

## **REVIEW ARTICLE**





# The Potential of Adsorption Technology for Batik Wastewater Treatment: A Review

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#### **ABSTRACT**

The Indonesian batik plays a crucial role in supporting the country's economy. However, its production often leads to environmental problems. As sustainable development implies the need for economic benefits equally accessible by all people without compromising the environment for the future of the next generation, the sustainability of batik means that batik, as a cultural product, should be preserved, and its production can bring economic benefits without harming the environment. Therefore, environmental issues related to batik should be overcome. Studies addressing the problem of batik wastewater have been conducted; however, adsorption technology is gaining popularity due to the benefits it offers. This review examines the characteristics of batik wastewater, identifies existing batik wastewater treatment technologies, and evaluates the potential of adsorption technology for batik wastewater treatment. This literature review was conducted using Science Direct and Directory of Open Access Journals (DOAJ) search engines, which initially collected 78 articles, and finally, 58 articles were found to be suitable for the review. An Excel-based matrix was then created to analyze the literature manually. It is found that batik wastewater is usually alkaline; the Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and Total Suspended Solids (TSS) usually exceed the quality standard regulated by the Indonesian government, and are usually non-biodegradable, as indicated by the low BOD/COD ratio. Adsorption is widely applied, economically feasible, and can be easily operated by batik entrepreneurs. The performance of this technology is best when combined with other processes.

#### Introduction

Batik is one of Indonesia's cultural products that plays an important role in supporting the country's economy. It is reported that in 2022, the export of batik and batik products reached USD 64.56 million, representing a 30.1% increase from the export value in 2021. In 2023, the Minister of Industry and Trade of the Republic of Indonesia made an effort to reach the USD 100 million export target [1]. The batik industry is also considered a labor-intensive sector, as it can absorb millions of workers [1]. The potential of batik in supporting Indonesia's economy is also reported in a previous study and is considered inseparable from its recognition by UNESCO as a World Intangible Heritage in 2009 [2].

In Indonesia, batik is commonly produced by Small and Medium Enterprises (SMEs) by the application of dyes, both synthetic and natural dyes (Figure 1). Previous studies have indicated that SMEs can contribute to the deterioration of environmental quality [3–5], a phenomenon also observed in the case of batik SMEs [2]. Environmental contamination of batik wastewater has been reported in some batik-producing regions, including Cirebon, Surakarta (Solo), Yogyakarta [2], Pekalongan [2,6], Sragen [7], and Klaten Regency [8]. In Pekalongan, the pollution has even been reported to decrease the water quality of the people's dug well, indicated by turbid (3.6%), smelly (16.1%), colored (9.8%), and tasteless (10.7%) water [6].

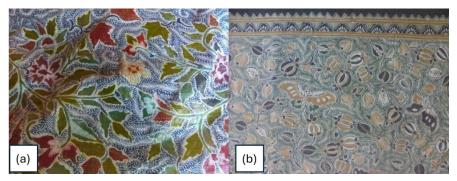


Figure 1. A prepared batik cloth applied by (a) synthetic dyes and (b) natural dyes.

The implementation of sustainable development should ensure that development can give economic benefits equally accessible to all people without deteriorating the environment for the future of the next generations. In the case of batik as a cultural product, it should be conserved, and its production to support the economics of Indonesia should not endanger the status of the environment. Therefore, the sustainability of batik as Indonesia's cultural heritage could go hand in hand with environmental and economic sustainability.

Studies were conducted to find the most suitable technology that might involve physical, chemical, and biological processes to address the problem. Some offered processes include coagulation [9–12], membrane filtration [13,14], advanced oxidation [15,16], ozonation [17], biological processes, both in the form of activated sludge process, attached growth, phytoremediation, or bioremediation [7,18,19], and adsorption process [2]. Recently, the adsorption process got more attention because of its efficiency in removing non-biodegradable pollutants [20], and this process could become a good combination if it is applied together with another process. Wastewater treatment, in general, could not merely involve a single use of technology, and hence, a combination of processes is preferred to provide better results. Moreover, although there might be many batik wastewater technologies available, the technology should be selected based on the characteristics of the wastewater. Therefore, this review will explain the characteristics of batik wastewater, identify the available batik wastewater treatment technologies, and explore the potential of adsorption technology for batik wastewater treatment.

#### **Materials and Methods**

The literature for this review was collected from three search engines: ScienceDirect, Research Gate, and the Directory of Open Access Journals (DOAJ). An exploration by Science Direct was conducted using the keyword "adsorption technology for batik wastewater", which found 78 articles on batik wastewater and textile wastewater in general. The articles selected for this study are Open Access articles and those with topics related to the use of technologies to treat dye-containing wastewater, and finally, 23 articles were found appropriate for this review. Meanwhile, the exploration by DOAJ was conducted using the keyword "batik wastewater treatment," which resulted in 37 articles. The articles included for this review are those written in English and those with topics related to the use of technologies to treat dye-containing wastewater. Finally, 30 articles were selected for this review. In addition, more articles are explored from Research Gate to find limitations of adsorbent, advanced oxidation process, and membrane technology, which found 5 suitable articles. Therefore, 58 articles in total were used for this review. The articles were put into an Excel-based matrix to summarize their abstracts, research methodologies, and research findings. These findings are then included in the writing of this paper.

#### **Results and Discussion**

#### Results

## The Characteristics of Batik Wastewater

Although there are media on which the batik technique could be applied, commonly, batik is made upon a cloth, both silk and cotton. Technically, batik cloth is made by creating a motif using wax as the dye-resisting material, and the batik-making process has been explained previously [8]. The batik wastewater usually

results from three processes, i.e., (1) the cloth preparation stage, which involves washing the cloth with Turkey Red Oil detergent; (2) the dyeing and fixation stage; and (3) the wax-removal and washing stage [8,21]. As SMEs are usually not accustomed to using the standard operating procedure, variations among SMEs in using dyes (both synthetic or natural dyes) and chemicals are usual. Therefore, the wastewater characteristics could differ among SMEs, as presented in Table 1.

Table 1. Batik wastewater characteristics.

Wastewater quality	Batik wastewater parameters concentration				Quality standard	
parameters	[8]	[11]	[22]	[23]	[24]	[25]
рН	9.8	10.7	9.8	12.1	5.8	6–9
Total Suspended Solids (mg/L)	1,400	72	388	NA	972	50
Chemical Oxygen Demand (mg/L)	6,960	867	870	13,600	2,870	150
Biological Oxygen Demand (mg/L)	21.2	NA	552	NA	5.50	50
BOD/COD ratio	0.003	NA	0.634	NA	0.002	0.333

NA = not available.

It is indicated from Table 1 that batik wastewater tends to be alkaline and contains a high concentration of organic matter represented by Chemical Oxygen Demand (COD). The alkaline properties of batik wastewater might relate to the use of certain chemical, such as the soda ash which are commonly used in the wax removal process [8]. However, there is possibility that batik wastewater could show an acidic tendency instead of alkaline because the use of hydrochloric acid (HCl) as a fixative agent for indigo sol dye [24].

Based on Table 1, the concentration of Total Suspended Solids (TSS) and COD is mostly higher than the quality standard regulated by the Indonesian government [25]. Higher COD indicates a higher concentration of organic matter contained in the wastewater. In addition, the wastewater's biodegradability indicates that batik wastewater tends to be non-biodegradable, as indicated by a low BOD/COD ratio. It is reported that a ratio BOD/COD of less than 0.30 corresponds to low biodegradability of the wastewater [26]. By understanding the characteristics of the wastewater, the required process to treat the wastewater can be decided.

## Wastewater Treatment Process and Batik Wastewater Treatment Technologies

The wastewater treatment requires technologies to eliminate or reduce the pollutants it contains. Based on the advanced characteristics of these technologies, three types of technologies can be applied. The first is the conventional techniques such as the coagulation-flocculation, precipitation, and sand filtration. The second is the established recovery process, such as oxidation technique, electrochemical method, membrane technology, and incineration; and the third is the emerging removal methods, which are represented by advanced oxidation technologies, adsorption, biosorption, biomass application, and nanofiltration [27].

Generally, the wastewater treatment consists of some steps, which are usually called primary, secondary, and tertiary treatments. When the physical and mechanical processes usually take place at the primary treatment (which typically removes 30–40% BOD), the secondary process usually involves a biological process [28]. Despite how many treatments there are, prior to the treatment, the wastewater usually passes through the preliminary treatment to prepare it for the next treatment.

Preliminary treatment is designed to remove large solids, scum, and grit (inorganic-non-biodegradable materials) from the wastewater. The process usually takes place using screens to remove debris, such as cans, rags, rocks, etc., and grit removal units [28]. In addition to this process is the equalization treatment, which plays an important role in wastewater treatment. The flow equalization and chemical neutralization are two important steps in wastewater treatment to control flow velocity and composition, while the other was meant to balance the acidity or alkalinity of the wastewater [29]. These processes bring some benefits, i.e., improving the wastewater's treatability, improving sedimentation efficiency, and providing an appropriate condition for microbial process if the biological method is used [29]. In terms of batik SMEs, the wastewater usually contains wax, particularly after the wax-removing process takes place. However, the wax is usually recovered by the workers for the recycling process [24], and therefore, the preliminary treatment in terms of removing wax from the wastewater is no longer a problem. The important thing is probably regarding the chemical neutralization, considering the pH of the alkaline tendency of batik wastewater.

After the equalization, the wastewater enters the first step, called primary treatment, which involves the elimination of solid particles from the wastewater. This process is designed to separate and remove settleable and floatable solids, which are usually indicated by the suspended solids, while allowing the sludge-thickening

process [28]. The process could be conducted by physical and chemical processes such as sedimentation or coagulation [27]. It is reported that by gravity settling, 40–60% of suspended solids could be removed, while BOD could be reduced by 30–40% [28]. However, if more suspended solids were removed, the addition of chemicals, such as alum, might be considered. It is reported that the addition of alum or other coagulants could precipitate suspended solids to 80% or 90% [28]. In case of batik wastewater, a recent study indicates that the use of 1.5 g/L of alum as a coagulant applied at pH 8, mixed at 100 rpm, and settled for 4h could reduce COD, turbidity, color, and TSS by 70.7%, 92.2%, 88.4%, and 100%, respectively [11]. Previous studies indicate the advantages of coagulation, i.e., (1) effective in removing pollutants, including dye substances; (2) producing less sludge if compared to chemical coagulants; and (3) less hazardous degradation products for the electrocoagulation technique [30]. Considering that alum is commonly found at an affordable price, the application of alum as a pre-treatment for batik wastewater is quite promising for batik SMEs.

As the COD and BOD concentrations are reduced by primary treatment, the treatability of wastewater is increased, and the wastewater is ready for secondary treatment, which typically involves a biological process. Basically, the biological process involves the biochemical oxidation by the role of microbes, both anaerobically and aerobically. Some biological process technologies include the use of aeration, attached growth systems, such as trickling filters and Rotating Biological Contactor (RBC) [28]. Our previous study indicates that the combination of Anaerobic Baffled Reactor (ABR) to treat batik wastewater could reduce COD to 45.4%, 61.7% Total Dissolved Solids (TDS) reduction, and 71.8% turbidity reduction, while the application of RBC could only reduce COD to 15.2%, 57.1% TDS reduction, and 19.4% turbidity reduction [7]. Although the ABR and RBC could be used for batik SMEs, this kind of technology could be considered as advanced and high-cost technologies to batik home industry entrepreneurs who commonly graduate from high school, which implies difficulty in tackling and maintaining the technologies, particularly for possible technical troubleshooting. Moreover, the biological process needs a spacious area to construct ponds or lagoons, which is not flexible for home industries. Therefore, innovations to solve this situation are now explored (Table 2).

**Table 2**. Possible batik wastewater treatment processes.

Batik wastewater treatment technology	Perf	ormance
Adsorption	a)	A minimum dye decolorization of 90% achieved after 144 h of adsorption by fungal myco- LECA composite [31].
	b)	Adsorption by Palm Shell Activated Carbon reduced COD to less than 50 mg/L after acidification [23].
	c)	The application of Palm Oil Fuel Ash-based adsorbent could adsorb the dye in batik wastewater up to 22% removal efficiency and 62 mg/g adsorption capacity [32].
	d)	Dye removal of batik wastewater using sewage-sludge biochar achieved 42.30 mg/g adsorption capacity by 16 L/h flowrate and 12 cm of bed depth [33].
	e)	Color removal from 496 mg/L to 147 mg/L (70.36%), neutralized pH (7.34) from alkaline condition (10.9), and COD reduction from 9,800 ADMI to 128 ADMI (98.69%) were achieved by the application of zwitterionic adsorbent coating [34].
	f)	COD reduction increased from 19–67% after the application of geopolymer/alginate spheres (GSA) adsorbent [35].
	g)	The application of teak sawdust-based activated carbon reduced the COD from 1,862.66 mg/L to 230.9 mg/L (87.60%), BOD from 569.97 mg/L to 67.04 mg/L (88.24%), and Zn from 22.75 mg/L to $1.84$ mg/L ( $91.91\%$ ) [36].
Advanced oxidation process by catalysis and	a)	The batik wastewater was degraded by 50.41% for 5 days of irradiation by TiO <sub>2</sub> -based photocatalysis [15].
ozonation	b)	COD, BOD, and TSS were reduced by 97, 23, and 71 points, respectively, by TiO <sub>2</sub> -based photocatalysis [15].
	c)	A COD reduction from 72.9 mg/L to 39.2 mg/L (46.22%) was achieved by TiO <sub>2</sub> -based photocatalysis [16].
	d)	A BOD reduction from 23.2 mg/L to 11.7 mg/L (49.56%) was reached by TiO <sub>2</sub> -based photocatalysis [16].
	e)	Complete decolorization of batik wastewater and 60.80% of COD removal were achieved by electrocatalysis performed at 5V, 120 min HRT, 4,000 mg/L salt concentration, and pH 5 [37].
	f)	A Remazol Blue color reduction of 99.70% and a reduction of 4-chlorophenol reached 62.79% after 60 minutes of ozonation under alkaline conditions [17].
	g) h)	A color reduction from 4,240 mg/L to 70 mg/L (98%) after 10 minutes ozonation [38]. A reduction of COD from 86 mg/L to 63 mg/L (26.74%) after 15 minutes of ozonation [38].

Batik wastewater	Perf	ormance
treatment technology		
	i)	A reduction of Total Organic Carbon (TOC) from 19.9 mg/L to 13.1 mg/L (34.17%) after 10
		minutes of ozonation [38].
	j)	Using a PSf/Ni@ZnO 1 wt-% membrane of 28.8 nm pore size under UV light exposure, TDS,
		COD, and dyestuff concentration were reduced by 26.4%, 34.7%, 92.1%, respectively [39].
	k)	Photocatalytic degradation-filtration combination using the PSf/Ni@ZnO 1% (w/w) showed
		the removal of total dissolved solid, chemical oxygen demand, and dye removal of 26.4%,
		33.5%, 92.2%, respectively [39].
Coagulation –flocculation	a)	The use of tofu bittern as a coagulant reduced Pb2 <sup>+</sup> and turbidity by 99% and 93%,
		respectively, at a coagulant dose of 25% with 55 rpm [12].
	b)	Heavy metals removal and COD reduction of 70% were achieved by the addition of MgO
		after acidification at pH 3 [23].
	c)	COD reduction of batik wastewater by 27% was achieved by the application of 1,500 mg/L
		MgO after acidification [35].
	d)	The COD, BOD, and Zn were reduced by 73.28%, 73.62%, and 79.21% respectively, after
		alum was applied at pH 6 [36].
Acidification	a)	A COD reduction of 98% (from an initial concentration of 4,915 mg/L) was achieved under
		acidification at pH 3 [23].
	b)	Acidification to pH 3 removed COD of batik wastewater by 93% [35].
Biological process	a)	The application of Anaerobic Baffled Reactor (ABR) in reducing COD, turbidity, and color reached 45.4%, 71.8%, and 65.1% [7].
	b)	The application of Rotating Biological Contactor (RBC) in reducing COD, turbidity, and color
		reached 15.2%, 19.4%, and 22.7% [7].
	c)	Bioremediation by immobilized Bacillus licheniformis reduced COD up to 75% [40].
	d)	Lepiota sp. exhibits fungal decolorization of dye-containing batik wastewater, which
		reached maximum decolorization of 85.78% under 72 h of incubation and an addition of
		1% of glucose concentration [41].
Membrane Technology	a)	The application of Polysulfone (PSf)-based membranes with the addition of polyvinyl
		pyrrolidone (PVP) membrane filtration reached the optimum removal of COD, color, TDS,
		and conductivity by 80.4%, 85.7%, 84.6%, and 83.6%, respectively [14].
	b)	The application of PSf/Ni@ZnO 1 wt% membrane of 28.8 nm pore size under dark
		conditions reduced TDS, COD, and dyestuff concentration by 19.6%, 16.6%, and 95.6%
		respectively [39].

Based on Table 2, technologies for batik wastewater have been emerging in a wide variety. The processes are focused on reducing pollutants contained in batik wastewater, indicated mostly by COD, BOD, solids (TSS or TDS), and dyes. It is indicated that acidification to pH 3 could reduce COD more than 90% [23,35]. Those studies were conducted for silicate-containing batik wastewater because of the addition of sodium silicate as a color stabilizer [23]. However, the addition of a strong acid, such as HCl, could lower the pH of the wastewater. In a low pH, the conversion of silicate to silicic acid takes place, which further forms polymerized SiO2. The reaction of the silanol group with oxygen molecules of wax will form the coordination of wax ester and polymerized SiO2, indicated by the decrease of COD and Si concentration [23]. A similar study indicates that COD and color removal of batik wastewater was high in the acidic conditions—in this case is pH 5—with the removal percentage reached 89.71% (COD) and 93.89% (color), resulting to the increase of BOD5/COD ratio from 0.015 to 0.271 [42], which indicates the increase of batik wastewaters' biodegradability. However, the findings of the studies indicate that acidification might bring an advantage for the pre-treatment of batik wastewater.

Another common process usually involved in the treatment is coagulation and flocculation. This method is preferable because it can use any widely available coagulants, such as alum, MgO, etc. Although COD reduction of 27% was reported using 1,500 mg/L of MgO [35], other studies indicate that the use of MgO (applied after acidification at pH 3) or alum (applied at pH 6) could reduce COD by around 70% [23,36]. A study using 3,000 mg/L MgSO4–Aloe vera hybrid coagulant could reduce dye contained in textile wastewater (not specifically batik) to 70% under pH 12.5 [9]. Another study even indicates the use of bittern could reduce turbidity and Pb2+ contained in the wastewater up to 93% and 99%, respectively, under alkaline conditions because the bittern itself naturally contains magnesium, chloride, and sulphate ions [12]. The efficiency of coagulants, however, is seemingly influenced by the pH of the mixture and the dosage of the coagulant, which in the case of alum is optimum in alkaline conditions [43]. This understanding is important if additional treatment by coagulants will be required to treat the wastewater, particularly after pH adjustment.

Other technologies, such as membrane filtration, could help to reduce the COD concentration of batik wastewater up to around 80% [14] and remove color by 85–95% [14,39]. The advantages of using a membrane to treat wastewater fall to its capability to remove a wide spectrum of dyes and organic compounds [30,44], resistance to higher temperatures and adverse chemical environments, as well as good permeability [44]. However, there are some precautions for using this kind of technology, i.e., concentrated sludge production [30], membrane fouling, which needs to be replaced periodically, and high cost both for management and disposal [44].

Another promising technology is Advanced Oxidation Process (AOPs). The AOPs are new introduced technology that include catalysis, both photocatalysis and electrocatalysis, and chemical oxidation, such as ozone oxidation. It involves the generation of highly oxidizing radicals (such as hydroxyl and sulphate radicals) under certain conditions involving temperature, pressure, UV light, or oxidizing agents [44]. Based on Table 2, it is indicated that ozonation could remove the color of batik wastewater around 98% [17,38], while the combination of filtration and photocatalysis exhibits 92% dye removal [39]. The advantages of AOPs are fast process, and eco-friendly because sludge is minimally generated during the process [44]. However, the process needs chemicals, is costly, and requires skillful human resources to operate the process [44].

In addition to those processes, the adsorption technology offers COD removal from at least around 87% to 98% [34,36] and color removal by at least 90% [31]. The adsorption process has advantages, such as high removal, and could remove a wide spectrum of dyes [30,44], regenerable, simple, and flexible, and low cost [44]. However, there is a problem regarding the use of adsorbents, i.e., some adsorbents are quite costly as well as require long exposure to reach the expected removal and need further treatment for the pollutants adsorbed to be completely removed [44].

The biological process offers wastewater pollutants removal up to 75% or even up to 85.78% [40,41]. It is cost-effective and possible to implement, mainly in developing countries [30,44]. However, it needs longer operation time in comparison to the physicochemical approach [44]. Moreover, it is only suitable for wastewater of good biodegradability, indicated by a high BOD5/COD ratio, because in lower biodegradability wastewater, the microbes could not grow well, as the condition is unfavorable for microbial growth [30,44].

Among all the processes offered, the batik wastewater treatment needs an appropriate technology, particularly for the batik SMEs, because they need a simple, low-cost, and easy-to-handle kind of technology or process, except if the technology needs to be tackled by a third party, such as the government or private sector. The use of advanced oxidation and biological processes will be suitable for the latest case because the process needs the assistance of a skilled person to tackle technical issues related to the process. Therefore, the suitable processes for batik SMEs are acidification, coagulation-flocculation, and adsorption.

#### Adsorbents and Their Performance for Wastewater Treatment

Adsorption is defined as a process in which a component in a gas or liquid form is attached to the surface of an adsorbent (solid form) by the contact of the component (usually called the adsorbate) and the adsorbent. Simply said, adsorption is the adhesion of atoms, molecules, or ions to a surface. The process accumulates particles removed from the bulk phase because of interactive physical forces between the porous solids' surface and the removed molecules. Based on this principle, adsorption technology is promising for separating gases and liquids [45], and it is gaining popularity worldwide. The performance of some adsorbents is presented in Table 3.

There are at least three mechanisms of how the adsorption takes place, i.e., physisorption [30,45], chemisorption [30,45], ion exchange [30,44,45], and precipitation, in addition to the previous three mechanisms [30]. The physisorption involves the electrostatic interaction and Van der Waals force [30,45,46], diffusion, and surface adsorption [30]. The chemisorption relates to involvement of chemical bonding, both ionic and covalent, which also requires high activation energy [30,45,46], as well as chelation, coordination bonding, and oxidation-reduction [30,46]. The ion exchange involves the exchange of ions between liquid and solid phases and is usually involved in dissolved contaminants in water [45]. It is also reported that dye pollutants contained in wastewater are usually removed by this mechanism [30,44]. However, regarding heavy metals from wastewater, the chemisorption is preferable because it shows stronger interactions and higher adsorption capacity toward heavy metals. The process involves (1) transporting pollutants from bulk solutions to the external surface of the adsorbent, and (2) adsorbing the pollutants on the active sites of the adsorbent's pore [46].

As adsorption is a surface phenomenon, the extent of the process occurs, or the quality of the process is influenced by the characteristics of the adsorbent and the adsorbate [45]. The adsorbent characteristics

include porosity, pore structure, pore size, and the nature of the adsorbing surface [30]. It is reported that the surface area of the adsorbent is equivalent to the adsorption [45]. Regarding the pore size, there are macropores (> 50 nm in diameter), mesopores (2–50 nm in diameter), and micropores (< 2 nm in diameter) types of adsorbents [30].

**Table 3.** Performance of adsorbents for the wastewater treatment process.

Type of adsorbent	Perfo	ormance	Ref.
Bulk adsorbent: Palm shell-	a)	The process could reduce COD to less than 50 mg/L following acidification at pH	[23]
based activated carbon (PSAC)		3 and application of MgO coagulant.	
	b)	Low pH is favorable to remove reactive dyes contained in batik wastewater by PSAC.	
	c)	Electrostatic interaction and hydrogen bonding mechanisms are involved in the process.	
	d)	Adsorption of dyes by PSAC is also affected by organic groups, such as wax	
		contained in the wastewater.	
Bulk adsorbent: Biochar made	a)	Surface area of the biochar was 117.7 m <sup>2</sup> /g.	[33]
of sewage sludge	b)	A 42.30 mg/g adsorption capacity of dye (234 Pt-Co of initial concentration) was achieved by 16 L/h flowrate and 12 cm of bed depth.	
	c)	The adsorption mechanism involves hydrogen bonding, electrostatic	
		interaction, functional group interaction, and $\pi$ - $\pi$ interaction.	
Bulk adsorbent: Zwitterionic	a)	The external surface area was 4.64 m <sup>2</sup> /g.	[34]
adsorbent made of bentonite	b)	The adsorbent performs COD removal from 496 mg/L to 147 mg/L (70.36%),	
clay		neutralized pH (7.34) from alkaline conditions (10.9), and color reduction from 9,800 ADMI to 128 ADMI (98.69%).	
	c)	Highest reduction of COD takes place at pH 5 and pH 11.	
	d)	Mechanism of adsorption by the adsorbent involves electrostatic attraction,	
		surface area, chemical bonding, and hydrogen bonding.	
Bulk adsorbent: Geopolymer	a)	Surface area of adsorbent was 12.874 m <sup>2</sup> /g.	[35]
alginate adsorbent	b)	COD reduction from 175 mg/L to 70 mg/L was achieved after the application of	
	•	10 g/L geopolymer/alginate spheres (GSA) adsorbent.	
Bulk adsorbent:	a)	The surface area of TSAC was 25.441 m <sup>2</sup> /g.	[36]
Teak sawdust activated carbon	b)	The TSAC application reduced the COD from 1,862.66 mg/L to 230.9 mg/L	
(TSAC)	,	(87.60%), BOD from 569.97 mg/L to 67.04 mg/L (88.24%), and Zn from 22.75	
		mg/L to 1.84 mg/L (91.91%).	
	c)	The highest reduction of COD, BOD, and Zn occurs at 26 g/L TSAC at 50–100	
	•	minutes exposure.	
	d)	Adsorption mechanisms involve chemisorption.	
Bulk adsorbent: Bio-sorbent	a)	The composite is constructed to exhibit functions of adsorption, photocatalysis,	[47]
made of basil ( <i>Ocimum</i>		and self-cleaning processes.	
basilicum) seeds combined to	b)	The adsorption of Methylene Blue (MB) dye from 5 ppm to 0.053 ppm (98.95%	
immobilized nano-TiO <sub>2</sub> (B-F-		reduction) by B-F-TiO <sub>2</sub> occurred in 90 minutes under direct sunlight exposure.	
TiO <sub>2</sub> )	c)	The maximum capacity of the adsorbent for MB dye was 49.47 mg/g.	
	d)	Adsorption of MB dye merely using basil seeds as an adsorbent indicates	
		74.74% reduction by the chemisorption mechanism.	
	e)	The removal of MB dye is increased by the increase in surface area of the composite.	
Bulk adsorbent: Bio-sorbent	a)	The adsorption of MB dye (800 mg/L as initial concentration) was optimum at	[48]
made of activated corn husk	u,	pH 6, 60 minutes contact time at room temperature (298 K) and 100 g/L adsorbent.	[ 10]
	b)	The adsorption capacity of the bio-sorbent was 41.06 mg/g.	
	c)	Under neutral pH (6–7), the MB dye (laboratory wastewater) removal could	
	c,	reach 98–99%.	
	d)	Under pH 6, the bio-sorbent could remove 50.41% MB dye from batik	
		wastewater. However, the removal of MB dye could only achieve 13.94% when	
		the bio-sorbent applied for real batik wastewater (pH 10).	
	e)	The adsorption mechanisms involved are hydrogen bonding, electrostatic	
		interaction, and Van der Waals force.	
Nano adsorbent: Reduced	a)	The adsorption of MB dye for 98.78% was optimum at pH 11, by 5 mg/L	[49]
graphene oxide		adsorbent for 20 minutes contact time.	
	b)	The maximum capacity of the adsorbent was 50.07 mg/g.	
	c)	The adsorption mechanism involved is physisorption in the form of electrostatic interaction, hydrophobic bonding, and $\pi$ - $\pi$ interaction.	

Type of adsorbent	Perf	ormance	Ref.
Bulk adsorbent: Biochar made	a)	The specific surface area was 174.67 m <sup>2</sup> /g.	[50]
of bamboo stem	b)	Maximum adsorption capacity was 114.75 mg/g at 0.02 g adsorbent loading for	
		initial Reactive Violet 5 dye concentration 10–50 mg/L.	
	c)	The adsorption mechanism involves hydrogen bonding and $\pi$ - $\pi$ interaction.	
Bulk adsorbent: Biochar made	a)	The specific surface area was 44.78 m <sup>2</sup> /g.	[50]
of calabash	b)	Maximum adsorption capacity was 0.0385 mg/g at 0.02 g adsorbent loading for	
		initial Reactive Violet 5 dye concentration 10–50 mg/L.	
	c)	The adsorption mechanism involves hydrogen bonding and $\pi$ - $\pi$ interaction.	
Bulk adsorbent: Pineapple	a)	The impregnation ratio influences the performance of the adsorbent in	[51]
leaves-based activated carbon		adsorbing dye molecules.	
	b)	The dye removal increased as the carbonization temperature increased.	
	c)	Adsorption capacity 50 mg/g.	

The adsorbents could be made of wide variety of materials, and are usually categorized into two groups, i.e., (1) bulk adsorbents and (2) nano-adsorbents represented by nanoparticles, nanomaterials (such as graphene), nanofibers, nano-clays, polymer composites, and aerogels [45]. The bulk adsorbent could be classified further into conventional and non-conventional adsorbents [45]. Those of conventional adsorbents are (1) commercial activated carbon made of wood, coals, shells [45]; (2) inorganic materials, such as commercial activated alumina, zeolites, silica gels [30,45]; (3) and ion exchange resins [45]. The nonconventional adsorbents are (1) waste-based activated carbon; (2) bio-sorbents, such as chitosan, bacteria, fungi, algae, yeasts, lichens, rice husks, coconut shells, peat moss [45,52], other materials of natural origin or derived from industrial by-products, such as clay, red mud, sludge, etc [45]. The bio-sorbents are usually made of dead biomass and the adsorption by this kind of bio-sorbent is usually called biosorption [46], that differs it from the bioremediation or phytoremediation which usually take place in the living cells. The performance of various adsorbents in treating wastewater is presented in Table 3. The performance of adsorbents to remove pollutants is influenced by some factors. The surface area of the adsorbent influences the adsorbent's performance. As previously mentioned, the greater the surface area, the greater the process, and conversely [45]. This is indicated by the performance of biochar made of bamboo stem, by 174.67 m<sup>2</sup>/g surface area, which exhibits a higher adsorption capacity (114/75 mg/g) compared to the surface area of biochar made of calabash (44.78 m<sup>2</sup>/g), by 0.0385 mg/g adsorption capacity [50]. Furthermore, membrane adsorbents made of chitosan and nano materials are reported to possess a large surface area [46]. However, another study indicated that even a smaller surface area (100-10 m²/g) could exhibit higher adsorption performance (460.5 g/m²/min) compared to a larger surface area (1,000-100 m²/g), which adsorbs 12.52 g/m<sup>2</sup>.min when the pore size is favorable for rapid uptake, which tends to be micropore [53]. Therefore, the size of the pore contributes to the performance of the adsorbent in addition to surface area.

The existence of functional groups might also impact the ability to adsorb different kinds of pollutants. Activated carbon is a good adsorbent for heavy metals because it has a large surface area with a variety of functional groups—including carboxyl, carbonyl, phenol, quinone, lactone, and other groups—attached to its structure [46]. The adsorption of dyes contained in batik wastewater by zwitterionic adsorbent is reported to occur because negatively charged groups originated from bentonite materials of the adsorbent, attracting positively charged dyes that induced electrostatic interaction [34]. The role of functional groups has also been reported previously to influence the adsorption performance of adsorbents [45].

Another factor influencing adsorption is pH of the solution. As reported, in a lower pH or acidic medium, the abundance of H+ ions will protonate the adsorbent surface, which eventually attracts anions from the medium. However, alkaline conditions weakened the electrostatic interactions between dye molecules and adsorption sites on the adsorbents, resulting in the desorption of dye molecules from the adsorbents [34]. Another study also found that biosorption is better to occur at pH 3–9, and the pH plays a key role in speciation and biosorption affinity of metal ions [48].

## Discussion

It is generally understood that the option to use specific technology for wastewater treatment should be determined based on the characteristics of the wastewater itself. In the case of batik wastewater, it is presented in Table 1 that batik wastewater tends to be alkaline and contains high Total Suspended Solids. Furthermore, it is also indicated that the wastewater has low biodegradability as its BOD/COD ratio value is usually less than 0.30 [26]. This means that biological processes might not be suitable to treat the wastewater, unless there are physical and/or chemical treatments to reduce the COD, and after these treatments, biological treatment might be applied. Even though the BOD/COD ratio is higher than 0.30 [22], it is not

automatically suitable for biological process to take place because the alkaline condition or high pH value [22] might not be appropriate to support the growth of microbes, the common biological agent for the biological wastewater treatment process. Furthermore, the use of biological treatment requires a particular Wastewater Treatment Plant (WWTP), which technically could be difficult to handle by batik entrepreneurs. Our previous study indicates that batik entrepreneurs usually graduated from primary school or high school [21]. This implies that the commonly used WWTP might not be suitable for SMEs because very often SMEs do not have the knowledge and technical capacity to operate the WWTP [54]. Therefore, other options left is the use of simple and practical technologies that could be applied by batik SMEs, such as the chemical and physical options.

Among those options, this study identifies chemical and physical options such as the adsorption, advanced oxidation by catalysis or ozonation, coagulation—flocculation, acidification, and membrane technology. Table 2 indicates that advanced oxidation by TiO2-based photocatalysis can reduce BOD, COD, and TSS, while the ozonation is very promising to remove the dyes contained in the wastewater as its application could reach more than 90% of dye removal. However, previous study indicated that application of TiO2 as a catalyst has not conducted yet in a full-scale application, while the process needs lots of study in determining the optimum concentration of catalysts, and further separation step will be required if the catalysts is added as slurry [55]. In addition, although ozonation is very promising for dye removal of wastewater, its application needs a high cost and may form a toxic byproducts [55].

The use of membrane technology is also promising in reducing COD, TDS, conductivity, and dyestuff contained in the wastewater by removal percentage around 80% or higher (Table 2). However, its application is limited by the high cost of implementation and the challenges of technical issues, such as membrane fouling, as the process is influenced by factors including pH, ionic strength, membrane roughness, and temperature [56]. Therefore, the advanced oxidation and membrane filtration are not appropriate for batik SMEs, and the remaining possible options are adsorption, coagulation—flocculation, and acidification, which could be combined in order to treat batik wastewater as presented in Figure 2.

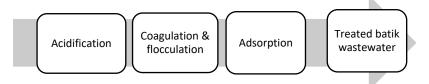


Figure 2. The proposed batik wastewater treatment process for batik SMEs.

The studies indicate that the use of adsorbents is very promising to treat wastewater, particularly to remove COD, BOD, heavy metals (Zn), and dyes to around 90% removal. Although the adsorption performance of adsorbents is affected by many factors, adsorption is still a promising technology available, particularly to treat wastewater. First, it can be produced from many varieties of sources, even agricultural wastes. Commercial activated carbons are also available widely at a relatively affordable price. Second, it can be used easily by batik entrepreneurs, and technical issues related to using activated carbon can be eliminated or at least will not burden the batik SMEs because of the difficult infrastructure technologies to handle. In addition, the cleaner production needs awareness and knowledge of technology, in addition to an investment [57]. Here, the knowledge on the latest technology appropriate for SMEs becomes important to help them not to rely on outdated and expensive know-how. The third, some adsorbents are reusable, making it economically feasible than other advanced technologies. The advantages of adsorption have been reported, such as wide applications, easy operation, economic feasibility, and simple design [46]. However, the use of adsorption alone, of course, is not suggested because batik wastewater needs to pass pre-treatment procedures.

The combination of acidification, coagulation, and flocculation—adsorption might bring promising results to treat batik wastewater (Figure 2). Those three processes are selected mainly because of their simple design that can be easily operated by batik SMEs and their effectiveness in removing pollutants. Dye is the major pollutant contained in batik wastewater; therefore, acidification is selected because an acidic medium could significantly increase the removal of dyes [33], which will also reduce the COD concentration of the wastewater. Acidification is also needed to provide favorable conditions for coagulation and flocculation, as reduction of COD, BOD, and Zn takes place after alum is added at pH 6 [36]. Other studies also indicate that coagulation flocculation could optimally reduce pollutants under acidic conditions [23,35]. When the COD concentration is decreased, the BOD/COD ratio could be increased, implying higher biodegradability of the

wastewater. Further processing using coagulation is intended to reduce the COD concentration of the wastewater. Finally, after COD reduction, the adsorption process is used to complete the removal process. However, it is commonly understood that the adsorbent will be saturated, and in the long term, the adsorbent should be replaced or removed. This means that the use of adsorbents will leave another kind of waste. However, there is another option to regenerate adsorbents and release the adsorbed pollutants, i.e., in the form of solid dyes, which could be dried and incinerated as well as immobilized as bricks or concrete [58]. If the adsorbent is not regenerated, then the saturated adsorbents can further be processed for other applications, such as materials for construction, fertilizer, and other applications [58].

#### **Conclusions**

The batik wastewater is usually alkaline and contains pollutants measured as TSS, COD, and BOD that exceed the quality standard regulated by the Indonesian government. It is also non-biodegradable, as indicated by a low BOD/COD ratio. The batik wastewater could be treated by some process, such as acidification, coagulation—flocculation, Advanced Oxidation Process, membrane filtration, adsorption, and biological process. Adsorption is a promising wastewater treatment technology as it is widely applied, economically feasible, and easily operated, and therefore, it could be recommended for batik SMEs. The adsorbents are in the form of activated carbon, nano adsorbent, polymer-based adsorbent, biochar, and bio-sorbent. The adsorbents exhibit a high capacity to treat dye-containing wastewater, which is promising for treating batik wastewater. However, the use of adsorbents for the batik wastewater treatment process should be combined with other simple and easily operated processes; therefore, it is suggested to use a sequential process of acidification, coagulation, and flocculation, followed by adsorption.

#### **Author Contributions**

**WH**: Conceptualization, Methodology, Investigation, Analysis and Interpretation, Writing - Original Draft; **DS**: Analysis and Interpretation, Writing - Review & Editing; **BW**: Conceptualization, Analysis and Interpretation, Writing - Review & Editing, Supervision.

## **Conflicts of Interest**

There are no conflicts to declare.

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