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Color and Chemical Oxygen Demand Removal of Strobilanthes cusia Fermentation and Natural Indigo-based Batik Dyeing Wastewater

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Abstrak

Strobilanthes cusia is the plant which has been cultivated at the District of Temanggung, Indonesia and used as a natural source for indigo dye. The use of natural dyes for Batik Industries are expected to prohibit environmental damage. However, the wastewater generated from the indigo extraction and Batik dyeing process is still showing high COD value (768-3.893 ppm). In the present study, color and COD removal from *Strobilanthescusia* processing (settling pond) and Indigo-based Batik dyeing (equalization tank) wastewater have been studied. The treatment involving the use of $FeSO_4$, Alum, and *Cyclea Barbata Miers.* powder (CBM) as coagulation-flocculation agents. Alum was efficiently reduced color up to 97% and 93% for settling pond and equalization tank effluent, respectively. The highest COD removal efficiencies of 87 % and 63% were observed for settling pond and equalization tank effluent, respectively.

Kata Kunci : Indigo dye; batik wastewater; color removal; coagulant; bio-flocculant.

INTRODUCTION

Water pollution is one of the most prominent problems that often occur in developed countries, including Indonesia (Montgomery & Elimelech 2007). Compared to the other Southeast Asian countries, Indonesia is a country with the most considerable wastewater burden in the textile industries. A load of textile wastewater produced in Indonesia is almost 900 tons/day, of which 30% of this burden comes from the batik industries (Nora, 2007).

Batik industries usually produce liquid wastes that are concentrated in color and affect the value of BOD (*biochemical oxygen demand*), COD (*chemical oxygen demand*), pH, temperature, turbidity, salinity, and sometimes contain toxic chemicals (Kusumastuti *et al.,* 2017; Riyanto *et al.,* 2017; Katheresan *et al.,* 2018). The wastewater has a negative impact once they discharged into an environment without treatment (Pastakia & Jensen 1998). One of the direct impacts is shallow groundwater pollution due to the process of moving wastewater from the surface into the soil (Narr *et al.*, 2019). This impact has been seen in the research sites, namely the batik industries in Malon, Gunungpati, Central Java.

Malon is one of the batik industry centers in Indonesia, which are generally produced batik at *home scale* (Pudjowati *et al.,* 2018). Some of the batik industries keep the tradition of utilizing natural dyes; for example, the use of Indigo from *Indigofera tinctoria and Strobilanthes cusia* (Ariyanti & Asbur, 2018). This plant has been cultivated and harvested in some districts in central Java, including in Temanggung (Hidayati *et al.*, 2018). This plant has been cultivating intensively between another productive tree such as coffee and cocoa. The farmer then sold the harvested *Strobilanthes cusia* to the Batik industries for being processed and extracted (Tangahu *et al.*, 2019). However, the processing of indigo dyes also generates wastewater that contributes to the high value of BOD and COD value (3.893-5.768 ppm). In advanced, batik industry produces a lot of wastewater, most of which comes from the process of dye extraction, dyeing, and washing fabrics (Tangahu *et al.*, 2019).

An initial field survey of natural indigo dye production in Temanggung, Central Java, shows that the indigo handicrafter *strobilanthes* cusia plant biomass because of the indigo yield is higher than the other plants. In this agro-climatic condition, the *strobilanthes cusia* is sown from February to, and the biomass is harvested for indigo dye production from May to August each year. Dye extraction process from fresh *Strobilanthes* biomass (3 months age old with flowering) is carried out by following three steps, i.e., steeping, beating, and dye recovery (Figure 1). In the former process, freshly harvested plant biomass containing Indican is immersed in water for 48 h. During this process, Indican is hydrolyzed to glucose and indoxyl. The fermented liquid color was observed to change into yellow-green, and the biomass is then separated. In the second process, the fermented liquid from the previous step is aerated mechanically in order to increase the dissolved oxygen to promote dimerization of unstable indoxyl molecules into indigo dye. In the last stage, the pH of liquid was adjusted into the value of 11-12, then the settled indigo dye is collected. Indigo dye is pressed in forms of pasta and stored at room temperature. The produced waste was in the form of solid and liquid waste.

The hydrogeological analysis shows that soil has a slow infiltration rate (Hardie & Almajmaie, 2019). Soil with a slow infiltration value should be able to resist the movement of pollutants polluting groundwater. However, the land also has a full capacity once this has been reached, pollutants in water can easily get into groundwater. In this condition, all the types of pollutants can penetrate groundwater, including batik industries wastewater as pollutants (Harren 2019). This implies that batik wastewater treatment is then necessary to overcome these issues.

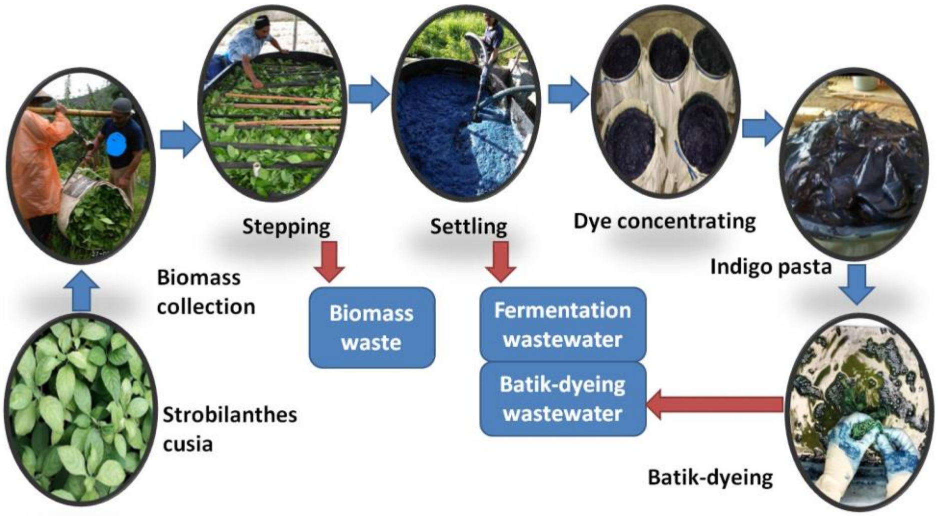


Figure 1. Schematic of *Strobilanthes* processing for indigo extraction at CV Isuga, Temanggung district and Indigo uses for batik dyeing at Malon district.

Coagulation-flocculation is one of the processes of the wastewater treatments that can be used in this study. The selection of this method is because coagulation-flocculation is simple, easy to apply, relatively inexpensive, and able to process waste to meet quality standards (Riyanto *et al.,* 2017; Crini & Lichtfouse, 2018; Oraeki *et al.,* 2018). Coagulation is the process of adding coagulants or chemicals into a solution to form colloid and suspended material for further processes, namely flocculation. Then, flocculation is the process of collecting particles with unstable charges, which then collide with each other to form a collection of particles of a larger size, also known as flock particles (Oraeki *et al.,* 2018).

The problem in chemical treatment is the selection of the chemicals, which must be added at specific condition and amount to the wastewater for separation of dispersed content (Katheresen *et al.,* 2018). On the other hand, suitable coagulant must be natural to handle, prepare, and handle (Tetteh & Rathilal, 2019; Freitas *et al.,* 2018). Aluminum-based coagulant, known as potassium aluminum sulfate ($KAl_2(SO_4)_3$) or alum, is the most well-known coagulant (The *et al.,* 2016). Alum and $FeSO_4$ have been widely used as a coagulating agent on various wastewater treatment. The activities and dosage of both chemicals depend on the characteristic of the treated waste. In this study, their activities were compared to the natural coagulant/bio-flocculant from *Cyclea Barbata Miers* (CBM).

The study aimed to find the right dose of chemicals ($FeSO_4$, alum, and CBM) in treating Indigo dying-batik wastewater, in order to reduce the intensity of color and COD levels to meet waste quality standards to be safely disposed of into the environment.

METHOD

The subject of this study was focused on *Strobilanthes cusia* fermentation and indigo-dying batik wastewater outlet, from Malon, Gunungpati district, Central Java.

Chemicals used are analytical grade including are $FeSO_4$ (Merck), $KAl(SO_4)_2.12H_2O$ (Alum, Merck), *Cyclea Barbata Miers*. Powder (self-prepared), $NH_4Fe(SO_4)_2.12H_2O$ (Merck), $K_2Cr_2O_7$ (Merck), 50% H_2SO_4, the aqueous solution of HCl 1M and NaOH 1M as pH controlling solution. The selection of chemicals in processing was based on reported work regarding the processing of textile wastewater.

The parameters of raw and treated wastewater samples were determined by Indonesian pollution control board limits, and these were COD, BOD5, TDS (total dissolved solids) and pH value.

Coagulation processing was carried out in batch system by adding chemicals (Alum, $FeSO_4$, or CBM) to 100 mL of wastewater cupped-bottles then irradiated with ultrasonic (type BQ 910S, 50 kHz, 100 watts) for 1 hour. Further, the flocculation was done by stirring the suspension at 100 rpm for 30 min. The flock was then settled for another 2 hours. Visual evaluation of the coagulation-flocculation process of tested wastewater samples was focused on flock formation and sedimentation. The influence of coagulant both on wastewater color as well as the removal of turbidity was also studied. The pH for the coagulation-flocculation process was adjusted at 11.

The wastewater color changes were compared to the absorbance of synthetic indigo dyes solution and measured as the change of UV-vis absorbance at 603 nm. The COD value was determined from the number of $K_2Cr_2O_7$ after oxidizing organic and other oxidizable substances in H_2SO_4 at reflux temperature. The excess $K_2Cr_2O_7$ was then titrated with standard $NH_4Fe(SO_4)_2.12H_2O$, using ferroin as an indicator (Tak *et al.,* 2016).

RESULTS AND DISCUSSION

The UV-vis spectra of standard Indigo are shown in Figure 2. The characteristic absorbance band appears at 610 nm. The diluted fermentation settling tank shows the broadband and peak at 610 nm indicate that some indigo is remaining on the wastewater. During fermentation, Indigo is not the only product extracted from the plant. The existence of other compounds was observed from the band shape that is different from standard indigo spectra. Further, the batik-dyeing wastewater contains high indigo dyes signed by the appearance of a similar band at 610. In this study, then the remaining Indigo will become a basic calculation for wastewater decolorization.

Kesalahan! Sumber referensi tidak ditemukan. shows the values of the determined parameters of the raw wastewater from *Strobilanthes cusia* fermentation and indigo-dying equalization tank. The values are typical for batik industry effluents and indicated relatively high variability between examined samples. The value of BOD_5 was 3-4 times higher than the standard and COD were also 10-25 times rather high, this indicates that the wastewater potent as a pollutant and therefore should be treated before discharge into the body of water. The absorbance at 610 nm indicates that a load of Indigo on each wastewater is quite high.

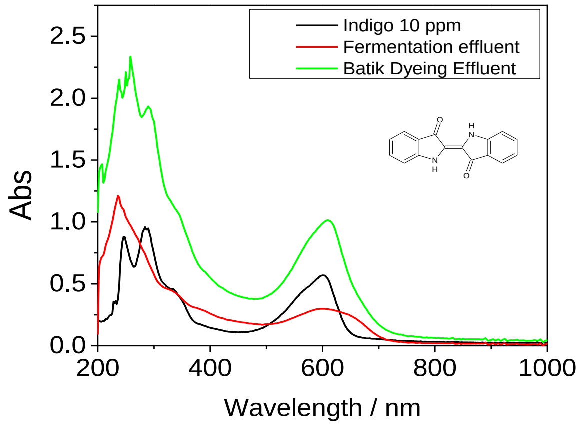


Figure 2. UV-Vis spectra of standard indigo solution (black line), dissolved Indigo in fermentation settling tank (red line), and batik dyeing effluent (green line) after dilution of 20 times and 50 times, respectively.

Table 1. Physico-chemical characteristics of raw wastewater.

Parameter	Unit	Standard*	Fermentation oulet	Indigo-dying outlet
pH	-	6.0-9.0	12.0±0.3	10.3±0.7
COD	Ppm	250	768±27	3.893±214
BOD	Ppm	85	243	355
TSS	Ppm	60	191.3±0.03	189.8±0.1
Abs$_{610}$	-	-	0,341 (after dilution 20x)	1,043 (after dilution 50x)

*Ministry of Environment No. : KEP-51/MENLH/10/1995

Color Removal

Figure 3 shows the change of indigo concentration from fermentation settling tank before and after coagulation-flocculation. The concentration of indigo dyes was exponentially decreased after addition of both alum and CBM up to more than 90% at coagulant addition 500 ppm. This result shows that Alum and CBM perform well as a coagulating agent. On the other hand, when the $FeSO_4$ concentration is small, the indigo concentration seems not to be changed. In some case, it was observed that the absorbance of the wastewater slightly increases. Textile industries, sometimes, also use $FeSO_4$ as a mordant. Addition of fixation agents aims to make the color appear brighter as well as its bind stronger to the fabrics. However, at the high concentration, the indigo concentration was decreased by about 50%.

The color characteristic of wastewater from batik-dyeing was five-time heavier than fermentation settling tank. The original remaining indigo content was about 1200 ppm. It is explained by the batik handcraft, that only 20-30% of dyes were adsorbed after 5-10 dipping process on the fabrics, the rest will be thrown as waste. The recovery of batik-dyeing is not easy since the wastewater containing various chemicals as a batik additive (Riyanto *et al.,* 2017; Harren, 2019; Lestari & Riyanto, 2004)s. However, the coagulation-flocculation process affects the color change of wastewater significantly. Figure 3b shows the color removal from the batik-dyeing process. CBM, natural coagulant, remove the color up to 63% at the concentration of 1000 ppm. On the other hand, at a similar concentration, Alum and $FeSO_4$ contribute color removal more than 91% and 93%, respectively.

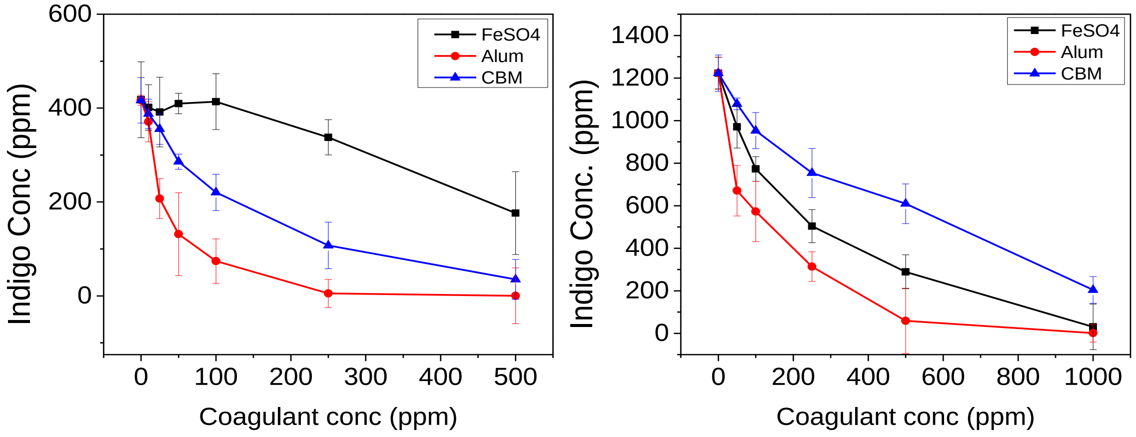


Figure 3. Indigo dye's concentration changes of (a) *strobilanthes* fermentation settling tank and (b) batik-dyeing equalization tank after coagulation-flocculation.

Alum performed well on both *strobilanthes* fermentation and indigo-batik dyeing wastewater. This behavior also claimed for textile wastewater treatment. Another benefit of alum is that the alum sludge can also be re-used for coagulation (Chu, 2001).

Chemical Oxygen Demand (COD) Removal

The organic load changes not only observed for indigo content but also for all oxidizable compounds in wastewater. It is shown in Figure 4, that the COD value decreased after addition of coagulant.

CBM perform continuous exponential decreases of COD value at all range of concentration for both fermentation and batik-dyeing wastewater. The COD value was decreased more than 66% after addition of high concentration of CBM for both waste water. Compare to other coagulants, this COD value is still high and not fulfilling the minimal requirement. Some important coagulation-flocculation process parameter needs to be optimized in the future study. Another factor which probably influenced is that CBM as a natural product, then the chemicals contents probably not stable during the storage and causing the ineffectiveness.

The lowest COD value was achieved after alum addition, which gave the number of were 87% and 63% for fermentation effluent and batik-dyeing effluent, respectively. Moreover, alum addition at high concentration leads to the increase of the COD value. The excess of Al^{3+} ion will dissolved in water and contribute the number of oxidizable inorganic content in wastewater, and directly affect the COD value (Tangahu *et al.,* 2019; Tak *et al.,* 2016).

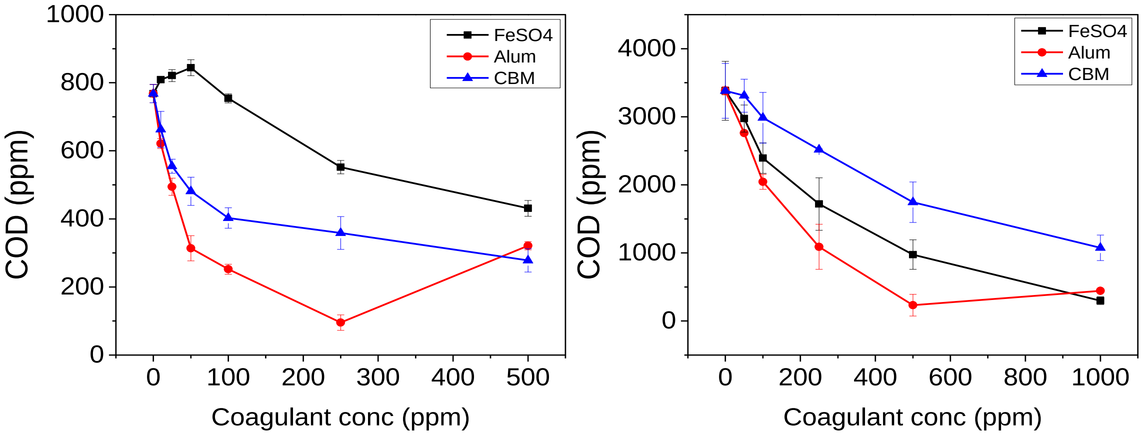


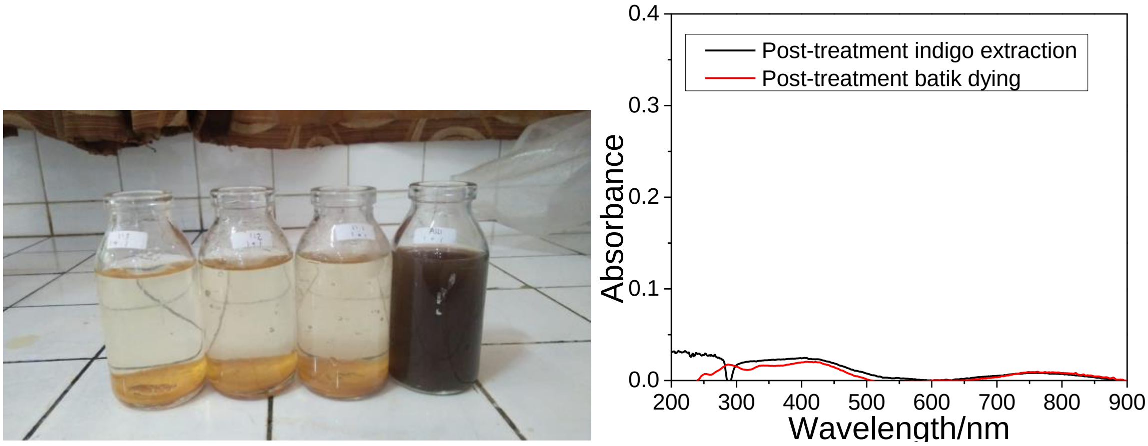
Figure 4. Chemical oxygen demand (COD) changes of (a) *strobilanthes* fermentation settling tank and (b) batik-dyeing equalization tank after coagulation-flocculation.

The decreased COD value shows that the organic and oxidizable component of wastewater were forcefully removed. However, from Figure 4 also seen that the addition of $FeSO_4$ the COD of the wastewater slightly increased (16%) at low concentration. The fixation behavior of $FeSO_4$ can explain this phenomenon. The existence of Fe^{2+} will interact with Indigo to form complex compounds, Fe(indigo)n, which highly stable (Lestari & Riyanto, 2004; Siagian *et al.,* 2017). The species which is stable in the solution will contribute to the number of COD (Tangahu *et al.,* 2019; Tak *et al.,* 2016). However, this phenomenon was not observed for batik-dyeing wastewater treatment. Batik-dyeing wastewater contains various chemicals. Fe^{2+} ion will then interact not only with Indigo but also another species which lead to the formation of flocks.

Wastewater Characteristic after Treatment

As the aim of this research is to remove the color, Figure 5 shows the UV-vis spectra of wastewater after treatment. In advanced, the wastewater parameters were evaluated after the coagulation-flocculation process, as shown in Table 2.

After coagulation and flocculation, the blue color of wastewater was decreased. The peak at around 610 nm is almost not observed. The peak at UV region also disappeared. This indicate that the compounds with chromophore moieties were removed from the wastewater. The pH of wastewater was significantly changed after coagulation-flocculation treatment with alum and $FeSO_4$. The pH changed can be explained by the water hydrolysis in the presence of metal salts (Rusydi *et al.,* 2016). The hydroxyl ions (OH^-) of water formed hydroxide with a metal ion (Al^{3+} and Fe^{2+}). The hydronium ion (H_3O^+) then acted to low the pH. Further, the TSS value indicates that the suspended solid was very low. Suspended solid was successfully aggregated and precipitate during coagulation and flocculation. After treated with alum, both fermentation effluent and batik-dyeing effluent were fulfilled the minimum requirement of wastewater disposal. Slight pH adjustment probably still required before disposal.



(a) (b)

Figure 5. (a) Final jar test result on batik wastewater and (b) UV-Vis spectra of post-treatment of wastewater.

Table 2. Physico-chemical characteristics of wastewater after treatment.

Parameter	Fermentation oulet			Indigo-dying outlet		
	250 ppm Alum	500 ppm FeSO4	500 ppm CBM	500 ppm Alum	1000 ppm FeSO4	1000 ppm CBM
pH	8.9±0.5	9.9±0.1	10.1±0.5	8.6±0.3	8.7±0.3	9.3±0.2
COD / ppm	95±12	431±23	230±34	233±59	298±56	1076±297
BOD / ppm	25.4	80.1	101.9	51.1	190.3	125.2
TSS / ppm	1.55±0.03	10.45±0.12	4.31±0.13	0.39±0.03	21.53±0.03	55.38±0.03
Abs_{610}	0,013	0,013	0,19	0,088	0,212	0,281

CONCLUSIONS

The current study was focused on the coagulant dosage effect on decolorization of wastewater from settling tank of *strobilanthes cusia* fermentation and equalization tank of batik-dyeing industry. Color and COD load indicate that the wastewater needs further treatment before disposal. The coagulation-flocculation process was chosen to minimize the color and COD loading. Alum, $FeSO_4$, and CBM perform as a right coagulation agent. Almost all parameters were eased up, including color, pH, COD, BOD, and TSS.

Future study is needed to obtain comprehensive information about coagulation-flocculation factors including initial pH effect, flocculation stirring rate, and a combination of coagulant.

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