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ADSORPTION OF ANIONIC AND CATIONIC DYES IN BATIK WASTEWATER USING BIOMASS ADSORBENTS: LITERATURE REVIEW

ABSTRACT

This literature review aims to determine 1. the content of chemical compounds in biomass waste, 2. the modification methods of biomass waste to be used as an adsorbent, 3. the suitable parameters for adsorbing anionic and cationic dyes. This literature review was conducted by Seven Steps Comprehensive Literature Review and reviewed 41 journals. The results of this literature review show that: 1. Sources of biomass adsorbents include tea waste, peanut shells, cassava dregs, cassava peels, oil palm empty bunches, coffee grounds, corn cobs and coconut shavings. The content of chemical compounds in biomass waste include cellulose, hemicellulose and lignin. The highest content of cellulose was found in peanut shells at 63,5%; hemicellulose was in coffee grounds at 40,55%; and lignin was in wood shavings at 17-35%. The content of cellulose in the adsorbent source affects the adsorption ability of the adsorbent produced. 2. The modification methods of biomass adsorbent include carbonization, physical and chemical activation, and nanocomposites. The adsorption capacity of the adsorbents made by the carbonization-activation, chemical activation, and nanocomposite manufacturing method are 102,77 – 332,6 mg/g; 26,67 – 236,6 mg/g; and 12,42 mg/g, respectively. 3. Parameters that affect the adsorption of anionic and cationic dyes are pH, contact time, adsorbent mass, and initial concentration of the adsorbate solution. The optimum conditions for anionic dyes adsorption by biomass adsorbents occurred at pH 2-4, contact time 30 – 40 minutes, 0,1 – 0,2 g of adsorbent mass, and initial concentration 80 – 100 mg/L. While the optimum conditions for cationic dyes adsorption occurred at pH 5-9, contact time 60 – 90 minutes, 0,2 – 0,3 g of adsorbent mass, and initial concentration 100 – 120 mg/L.

Key word: *adsorption, anionic dyes, batik wastewater, biomass adsorbents, cationic dyes*

INTRODUCTION

Since UNESCO established batik as Indonesian culture on October 2, 2009, the batik industry in Indonesia has experienced growth and development every year which is marked by the increasing number in each region, ranging from home industry to large scale industries [1]. However, the growth and development of the batik industry are not accompanied by increased efforts to treat the resulting waste. Most of the batik liquid waste contains dyes produced from the washing and rinsing process of batik cloth, where these dyes are toxic and carcinogenic [2].

Dyes are organic compounds that have double bonds in their molecular structure. This double bond causes the dye to have color because the double bond electrons can absorb energy from light or light in the visible spectrum, namely at wavelengths between (400-700 nm) [3]. Based on the general structure, textile dyes are classified into anionic, nonionic, and cationic dyes. Anionic dyes include direct, acid, and reactive dyes. Nonionic dyes include dispersion dyes that are not ionized in water in the environment. Cationic dyes include azo, basic dyes, anthraquinones, and reactive dyes [4].

Dye waste can be treated using several techniques, such as adsorption, coagulation, chemical oxidation, electrochemistry, and others. Among the various removal techniques above, the adsorption technique is preferred because the process is easy, effective, and relatively inexpensive [5]. However, now there is a new trend to produce alternative processes that are in line with the principles of "Green Chemistry" or "Sustainable Chemistry". Some of the principles of Green Chemistry are as follows [6]:

1) Reduce concumption of toxic chemical reagents such as conventional organic solvents,
2) Use safer reagents,
3) Avoid the generation of non-recyclable waste,
4) Reusing reagents,
5) Reduce energy consumption,
6) Selecting environmentally friendly analytical techniques to detect analytes,
7) Use of automation and development at the micro-level.

Further waste treatment can be carried out with biosorption technology by utilizing waste biomass as a biosorbent. The use of biosorbents in water treatment technology has several advantages compared to conventional chemical adsorbents, such as biosorbents are biodegradable, highly abundant in nature, and have simple collection and preparation procedures. Biosorbents include bacteria, fungi, algae, industrial waste, agricultural waste, and other biomaterials [6].

Lignin and cellulose are the main constituents of a plant and include the main component of biomass [7]. Lignin and cellulose as the main constituents contain functional groups including alcohol, aldehyde, ketone, carboxylic, phenolic, and ether groups. These functional groups can bind water pollutants through different binding mechanisms [8].

As an alternative, a lot of research has been done on wastewater treatment using biomass waste. Sudarja and Caroko [9] used sawdust adsorbent to adsorb dyes in batik wastewater, where sawdust contains cellulose which generally has –COOH and –OH functional groups that can bind to dyes. The adsorbent from teak sawdust has an adsorption efficiency of 99,98% from batik wastewater. Tran et al. [10] reported the adsorption of methylene blue (MB) used activated carbon from coffee husk waste. The result of the study showed the maximum adsorption ability of MB was 418,78 mg/g, and the activated carbon produced has a surface area of 862,2 m^2/g.

Anionic and cationic surfactants can affect the adsorption of dyes depending on the type of dyes. The adsorption of cationic dyes can increase in the presence of anionic surfactants. Meanwhile, the adsorption of anionic dyes can increase in the presence of cationic surfactants [5]. Therefore, it is necessary to conduct a study to estimate the interaction between various types of dyes and the surface of the biomass adsorbent so that it can remove dye wastes optimally. The researcher intends to conduct a review that focuses on utilizing biomass waste as a biosorbent and its modification method to remove various cationic and anionic dyes in batik industrial wastewater.

METHODS

This literature review used the Seven Steps Comprehensive Literature Review method developed by Onwuegbuzie & Frel [11]. The seven stages of the literature review describe as follows.

1. Exploring Beliefs and Topics

At this stage, the researcher set a question or research topic that stems from a dilemma or lack of knowledge about something. This literature review is a comprehensive summary of several research studies selected based on the theme of "Adsorption of Anionic and Cationic Dyes in Batik Wastewater using Biomass Adsorbents".

2. Initiating the Search

The search process was carried out from August to Oktober 2020. The type of data used in this study was secondary data, which was not obtained from direct observation of the researcher but was obtained from the results of research that had been carried out by previous researchers. The search process in this literature review used the Google scholar database, used the following Indonesian keywords: adsorpsi DAN limbah zat warna DAN batik DAN adsorben selulosa, and also used the following English keywords: adsorption AND dye waste AND batik AND cellulose adsorbent.

3. Storing and Organizing Information

In this stage, the storage and organization of information are carried out. The articles that have been collected are then saved into Mendeley software to help make it easier to organize information.

4. Selecting/ Deselecting Information

This stage involves establishing criteria of determining which sources to use or not to use in the literature review. The selection criteria is seen in Figure 1.

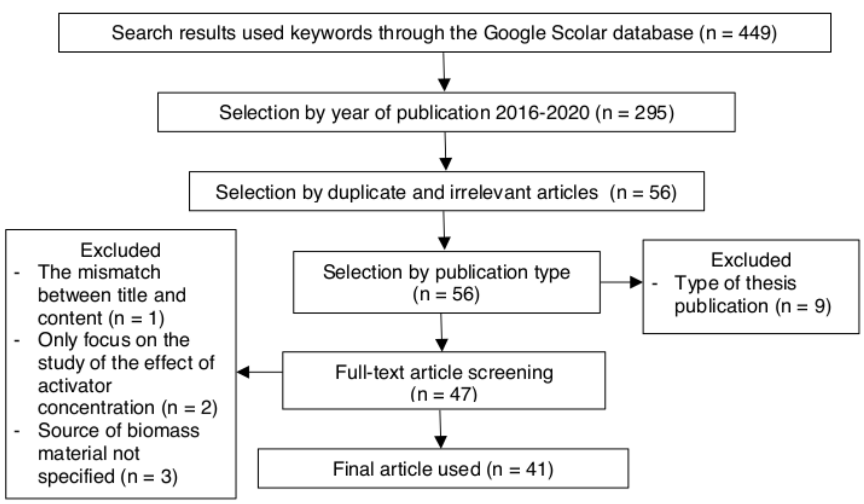

Figure 1. Flowchart of Article Selection

5. **Expanding the Search**

This stage was carried out if the information provided in the initial study is not sufficient to explain the information that will discuss in this study.

6. **Analyzing/ Synthesizing Information**

This process was carried out by making tabulations to organize the essential findings. These findings will be used as citation material to be combined with other literature results that will form information to answer the questions in this literature review.

7. **Presenting the Literature Review**

The last stage is to present the results of literacy study to the audience by writing a literature review. The literature review that had compiled into a report then be presented.

RESULTS AND DISCUSSION

1. Biomass Adsorbent Chemical Compound Content

The value of chemical compounds in several sources of biomass adsorbent are presented in Table 1. Table 1. shows that based on the cellulose content, peanut shells have the highest cellulose content of 63,5% with an adsorption percentage of 97,52%. Cassava pulp and cassava peel have low cellulose content, at 11% and 13,75%, respectively. From the data obtained, the adsorption capacity of the cassava pulp adsorbent is greater than that of the cassava peel adsorbent, namely 16,878 mg/g and 19,59 mg/g according to the cellulose content, where the cassava pulp is larger than the cassava peel.

Corn cobs contain cellulose by 41%, higher than the cellulose content in tea waste, which is 37%. Table 1. shows that the adsorption efficiency of corn cobs adsorbent is higher than the adsorption efficiency of tea waste adsorbent, 64% and 46,72%, respectively.

Table 1. Content of Chemical Compounds in Several Sources of Biomass Adsorbents

Sources of Biomass	Cellulose (%)	Hemi-cellulose (%)	Lignin (%)	Mod*	Adsorption capacity (mg/g)	Adsorption efficiency (%)	Ref
Tea waste	37	24	14	A_C	-	46.72	[12]
Peanut shell	63,5	-	13,2	C-A_C	9,752	97,52	[13]
Cassava pulp	11	-	-	raw	16,878	-	[14]
Cassava peel	13,75	37,86	9,14	raw	19,59	-	[15]
Oil palm empty fruit bunches	45,95	16,49	22,84	C-A_C-A_P	-	99,5	[16]
Coffee grounds	51,5	40,55	-	raw	-	80-90	[17]
Corncob	41	36	16	A_K	-	64	[18]
Wood shavings	40-50	15-34	17-35	C-A_c	-	98,251	[19]

* Mod = Modification; A_P = Physics Activation; A_C = Chemical Activation
C = Carbonization; Raw = Without Modification

From the above description and information, it can conclude that agriculture waste biomass can be used as an adsorbent to adsorb dyes in the batik industry wastewater due to the high content of cellulose, hemicellulose, and lignin. The performance of each biomass adsorbent varies according to the amount of content.

However, some differences can be seen in Table 1., for example, is the information of oil palm empty fruit bunches adsorbent and the peanut shells adsorbent. The performance of the two adsorbents was not following the cellulose content of each adsorbent, which might be caused by differences in the adsorbent modification method used. So the performance of the biomass adsorbent, besides being influenced by the amount of cellulose content present, is also influenced by the modification method used to maximize the cellulose content.

2. Biomass Adsorbent Modification Method

Biomass wastes are usually not used in raw form without pre-treatment but are more often processed with physical or chemical modifications first. The modification process is needed to improve the surface properties of the adsorbent material [20]. Several studies of biomass adsorbent modification are listed in Table 2.

Table 2. shows the performance of the biomass adsorbent is also influenced by the modification method, besides being influenced by the cellulose content. The difference in cellulose content in corn cobs and wood shavings is slight, but the adsorption results are more different. The adsorption percentage of wood shavings adsorbent is higher than that of corn cobs, 98,251% and 64%, respectively, in the effect of differences in the adsorbent modification method carried out. The modification method in corncob adsorbent only used chemical activation, while wood shavings used carbonization and chemical activation.

Table 2. Biomass Adsorbent Modification Method

Sources of Biomass	Methods	Treatments	Results	Ref
Tea waste	Chemical activation	Chemical activation using 0,8 M of H_2SO_4 solutions	Adsorbents with an adsorption efficiency of 46.72%	[12]
Peanut shell	Carbonization - activation	Burned at 450°C, activated using 1 M of H_3PO_4 solution and 1 M of NaOH solution	Adsorbents with an adsorption capacity of 9,752 mg/g and adsorption efficiency of 97,52%	[13]
Cassava pulp	Drying	Dried in an oven at 80°C for 5 hours	Adsorbents with an adsorption capacity of 16,878 mg/g	[14]
Cassava peels	Drying	Dried in an oven at 100°C, for 24 hours	Adsorbents with a surface area of 0,85 m^2/g and adsorption capacity of 19,41 mg/g	[15]
Oil palm empty fruit bunches	Carbonization - activation	Carbonized in cans until the white smoke disappears, physical activation at 300°C for 1 hour, chemical activation using 5 M of H_3PO_4 solution	Adsorbents with an adsorption efficiency of 99,5%	[16]
Coffee grounds	Drying	Dried in an oven at 80°C for 8 hours	Adsorbents with an adsorption efficiency of 80-90%	[17]

Corncob	Chemical activation	Chemical activation using 1 M of HCl solution	Adsorbents with an adsorption efficiency of 64%	[18]
Wood shavings	Carbonization - activation	Carbonized at 500°C and chemical activation using 10% of H_3PO_4 solution	Adsorbents with an adsorption efficiency of 98,251%	[19]
Coconut shell	Activation - carbonization	Addition (impregnation) of NaCl with a ratio 1:1, and then burned in the furnace	Adsorbents with a surface area of 804,58 m^2/g and carbon content of 61,17%	[21]
Cassava peels	Carbonization - activation	Burned at 700°C, chemical activation using H_3PO_4 (40%, 50%, 60%), physical activation with N_2 flow 0,25 dm^3/min	Activated carbon with a surface area of 257,76 m^2/g	[22]
Tamarind seeds	Chemical activation	Chemical activation using 4 N of H_3PO_4 solution	Adsorbents with an adsorption capacity of 24,67 mg/g and adsorption efficiency of 98,827%	[23]
Tamarind seeds	Activation - carbonization	Chemical activation using two concentrations of H_3PO_4 solution, namely 30% and then 85%, and burned in a furnace at 500°C for 4 hours	Activated carbon with a surface area of 594,04 m^2/g and adsorption capacity of 102,77 mg/g	[24]
Peanut shell	Chemical activation	Chemical activation using 0,25% of sodium dodecylsulfate (SDS) solution	Adsorbents with a surface area of 11,023 m^2/g and adsorption capacity of 236,602 mg/g	[25]
Peanut shell	Drying	-	Adsorbents with a surface area of 7,341 m^2/g and adsorption capacity of 133,146 mg/g	[25]
Bagasse	Activation - nanocomposite	Chemical activation using citric acid (0,1; 0,3; and 0,5 mol/L), and addition of Fe_3O_4 nanoparticles	Nanocomposite with an adsorption capacity of 12,42 mg/g and adsorption efficiency of 98%	[26]
Corncob	Carbonization - activation	Burned at 300-400°C, chemical activation using 7 M of KOH solution, impregnation of Fe_2O_3	Activated carbon with an adsorption efficiency of 71,93%	[27]
Water hyacinth	Chemical activation	Chemical activation using 2% of NaOH solution for 24 hours	Adsorbents with an adsorption efficiency of 74,767%	[28]
Bintaro shell	Carbonization - activation	Burned at 400°C (1 hour), chemical activation using 20% of $ZnCl_2$ solution	Activated carbon with an adsorption capacity of 332,6 mg/g	[29]
Nata de coco	Drying	Dried in an oven at 80°C for 8 hours	Adsorbents with an adsorption capacity of 0,2066 mg/g and adsorption efficiency of 44,66%	[30]
Orange peels	Carbonization - activation	Burned at 120°C (24 hours), and addition of HNO_3 with a mass ratio of adsorbent:HNO_3 = 1:1	Activated carbon with a surface area of 15 m^2/g	[31]
Reed	Chemical activation	Chemical activation using 2M of HCl solution	Adsorbents with an adsorption capacity of 26,6758 mg/g	[32]
Nata de coco	Drying	Pressed with a press machine at a pressure of 250 kgf/cm, then dried in an oven at 80°C fot 30 minutes	Adsorbents with a surface area of 1,662 m^2/g, adsorption capacity of 7,45 mg/g, and adsorption efficiency of 75,66%	[33]

Canang (coconut leaves)	Delignification and chemical activation	Chemical activation using 12% of NaOH solution and NaOCl solution	Adsorbents with a surface area of 31,867 m^2/g	[34]
Siwalan peels	Chemical activation	Chemical activation using 5 M of H_2SO_4 solution	Adsorbents that can adsorb batik dye of 7,72 ppm from the initial condition of 12,45 ppm (adsorption efficiency of 62%)	[35]

Oil palm empty fruit bunches adsorbent has a cellulose content of 45,95%, lower than that peanut shells, 63,5%. However, the adsorption efficiency of oil palm empty fruit bunches was higher than peanut shells, namely 99,5%, and 97,52%, respectively. The modification methods used in the oil palm empty fruit bunches are carbonization, chemical, and physical activation. While peanut shells only used carbonization and chemical activation methods.

Both Rizki et al. [23] and Jamion et al. [24] research made adsorbents from tamarind seeds to adsorb methylene blue (MB) dye, but used different adsorbent modification methods. From the results of both studies, be concluded that the performance of the adsorbent by Jamion et al. [24] was better than the adsorbent by Rizki et al. [23], which has adsorption capacity of 102,77 mg/g and 24,67 mg/g, respectively. That's because, Jamion et al. [24] used carbonization and chemical activation methods, while Rizki et al. [23] only used the chemical activation method.

Both Astuti et al. [22] and Irawati et al. [15] made adsorbents from cassava peel biomass, but adsorbents produced by Astuti et al. [22] are better than Irawati et al. [15], which has a surface area of 257,76 m^2/g and 0,85 m^2/g, respectively. Astuti et al. [22] used carbonization, chemical, and physical activation, while Irawati et al. [15] only used the drying method.

Fatimah et al. [25] reported the peanut shells utilization as an adsorbent by the chemical activation method of 0,25% sodium dodecyl sulfate (SDS) solution. The produced adsorbent showed a surface area of 11,023 m^2/g and an adsorption capacity of 236,6 mg/g. This study also reported the peanut shell adsorbents with drying pre-treatment only, which showed a surface area of 7,341 m^2/g and an adsorption capacity of 133,146 mg/g. It concluded that the peanut shell adsorbent after chemical activation has a better surface area and adsorption capacity than the dried peanut shell adsorbent alone.

In addition to the modification methods described above, there is another modification method, namely the manufacture of nanoparticles or nanocomposites. For example, Anh et al. [26] synthesized nanocomposites using Fe_3O_4 and sugarcane bagasse. The produced adsorbent has a higher adsorption efficiency than natural bagasse without modification of 98%, while natural bagasse was 66%. These results were due to the addition of Fe_3O_4 nanoparticles attached to the surface of the bagasse added to the existing functional groups.

Overall, biomass can be used as an adsorbent to adsorb dyes in batik industrial wastewater through several modification methods.

3. Effect of Various Parameters in Dyes Adsorption Process

Parameters that affect the adsorption process include the solution pH, contact time, adsorbate mass, and the initial concentration of the solution used. Analysis of these parameters can provide information about the adsorption mechanism, which is very important when choosing adsorbent materials and the preparation conditions used in the adsorption process [36]. Several studies about the effect of various parameters on the adsorption of anionic and cationic dyes are listed in Table 3.

a. Effect of Solution pH

In Table 3., it can be seen that the optimal adsorption conditions for biomass adsorbents to adsorb anionic dyes occurred at low pH or acidic conditions. Wahyuningsih et al. [14] studied the effect of pH on the adsorption of remazol brilliant blue R dye using cassava pulp as an adsorbent with pH variations ranging from 1 to 10. The results showed that the optimum adsorption condition occurred at pH 1, with an adsorption capacity of 16,878 mg/g.

Aisyahlika et al. [29] reported the adsorption of reactive red-120 dye using bintaro shell adsorbent with pH variations from 2 to 12. The results showed that the optimum adsorption condition occurred at pH 2 with an adsorption capacity of 322,6 mg/g. Puspita et al. [37] also reported the adsorption of reactive red-120 dye using palm fiber as an adsorbent. The variations of pH used were from pH 2 to 8. The results showed that the optimum adsorption condition was at pH 3 with an adsorption capacity of 400 mg/g.

The adsorption mechanism of biomass adsorbents on anionic dyes, for example, reactive red-120 dye, is as follows:

At an acidic pH of 3, H^+ ions will protonate OH^- from the adsorbent functional group to become H_2O^+. This group will then bind to the sulfonate group (SO_3^-) in the dye.

$\square COOH + H^+ \rightarrow \square COOH_2^+$

$\square COOH_2^{+-} + \square SO_3^- \rightarrow \square COOH_2SO_3\square$

Table 3. Effect of adsorption parameters on the adsorption of anionic and cationic dyes by biomass adsorbent

Sources of Biomass	Adsorbate/ dyes	Variations: pH	Variations: Contact time (minutes)	Variations: Adsorbent mass (grams)	Variations: [adsorbate] (mg/L)	Adsorption capacity/ adsorption efficiency	Ref
Anionic dyes							
Cassava pulp	Remazol brilliant blue R	1-10 **(1)***	5-90 **(45)***	0,2	200	16,878 mg/g	[14]
Cassava peels	Naphthol blue-black	1-11 **(3)***	10-180 **(180)***	0,2	5-500 **(500)***	99,7%	[22]
Bintaro shell	Reactive red-120	2-12 **(2)***	10-90 **(40)***	0,05-0,175 mg **(0,1)***	100	322,6 mg/g	[29]
Coconut leaves	Remazol briliant blue	2-8 **(4)***	5-90 **(15)***	0,1-1 **(0,1)***	25	10,6 mg/g	[34]

Pineapple peels	Remazol red RB	1-11 **(2)***	60-180 **(120)***	-	10-100 **(80)***	21,9 mg/g	[38]
Palm coir	Reactive red-120	2-8 **(3)***	10-90 **(30)***	0,05-0,175 **(0,15)***	100	400 mg/g	[37]
Rice husk ash	Titan yellow	4-6 **(4)***	10-60 **(40)***	2,5	20-100	1,15 mg/g	[39]
Kawista fruit shell	Metanil yellow	4-8 **(7)***	15-120 **(90)***	0,5-2,5 **(1)***	25	5,48 mg/g	[40]
Cavendish banana peels	Methyl orange	-	30-120 **(120)***	0,5 and 1 **(1)***	50,27	28,15%	[41]
Corncob	Reactive blue 19	5-11 **(11)***	5-90 **(90)***	10	25-100 **(25)***	-	[42]
Rice bran	Congo red	4-8 **(6)***	5-30 **(30)***	-	-	7,19 mg/g	[43]
Nata de coco	Remazol yellow FG	1-10 **(2)***	45	0,1	100	11,264 mg/g	[44]
			Cationic dyes				
Tamarind seeds	Methylene blue	6	30-180 **(150)***	0,3-0,9 **(0,3)***	100	24,67 mg/g	[23]
Sugarcane bagasse	Methylene blue	3-9 **(9)***	30	0,05-0,5 **(0,2)***	30-75 **(50)***	12,42 mg/g	[26]
Corncob	Methylene blue	-	120	0,025	20	15,38 mg/g	[27]
Reed	Methylene blue	2-11 **(9)***	30-780 **(180)***	0,02	40-200 **(100)***	26,4472 mg/g	[32]
Kepok banana peels	Rhodamine B	-	10-120 **(120)***	0,1	2-10 **(6)***	4,55 mg/g	[45]
Pineapple leaves waste	Methyl violet	1-11 **(5)***	90	-	10-700 **(700)***	73,556 mg/g	[46]
Pineapple leaves fiber	Methylene blue	-	30-120 **(90)***	0,5	25-55 **(45)***	40,2 mg/L	[47]
Phytoremediation plant waste (Scirpus grouss)	Methylene blue	6	10-120 seconds **(30)***	0,5	5-15 **(15)***	100%	[48]
Areca fiber	Basic red 18	4-9 **(4)***	-	1-3 **(1)***	10-50	-	[49]
Reed ash	Methylene blue	3-10 **(3)***	15-90 **(75)***	0,5-3 **(0,5)***	5	0,4844 mg/g	[50]
Pondoh salak seeds	Methylene blue	-	15-60 **(60)***	1	25-100 **(100)***	4,924 mg/g	[51]
Coconut shell waste	Methyl violet	1-11 **(3)***	10-180 **(180)***	0,3	10-500	40 mg/g	[52]
Silk cotton tree	Methyl violet 2B	5-9 **(7)***	5-180 **(10)***	2	50-200 **(200)***	97,1%	[53]
Gumitir stem	Rhodamine B	1-11 **(3)***	30-180 minutes **(90)***	1	20 – 200 **(120)***	2,4 mg/g	[54]

Anh et al. [26] studied the effect of pH on the adsorption process of cationic dye methylene blue with bagasse adsorbent. The variations of pH used were from 3 to 9. The optimum adsorption occurred at pH 9 with an adsorption capacity of 12,42 mg/g. Huda and Yulitaningtyas [32] reported the adsorption process of methylene blue dye using reed adsorbent with pH variations from 2 to 11. The optimum adsorption occurred at pH 9, with an adsorption capacity of 26,4472 mg/g. Lanjar et al. [46] also reported adsorption using pineapple leaf waste adsorbent on methyl violet dye. The variations of pH used were from 1 to 11. The results showed that at pH 1 to 5, the adsorbed dye increased, but at pH above 5, were decreased. The optimum adsroption occurred at pH 5 with an adsorption efficiency of 99,45%.

The adsorption mechanism of biomass adsorbents on cationic dyes, for example, crystal violet dye, is as follows:

At pH 7, the surface of the adsorbent is deprotonated so that more carboxyl groups are formed and bind to crystal violet ions (N^+).

$$\square COOH + H_2O \rightarrow \square COO^- + H_3O^+$$

$$\square COO^- + \square N^+ \rightarrow \square COO\text{-}N\square$$

However, several studies showed that the adsorption of cationic dyes occurred at low pH or acidic conditions. For example, Riwayati et al. [50] reported the adsorption of cationic dye methylene blue was optimum at pH 3. According to them, at an alkaline pH, protonation of the methylene blue solution was disturbed, and the adsorption capacity of the dye decreased. Sahara et al. [54] reported that the adsorption of rhodamine B dye was optimum at pH 3. Although the condition was not favorable for electrostatic interactions, the amount of rhodamine B dye adsorption was still increasing. The results of this study indicate that electrostatic interactions are not the primary mechanism in adsorption. But adsorption can occur through other interactions such as hydrogen bonds and π-π bonds that can happen between several functional groups on the surface of the adsorbent.

b. Effect of Contact Time

Aisyahlika et al. [29] studied the effect of contact time on the adsorption process of reactive red-120 dye using a bintaro shell adsorbent. The variations of contact time used are 10-90 minutes. The results showed an increase in adsorption capacity at an interval of 10-30 minutes. Optimum adsorption conditions occurred at minute 40. After more than 40 minutes there was a decrease. This is caused by the desorption that occurred due to the reduced active site on the surface of the adsorbent. After all, the dye solution forms a new layer on the surface of the adsorbent so that it covers the adsorbent surface. Puspita et al. [37] researched the adsorption of reactive red-120 dye using oil palm coir adsorbent with contact time variations from 10 to 90 minutes. Optimum adsorption conditions occurred at contact time of 30 minutes.

Musafira et al. [45] did adsorption of rhodamine B dye using kepok banana peels as an adsorbent. The variations of contact time used are 10 to 120 minutes. Optimum adsorption conditions occurred at contact time of 120 minutes. Rizki et al. [23] varied the contact time on the adsorption process of methylene blue dye using tamarind seed adsorbent. The variations of time are from 60 to 180 minutes. The optimum conditions occurred at contact time of 150 minutes. The dye adsorption efficiency increased and was slower until constant at equilibrium. These because the adsorbent was saturated so that it was no longer able to adsorb the dye.

c. Effect of Adsorbent Mass

The adsorbent dose is also a significant parameter for the economic optimization of the adsorption process [36].

Mustikawati et al. [34] studied the effect of adsorbent mass on the adsorption of anionic dye, namely remazol brilliant Blue using canang (coconut leaves) adsorbent. The adsorbent mass variations used are 0,1 to 1 gram. The optimum adsorption occurred at an adsorbent mass of 0,1 grams. Aisyahlika et al. [29] also varied the mass of the adsorbent on the adsorption of reactive red-120 using bintaro shell adsorbents ranging from 0,05 to 0,175 grams. Optimum adsorption occurred at the adsorbent mass of 0,1 grams. The results of the study indicated that the addition of adsorbent mass would increase the adsorption of dyes. The surface area and the active sites of the adsorbent will increase, so will increase adsorption capacity.

Rizky et al. [23] studied the effect of adsorbent mass on the cationic dye, namely methylene blue, using tamarind seed adsorbents. The mass variations used were 0,3 to 0,9 grams, and the optimum occurred at 0,3 grams. By adding adsorbent mass, the adsorption process will quickly reach saturation, which makes the adsorbate easily separated from the surface of the adsorbent. Anh et al. [26] ivestigated the adsorption process of methylene blue dye with sugarcane bagasse as adsorbent and mass variations ranging from 0,05 to 0,5 grams. Optimum adsorption conditions occurred at a mass of 0,2 grams.

Thus, the mass of the adsorbent used influenced the adsorption process. However, for economic optimization of the adsorption process, a minimum of adsorbent mass is investigated to provide maximum adsorption results.

d. Effect of Initial Concentration of Dye

The effect of initial dye concentration is based on the direct relationship between the dye concentration and the active sites available on the surface of the adsorbent. Sukarta [38] investigated the effect of initial dye concentration on the adsorption of anionic dye, namely remazol red RB, using pineapple peel adsorbent with concentration variations of 10-100 mg/L. The results showed that when the concentration increased from 10 mg/L to 80 mg/L, the adsorption capacity of the dye increased. Huda and Yulitaningtyas [32] reported the adsorption of methylene blue dye using reed adsorbent with various concentrations of 40 mg/L to 200 mg/L. Optimum adsorption conditions occurred at a concentration of 100 mg/L. At concentrations higher than that, there was no significant increase or decrease.

In general, it can conclude that increasing the initial concentration of dyes, both anionic and cationic, will lead to an increase in the adsorption capacity of biomass adsorbents. The decrease in adsorption capacity is caused by the surface of the adsorbent that has passed the saturation so that the active sites on the adsorbent can no longer bind the dye molecules.

CONCLUSION

The adsorption of cationic and anionic dyes using various biomass adsorbents has been summarized in this study. The data that has been collected can be used as a reference in finding adsorbent materials from biomass waste to remove harmful dyes in batik wastewater. The selection of adsorbent biomass can be based on the content of cellulose, hemicellulose, and lignin. The modification method used must be considered, such as using activation, carbonization, and nanocomposite manufacturing. Variations of pH, contact time, adsorbate mass, and initial dye concentration also be considered. The most influential parameter in dye adsorption is pH. At low pH, the adsorption of anionic dyes is preferred. Meanwhile, at high pH, the adsorption of cationic dyes is preferred.

From the data that has been collected, it is concluded that the optimum adsorption conditions for biomass adsorbent to adsorb anionic dyes occurred at pH 2-4, contact time 30-40 minutes, adsorbent mass 0,1-0,2 grams, and initial dye concentration 80-100 mg/L. While for cationic dyes occurred at pH 5-9, contact time 60-90 minutes, adsorbent mass 0,2-0,3 grams, and initial dye concentration of 100-120 mg/L.

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