PROC. INTERNAT. CONF. SCI. ENGIN.
Volume 1, October 2017 | Pages: 125-130

ISSN 2597-5250 | EISSN 2598-232X

Study of Batik Wastewater Treatment Using PAC (Poly Aluminum Chloride) as Coagulant and Organoclay (Montmorillonite-polydadmac) as Floccullant to Reduce Total Suspended Solid (TSS) and Total Dissolved Solid (TDS)

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Abstract. *Sari N C, Nugraha I. 2017. Study of Batik Wastewater Treatment Using PAC (Poly Aluminum Chloride) as Coagulant and Organoclay (Montmorillonite-polydadmac) as Floccullant to Reduce Total Suspended Solid (TSS) and Total Dissolved Solid (TDS). Proc Internat Conf Sci Engin 1: 125-130.* Batik wastewater treatment using PAC (Poly Aluminium Chloride) as a coagulant and organoclay (montmorillonite- polyDADMAC) as flocculants was investigated in this study. The purpose of this study was to analyze the quality of batik wastewater effluent before and after coagulation-flocculation and analyze the effectiveness of organoclay as flocculants of batik wastewater. Organoclay (montmorillonite-polyDADMAC) synthesised by reacting natural bentonite with polyDADMAC 0.4%. Coagulation and flocculation used jar test method with a speed stirring at 120 rpm for 2 minutes and slow stirring at 40 rpm with a variety of types, masses of flocculants and flocculation time. At first, batik wastewater had high levels of TSS and TDS levels. TSS and TDS levels reduced after coagulation-flocculation. Effectiveness of maximum TSS reduced at 99,74% with the addition of organoclay flocculant 2.5 g/L and flocculation time for 80 minutes. Effectiveness of maximum TDS reduced at 93,57% with the addition of organoclay flocculant 2.5 g/L and 60 minutes flocculation.

Keywords: Organoclay, montmorillonite-polyDADMAC, polymer, flocculant, batik wastewater, intercalation, bentonite

INTRODUCTION

The fashion development in Indonesia has spurred the textile industry development, the example is the batik industry. Batik was recognized by UNESCO as a world cultural heritage from Indonesia. The process of batik manufacture produced wastewater. Batik wastewater from batik coloring process has the potential to damage the environment. Based on observations and interviews with batik business people, the conditions show most of the batik industry are not to process the wastewater before thrown away. This is because the wastewater processing techniques is expensive and difficult. Batik wastewater was produced the environment pollute because it has BOD (Biological Oxygen Demand) at 960 mg/L, COD (Chemical Oxygen Demand) at 1800 mg/L, TSS (Total Suspended Solid) at 540 mg/L , TDS (Total Dissolved Solid) at 1672 mg/L, pH 13 and temperature 30 ^{o}C (Pratiwi, et al. 2014).

Batik wastewater is an organic wastewater that has a high concentration of pH, BOD, COD, TSS, and TDS. One of dye used in the colloring process of batik is golden yellow and black remazol. The compound is only used about 5% and 95% will be disposed (Suprihatin, 2014).

Before disposal must to treated the wastewater because the concentration of COD, TSS, TDS, and turbidity are high and exceed the quality standard of batik wastewater. Batik wastewater treatment to reduce the environmental pollution. The batik wastewater treatment are chemically, biologically, and physics. Chemical processes include flocculation, adsorption, and coagulation. Physical processes include screaning, filtration, and membrane technology. Biological process with the activity of microorganisms and aquatic plants (Kurniawan, 2013)

Coagulation-flocculation process is a wastewater treatment to wastewater that containing hazardous chemical compounds from the coloring process (Gillespie, et al., 1970). Coagulation is a process of destabilizing colloidal particles by the addition of coagulants and stirring at high speed. A cationic coagulant is added to the water which forms the attraction force among the suspended particles. Flocculation is the process of forming clumps of solids in a solution (flocs) (Suharto, 2011).

Coagulation-flocculation process is done by adding polymers/surfactant as coagulants and flocculants to remove organic compounds and strengthen flocs. PAC (poly aluminum chloride) is a compound used as a coagulant. PolyDADMAC is a cationic polymer that can be utilized as a flocculant in water treatment (Bolto, B., et al., 2007). However, based on CAS: 26062, polyDADMAC is deficient because the boiling point value is 100^{o}C, so if waste treatment applied in high-temperature will damage the structure of polyDADMAC.

The addition of clays such as bentonite is good used as a flocculant in the waste treatment process. One of the utilization is as flocculant in paper wastewater processing (Gillespie, et al., 1970). The material can also be used in various applications according to the specification of the surface area and structure of clay type (Malik, 2003). Bentonite producer in Indonesia is very much and almost in all town but the utilization not optimal (Prasetyo, 2007).

Bentonite is a mineral of alumina silicate hydrate which is included in pilosilicate or silicate plated with Tetrahedral: Octahedral ratio = 2: 1. The composition of bentonite is dominated by montmorillonite (85%) and beidellite. Bentonite can be utilized as an adsorbent because has expandability and large surface area so it can accumulate metal ions and organic compounds (Konta, 1995).

Bentonite deficiency is easy to absorb water and less stable when used as an adsorbent. The expansion of the lattice from bentonite can be enhanced by modifying bentonite become organoclay minerals. Ganigar, et al. (2010) was modified the polydiallyldimethylammonium chloride (polyDADMAC) cationic surfactant with montmorillonite (MMT) to adsorb trichlorophenol and trinitrophenol from river wastewater. The modified bentonite produces organoclay with a larger lattice area.

Research needs to be done for batik wastewater treatment to reduce the concentration of TSS and TDS in batik wastewater using bentonite modification (montmorillonite-polyDADMAC) as flocculants and coagulation process using PAC (poly aluminum chloride). The expectation of this reasearch was produced the batik wastewater that below the quality standard (the decision of the governor of DIY No. 7 of 2010).

MATERIALS AND METHODS

Materials

This research used natural bentonite.The batik wastewater effluent used in this research from Kabul Art Gallery in Yogyakarta. The cationic surfactant used for modification is Polydiallyldimethylammonium chloride (polyDADMAC) 40%.

Preparation of Organoclay

Natural bentonite was added distillated water. A suspension of natural bentonite in distillated water was stirred for 1 h on magnetic stirrer at 70 °C to remove a soluble inorganic salts and any adhering materials. The natural bentonit suspension were modified with polyDADMAC 0,4 % by adding amounts of surfactant was stirred for 3 h on magnetic stirrer at 65 °C. Then the suspension was fitered, washed with hot distillated water and then dried at 80°C for 18h. The product (organoclay) was grinded and sized to get a particle size of 109 microns.

Analytical Methods

The composition of natural bentonite and organoclay was determined with FTIR and XRD. FTIR pectra for natural bentonite and organoclay were obtained using FTIR Shimadzu Prestige-21. XRD for natural bentonite and organoclay were obtained using XRD Shimadzu 600.

Coagulation and Flocculation Experiments

Coagulation and flocculation in this study used jar test methods. The batik wastewater was diluted up to 20x. The batik wastewater as much 500 mL was inserted in a 1 L beaker. Then added PAC 1,5 g/L as coagulant and stirred for 2 minutes on magnetic stirrer at constantly speed 120 rpm. After coagulation added flocculant with mass and type variation, then stirred for variation time on constantly speed 10 rpm. The mixture was precipitated at 1 h. A supernatant was analyzed parameter TSS (SNI 06-6989.03-2004) and TDS (SNI 06-6989.27-2004) concentration of batik wastewater.

Flocculant Type Variation

Coagulation and flocculation experiment with variation of type flocculant. The type of flocculant are montmorillonite-polyDADMAC (organoclay), natural bentonite, and polyDADMAC with the same mass 2,5g/L.

Flocculant Mass Variation

Coagulation and flocculation experiment with variation of mass flocculant. The mass of flocculant are 0,5 g/L, 1 g/L, 1,5 g/L, 2 g/L, dan 2,5 g/L with natural bentonite and montmorillonite-polyDADMAC (organoclay) as flocculant.

Flocculation Time Variation

Coagulation and flocculation experiment with variation of flocculation times. Flocculation used montmorillonite-polyDADMAC (organoclay) 2,5 g/L as flocculant at 20, 40, 60, 80, 100 minutes.

RESULTS AND DISCUSSION

Modification of (Organoclay) Montmorillonite-polyDADMAC

Montmorillonite-polyDADMAC was synthesized with method of Anirudhan, et.al. (2015). Montmorillonite-polyDADMAC was synthesized by natural bentonite dispersed into distilated water to occur swelling between bentonite layers, so that in bentonite dispersions can receive metal ions and organic compounds, including polyDADMAC. The cations on the interlayer will be replaced by the N group of polyDADMAC. The cation exchange process at 65°C so that the cation exchange reaction is faster and more optimal.

The results from the reaction between polyDADMAC and natural bentonite is a paste organoclay. The formation of the paste indicates that polyDADMAC has reacted with natural bentonite. Organoclay dried at 80°C to evaporate distilation water dispersed in organoclay. The dried organoclay was crushed and filtered using a 109 micron sized filter to has the same size and expand the surface. The results of montmorillonite-polyDADMAC synthesized (organoclay) were compared to their physic with natural bentonite before modified with polyDADMAC. Montmorillonite-polyDADMAC (organoclay) has a darker color than natural bentonite before modified.

FTIR (Fourier Transform Infrared Spectroscopy)
Characterization using the FTIR instrument to determine the functional groups in natural bentonite and montmorillonite-polyDADMAC (organoclay). Figure 1 shows the FTIR spectra in the 4000-400 cm-1 wavelength range. The specific vibrational energy of each element will be indicated by the magnitude of the infrared wave number on the FTIR spectra. From the FTIR spectra of montmorillonite-polyDADMAC (organoclay) and natural bentonite, there can be a shift in the absorption of wave numbers in some functional groups.

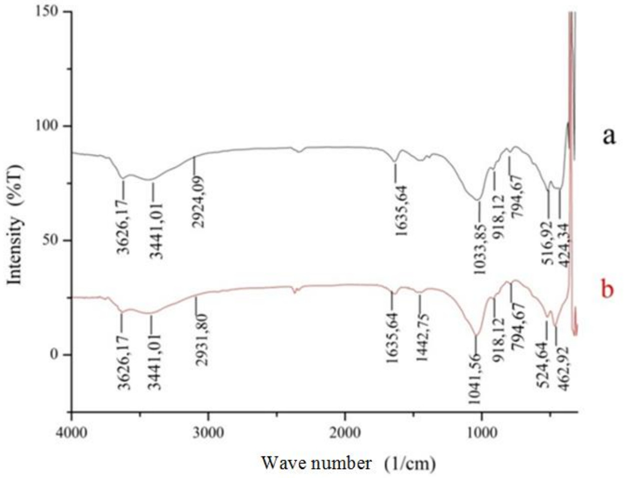

Figure 1. FTIR spectrum (**a**) natural bentonite, (**b**) montmorillonite-polyDADMAC.

There was a shift in the vibration of Si-O-Si from 1033,85 cm-1 to 1041,56 cm-1, vibration buckling of Si-O-Al from 516,92 cm-1 to 524,64 cm-1, and bending vibration of Si-O-Si from 424,34 cm-1 to 462,92 cm-1. Reaction of bentonite with cationic surfactant resulted the shift of the wave number. The FTIR spectra showed that no decomposed functional group in the sample and the structure of the bentonite does not change.

PolyDADMAC has a specific vibration at 3332.5 cm-1 which is a vibration of OH and 1644.2 cm-1 is the vibration of C-N (Mwangi I.W., et al., 2013). The presence of polyDADMAC in organoclay cannot be shown in the FTIR spectra because the polyDADMAC interaction on bentonite is an ion-exchange reaction. There is overlaping of functional groups of FTIR spectra between polyDADMAC surfactant and natural bentonite. Analysis using FTIR cannot show functional groups of polyDADMAC.

Based on the FTIR spectra of natural bentonite and montmorillonite-polyDADMAC, can be concluded that no significant changes in wave numbers and functional groups. The shift of wave numbers is a sign that the interacted bentonite with polyDADMAC is cation exchange.

XRD (X-Ray Diffraction)
Characterization using XRD is method for bentonite characterization. Qualitative characterization using XRD to determine the types of minerals from natural bentonite and montmorillonite-polyDADMAC (organoclay). In the XRD difactogram (Figure 2) natural bentonite has diffraction peaks at 2θ of 6.1o; 20.2o and 26.9o with a basal spacing at 14.48 Å, 4.38 Å, and 3.31 Å. While the spesific diffraction peaks organoclay at 2θ is 5.7o; 19.7o; and 26.4° with a basal spacing at 15.49 Å, 4.51 Å, and 3,37 Å.

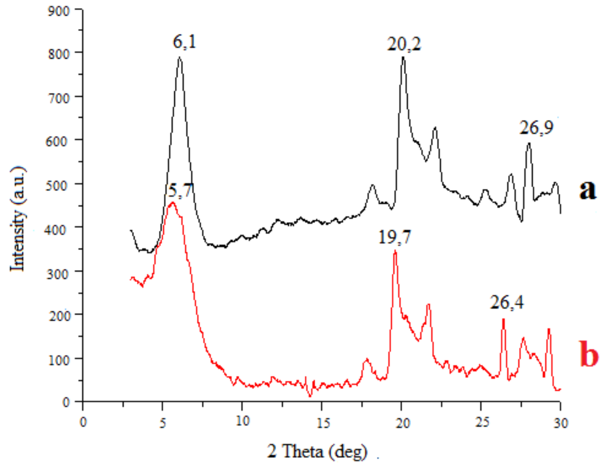

Figure 2. XRD diffractogram (a) natural bentonite; (b) *montmorillonite-polyDADMAC.*

Table 1. Comparison of 2Θ and basal spacing on natural bentonite and montmorillonite-polyDADMAC.

Natural bentonite		**Montmorillonite-*polyDADMAC* (*organoclay*)**	
2Θ	d (Å)	2Θ	d (Å)
6,1	14,4773	5,7	15,49233
20,2437	4,3831	19,6738	4,50879
26,93	3,31	26,3933	3,37416

The basal spacings was shifted because of interaction between natural bentonite with polyDADMAC. The research by Shen, Dazhong, et al. (2009) produces organoclay with a shift of diffraction peaks to the left. The shift to the smaller diffraction peaks indicates that the cation of the polyDADMAC replaces the cation on the natural bentonite interlayer. Table 1 assumed that montmorillonite-polyDADMAC (organoclay) has been successfully synthesized by intercalation reaction.

The organic compounds location in organoclay depends on the size of the organic compound cation, the length of the alkylammonium ion chain, and the layer charge of the clay (Bergaya, F., et al, 2016). Montmorillonite-polyDADMAC has been successfully synthesized by monolayer intercalation reaction because has a basal spacing at 15.49233 Å equivalent to 1.54923 nm.

Effectiveness of montmorillonite-polyDADMAC (organoclay) as Flocculant to Reduced TSS and TDS of Batik Wastewater

TSS (Total Suspended Solid) are particles suspended have a negative impact to aquatic ecosystem. TSS take a long time to precipitate and not through a filter (Fardiaz, 1992). The batik wastewater must be in accordance with the batik wastewater quality standard. The TSS level of batik wastewater quality standard based on the decision of the DIY governor number 7 on 2010 is less than 200 mg/L. TSS levels of batik wastewater the beginning has a high TSS level at 7145 mg / L, while the TDS level at 8080 mg/L. In this research used batik wastewater with 20x dilution which has a high levels of TSS at 5716 mg/L and a high levels of TDS at 6920 mg/L and not feasible to disposal and must to processed.

This research used variation of flocculant types, flocculant mass, and flocculation contact time to investigate the effectivity of montmorillonite-polyDADMAC flocculant (organoclay) to reduce TSS and TDS levels of batik wastewater. Flocculant types used montmorillonite-polyDADMAC (organoclay), natural bentonite, and polyDADMAC. The variation of flocculant types resulted in different TSS and TDS levels for each treatment.

Variation of Floccculant Type

Table 2 showed the montmorillonite-polyDADMAC (organoclay) flocculant is the best of flocculants to reduce TSS levels. Treatment with natural bentonite flocculants and polyDADMAC polymers is not able to reduce TSS and TDS in accordance with the batik wastewater quality standard. Batik wastewater with TSS levels at 25 mg / L and effektivness of TSS reduce at 99.5626% is feasible to be disposal because less than batik wastewater quality standard.

Table 2. Effectiveness of TSS levels reduce with variation of flocculant types.

Flocculant types	TSS levels (mg/L)	Effectiveness (%)
Montmorillonite-polyDADMAC (organoclay)	25	99,5626
Natural Bentonite	250	95,6263
PolyDADMAC	1575	72,4458

Table 3 showed the montmorillonite-polyDADMAC (organoclay) flocculant is the best flocculants to reduce TDS levels. Batik wastewater with TDS levels at 585 mg / L and evectiveness of TDS reduce at 91,5460% is feasible to be disposal because less than batik wastewater quality standard. This suggests that montmorillonite-polyDADMAC flocculant is a higher effectiveness than polyDADMAC flocculants and natural bentonite. Organoclay flocculant has a better performance because has a polymer on the interlayer that can bind to compounds contained in batik wastewater. Organoclay also has a function as an adsorbent because has a pores that can adsorb the compounds in batik wastewater.

Table 3. Effectiveness of TDS levels reduce with variation of flocculant types.

Flocculant types	TDS levels (mg/L)	Effectiveness (%)
Montmorillonite-polyDADMAC (organoclay)	585	91,5460
Natural bentonite	960	86,1272
PolyDADMAC	2020	70,8092

Variation of Flocculant Mass

Flocculants that used are montmorillonite-polyDADMAC (organoclay) and natural bentonite. The result of wastewater treatment of batik with variation of flocculant mass according to the Figure 3 and 4.

Table 4. TSS levels with variation of flocculant mass.

Flocculant Mass (g/L)	TSS with Addition Natural Bentonite (mg/L)	TSS with Addition Organoclay (mg/L)
0,5	710	620
1,0	325	555
1,5	260	315
2,0	215	100
2,5	250	25

Table 5. TDS levels with variation of flocculant mass.

Flocculant Mass (g/L)	TDS with addition natural bentonite (mg/L)	TDS with addition Organoclay (mg/L)
0,5	1560	1595
1,0	1510	1335
1,5	1100	1125
2,0	985	790
2,5	960	585

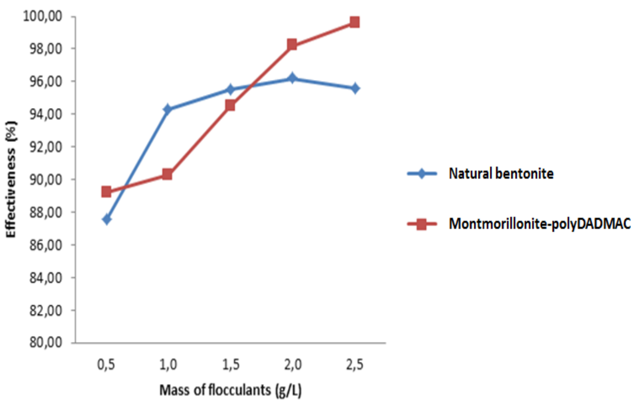

Figure 3. Influence of flocculant mass with effektiveness of TSS reduction.

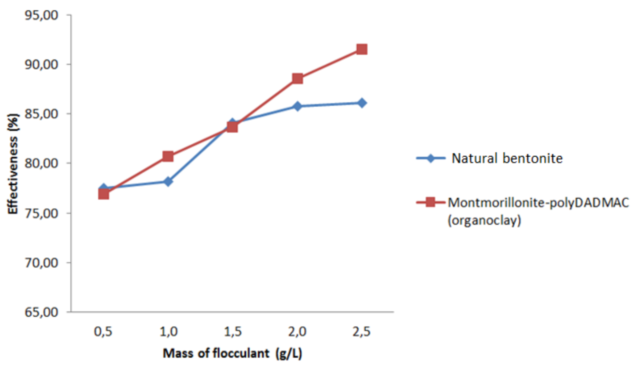

Figure 4. Influence of flocculant mass with effektiveness of TDS reduction.

Figure 3 and 4 are the maximum effectiveness of TSS and TDS reduced with addition of natural bentonite and montmorillonite-polyDADMAC flocculant. The mass used 2.5 g/L. TSS levels was reduced up to 25 mg/L while TDS levels up to 585 mg/L. Its feasible to be disposal because less than batik wastewater quality standard. This suggests that montmorillonite-polyDADMAC flocculants are better than natural bentonite flocculants to reduced TSS and TDS levels of batik wastewater. Organoclay flocculant has a better performance because has a polymer on the interlayer that can bind to compounds contained in batik wastewater. Organoclay also has a function as an adsorbent because has a pores that can adsorb the compounds in batik wastewater.

Variation of Flocculation Contact Times

Table 6. TSS levels based on variation of flocculation times.

Flocculation Times (menit)	TSS levels (mg/L)
20	125
40	25
60	20
80	15
100	20

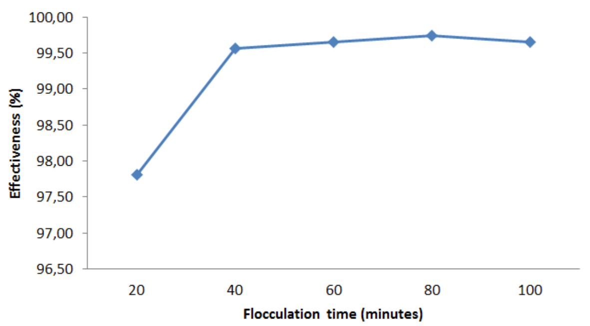

Figure 5. Influence of flocculation times with effektiveness of TSS reduction.

Figure 5 shows the infuence of flocculation times with effektiveness of TSS reduction. This treatment used 2,5 g/L of montmorillonite-polyDADMAC flocculant (organolclay). Effectiveness of maximum TSS reduced at 99,74% with the addition of organoclay flocculant 2.5 g/L and flocculation time for 80 minutes.

Table 7. TDS levels based on variation of flocculation times.

Flocculation Times (menit)	TDS levels (mg/L)
20	980
40	585
60	445
80	320
100	455

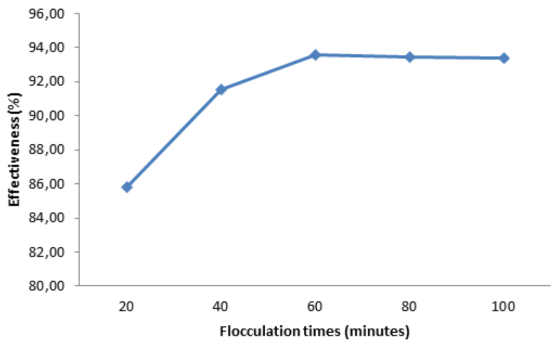

Figure 6. Influence of flocculation times with effektiveness of TDS reduction.

Figure 6 shows the effectiveness of maximum TDS reduced at 93,57% with the addition of organoclay flocculant 2.5 g/L and 60 minutes flocculation. If contact is too long cause the formed of flocks was decomposed again and more likely to form aggregates with wastewater. In addition, because all parts of the organoclay cannot binding the flock again.

CONCLUSIONS

1. TSS and TDS concentration of batik wastewater effluent before coagulation-flocculation is 7145 mg/L and 8080 mg/L, it means the concentration exceeds the quality standard.
2. TSS and TDS concentration of batik wastewater effluent after coagulation-flocculation with organolay flocculant is below the quality standard.
3. Organoclay characterization used FTIR and XRD indicates that modification of natural bentonite and polyDADMAC was succesfull with monolayer intercalation reaction.
4. Effectiveness of maximum TSS reduced at 99,74% with the addition of organoclay flocculant 2.5 g/L and flocculation time for 80 minutes. Effectiveness of maximum TDS reduced at 93,57% with the addition of organoclay flocculant 2.5 g/L and 60 minutes flocculation.

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