8] Lestari S Tandjung S D Santoso S J 2018 E3S Web of Conferences 2018 31 04010
[9] Buthiyappan A Raman A A Daud W M 2016 RSC Advances 6(30) 25222-4
[10] Sridewi N Tan L T Sudesh K S 2011 Clean–Soil, Air, Water 39(3) 265-273
[11] Warjito W Nurrohman N 2016 International Journal of Technology 7 898-909
[12] Yaacob M R Ismail M Zakaria M N Zainol F A Zain N F 2015 International Journal of Academic Research in Business and Social Sciences 5(4) 338-47
[12] R A Rahman C R Ngah N Baharom 2013 Eds. Putrajaya Jabatan Alam Sekitar Malaysia. *Garis Panduan Pelaksanaan Amalan Industri Hijau Bagi Industri Batik* (Malaysia: Jabatan Alam Sekitar)

[13] Rashidi H R Sulaiman N M Hashim N A 2013 *Advanced Materials Research* 627 394-398

[14] Khalik W F Ho L N Ong S A Wong Y S Yusoff N A Ridwan F 2015 *Sains Malaysia* 44(4) 607-12

[15] Sridewi N Tan L T Sudesh K 2011 *Clean–Soil, Air, Water* 39(3) 265-73

[16] Birgani P M Ranjbar N Abdullah R C Wong K T Lee G Ibrahim S Park C Yoon Y Jang M 2016 *Journal of environmental management* 15(184) 229-39

[17] Chaudhuri M Elmolla E S Othman R B 2011 *Nature Environment and Pollution Technology* 10 (2) 193-206

[19] Bhatnagar A Hogland W Marques M Sillanpää M 2013 *Chemical Engineering Journal* 219 499-511

[20] Hami M L Al-Hashimi M A Al-Doori M M 2007 *Desalination* 216(1-3) 116-22

[21] Matilainen A Vepsäläinen M Sillanpää M 2010 *Advances in colloid and interface science* 159(2) 189-97

[22] Pang Y L Abdullah A Z 2013 *Clean–Soil, Air, Water* 41 (8) 751-64

[23] Sulieman A M Yousif A W Mustafa A M 2010 Fourteenth International Water Technology Conference 2010 14 305-315