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Bentonite utilization to removal nitrogen from palm oil mill

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Abstract
Palm oil mill will give impact for environment such as nitrogen. This paper will describe clearly about ability of activated and natural bentonites to absorb nitrogen derived from palm oil mill wastewater. Sampling of bentonite was obtained from the Sungai Rengas in Jambi Province, Indonesia. Bentonite was smoothed and activated using a 1.6 M HCl. Measurement of nitrogen content using UV-vis instruments. Result of this study showed that activated bentonite can reduce 86% nitrogen and natural bentonite can reduce 85% nitrogen from anaerobic pond. This study showed that activated bentonite better than natural bentonite to reduce nitrogen at anaerobic pond from palm oil mill.

Keywords: bentonite, Activated bentonite, nitrogen, adsorption, wastewater, palm oil mill

Introduction

Nitrogen is the element in the earth's biosphere (Vincenzo et al., 2016) [20]. Nitrogen is one of six elements (C, H, O, N, P, and S) which are the main elements of living tissue (Watson et al., 2019) [21]. The atmosphere of the earth consists of 78% gas nitrogen (N_2), but most of these elements cannot be used by living things. Nitrogen in water can be found in organic nitrogen, ammonium, ammonia, nitrate, nitrite and molecular nitrogen in the form of gases. Excess nitrogen causes a decrease in dissolved oxygen levels due to two ongoing processes namely nitrification and eutrophication (Chai et al., 2019; Rivett et al., 2008) [20, 19]. Nitrification is a change in the chemical reaction of ammonium compounds into nitrates which requires a very large amount of oxygen (Rivett et al., 2008) [19]. This will cause a decrease in dissolved oxygen levels in the waters. Whereas eutrophication is a growth event of living things such as algae and algae that takes place rapidly when the nutrient content in the waters is in excessive amounts. Another impact caused is nitrogen pollution and ammonia toxicity. Ammonia contained in water in the form of NH_4 ions and NH_3 gas causes toxins in living things such as fish in these waters. From this explanation it can be identified that nitrogen compounds can cause environmental pollution. In general, these nitrogen compounds can be combined as total nitrogen (Ahn, 2006) [1].

Processing plants of liquid waste palm oil contain high organic matter, one of which is Nitrogen. The organic material is a nutrient so that the liquid waste has the opportunity to be used as a source of nutrients for plants. Therefore, if the nitrogen content in palm oil mill exceeds the threshold, it can pollute the environment, disrupt aquatic plants and animal ecosystems. Industrial activity will give negative impact for environment. Nitrogen content in oil palm mill was declared in Decree of the State Minister of Environment No. 51 of 1995 that quality standards of palm oil industry wastewater maximum levels of total nitrogen (N) is 50.0 mg/l with a maximum pollution load of 0.125 kg/ton.

Ammonia in wastewater is often formed due to chemical processes naturally (Karri et al., 2018) [10]. The effect of ammonia on human health, which can cause irritation to the eye if the ammonia content in water is greater than 0 mg/L (Li & Pauluhn, 2010) [1]. The effect of nitrites on human health, that is, can cause methemoglobinemia and the toxic effects of nitrite in water greater than 0 mg/L (Hord et al., 2009) [9]. Nitrite is a fertilizer in aquatic plants. Abundance of nutrient elements this nitrate in water is called eutrophication (Conley et al., 2009) [5]. The negative effect of this eutrophication is the change in the balance of life between aquatic plants and aquatic animals (Yang et al., 2008) [24]. The effect of nitrate on human health is that it can cause methemoglobinemia in infants who consume water with nitrate concentrations of more than 45 mg/L. One method that can be used to reduce the nitrogen content of palm oil mill wastewater is adsorption. Adsorption is the absorption of a substance (molecule or ion) on the surface of the adsorbent (Wibowo & Naswir, 2019; Wibowo et al., 2019) [22, 23]. In this study bentonite was used as an adsorbent. Bentonite is good adsorption properties because bentonite have high pores and surface area. Several studies on the use of bentonite have been applied for absorption of inorganic elements such as Cd^{2+} ions, Pb^{2+} and Cu^{2+}. Mn^{2+} and NO_3, Ni, and Fe (Naswir, 2016; Naswir et al., 2018; Naswir et al., 2014; Naswir et al., 2011; Naswir et al., 2013; Naswir et al., 2013) [13, 14, 16, 18, 15]. Utilization of bentonite applied to the absorption of organic compounds, there was no specific absorption on organic nitrogen elements. In this study an analysis of total nitrogen-organic matter was carried out on Palm Oil Mill wastewater. The sample used is wastewater taken in anaerobic ponds and aerobic pools of PT. Deli Muda Perkasa, Mersam, Jambi. Total nitrogen content was analyzed by UV-vis Spectrophotometry method. Bentonite is activated using HCl. The adsorption test will be carried out using bentonite with the mass and contact time obtained in previous studies. From this research, it is expected that bentonite has good effectiveness as nitrogen element adsorbent.

Materials and Methods

Tools and Materials

The tools used in this study are Erlenmeyer, clamp, beaker, measuring cup, measuring flask, measuring pipette, spatula, stirring rod, ball pipettes, glass funnels, analytic balance, ovens, shakers, crucible, mortal, desiccator, filter paper and watch glass. The materials used in this study were wastewater samples in aerobic and anaerobic ponds, bentonite, NaOH, KNO_3, $K_2S_2O_8$, HCl, and distilled water.

Sample Preparation

200 gr bentonite samples were cleaned and washed with distilled water, then dried in an oven at 105 °C for 24 hours to remove water content. The dried bentonite is crushed until smooth, then sifted with a 100 mesh sieve. Clean bentonite samples are stored in the desiccator.

Bentonite Activation

A total of 50 grams of 100 mesh bentonite was immersed in 200 mL of 1.6 M HCl that stirred for 1 hour at a speed of 200 rpm then filtered and washed with distilled water. The residue obtained is heated at 200°C for a hour. After drying, it is crushed and sifted with a 100 mesh sieve. Activated bentonites are stored in the desiccator and ready to be used for the next process.

Determination of total N-content in Palm Oil Mill wastewater

Determination of total N-level refers to the workings of JIS [K 0102-45.2.2002). Making the standard N-total solution was carried out by diluting the induction nitrogen solution 100 mg N / L to 0.2 mg N/L; 0.4 mg N/L; 0.8 mg N/L; 1.2 mg N/L; and 2.0 mg N/L. Then measured by a UV Vis spectrophotometer with a wavelength of 220 nm.

Hypothesis and Analysis

The method used in data analysis in the study of the determination of total N-organic matter content and its absorption test with bentonite were as follows: Total N-analysis was carried out using UV-vis spectrophotometry. Determination of total N-levels is known based on the standard curve, namely by plotting the absorbance value of the sample against the concentration of work or by using a straight-line equation bellow:

$$Y = ax + b$$

Note:
Y = Absorbance a = slope
b = intercept
X = Concentration

The total N-level in the sample is determined using the calibration curve method with the substitution of the Y value (absorbance) obtained from the absorbance measurement of the regression line equation from the calibration curve. So that the levels of N, P, and K can be determined by substituting the value of X in the following equation

$$\text{Sorption efficiency} = \frac{(Co - Ce)}{Co} x \ 100\%$$

Where, qe (mg/g) is the adsorption equilibrium of bentonite capacity; C_0 (mg/L) and Ce (mg/L) are the nitrogen concentrations at initial and equilibrium states, respectively; V is the solution in litter, and W is the mass of bentonite in gram.

Results and Discussions

Activated Bentonite

Bentonite was activated by HCl. The activation process functions to exchange cations in bentonite pores with H^+ ions and to cause dealumination (Didi et al., 2009) [6], namely the process of releasing Al^{3+}, Fe^{3+}, Mg^{2+} from bentonite ions and increase the acidic site of the bentonite itself (Durán, Bueno, Hermosín, Cox, & Gámiz, 2019) [7]. This acid site is a site that functions as the activated bentonite. It also increases the activity of bentonite. Addition of HCl too can clean the pore, remove impurities and rearrange the location of the exchanged ions

Cation exchange occurs from mineral salts (Ca^{2+} and Mg^{2+}) in the interlayer layer of bentonite with H^+ ions from acids, then followed by dissolving Al^{3+} and other metal ions such as Fe3 + from bentonite lattice layers (Fig. 1).

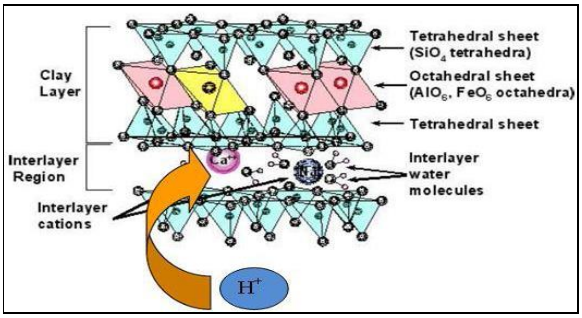

Fig 1: Bentonite reaction of HCl activation

Activated bentonite have montmorillonite, this content indicated that crystalline Na from montmorillonite, several study showed montmorillonite typical peaks around 3º and 5º. Characterization of bentonite inform that activated bentonite have small amounts of minerals such as quartz, illite and albite. FT-IR of activated bentonite remarkable peaks can be assigned to Si-O sretching and Si-O-Si bending according to literature (Askalany et al., 2017) [3]. Activated bentonite have strong intensity than natural bentonite as x-ray diffraction, peak of activated bentonite used HCl is in 28º. Activated bentonite have bigger pores than natural bentonite, HCl can clean the bentonite pores from residue and imputiry (Hebbar et al., 2018) [8].

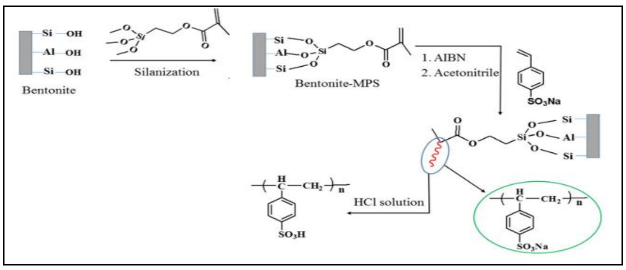

Fig 1: Bentonite activation use HCl

Determination of total N-content in Palm Oil Mill wastewater

Total nitrogen (N-total) is the total or total amount of nitrogen contained in waste water or samples, surface water and others. Curve of calibration made from a standard Nitrogen solution with a concentration of 02; 0.4; 0.8; 1, 2; and 2.0 mg N/L. Then the absorbance was measured by UV-vis spectrophotometry at a wavelength of 220 nm (Table 1)

Table 1: Absorbance of the Nitrogen standard

Concentration	Absorbance
0.2	0.217
0.4	0.355
0.8	0.646
1.2	0.921
1.4	1.416

The standard solution curve made by x-axis concentration and absorbance y-axis, then the regression equation y = 0.6684x + 0.0961, with the price of R2 = 0.9986. The absorbance produced is directly proportional to the concentration of the standard solution, namely the greater the concentration used, the greater the absorbance. This is in accordance with the law of Lambert-Beer, namely A = a, b and c, where the value of absorbance (A) is directly proportional to the value of concentration (C). Palm oil mill wastewater contains nitrogenous organic matter based on the Decree of the State Minister of Environment No. 51 of 1995.

Table 2: Nitrogen in Palm Oil Mill

Sample	Absorbance	Kons (Mg/L)	FP	Result (Mg/L)
Blanko	0.089	-0.010	1.0	-0.010
Wastewater in Anaerobic pond	0.806	1.061	100.0	106
Wastewater in Anaerobic pond	0.933	1.341	10.0	13.4

Absorption of Bentonite against N-Total in Palm Oil Mill Waste Water

Determination of absorption of bentonite against N-total was carried out with a mass of 1 gram bentonite for 90 minutes contact time.

Table 3: N-Total analysis after adsorption

Organic Matter	Natural Bentonite	Activated Bentonite
N	19.7	18.6
Efficiency	81%	82 %

Activated bentonite have stronger sorption than natural bentonite (Table 3). Activated bentonite by HCl showed affects mineral acid, this treatment showed that activated bentonite can dissolve the components of SiO_2 and Al_2O_3 which fill the adsorbent pores. This research inform that activator (HCl) can open the pores, opened pores in bentonite can make bentonite more powerful to nitrogen content. Activation of bentonite using acid also produces bentonite with larger active sites and greater surface similarity, resulting in higher bentonite yields than natural bentonite (Al-asheh et al., 2003) [2] .

Nitrogen in excess conditions is one of the pollutant parameters of the waters because it can reduce dissolved oxygen concentration through the process of nitrification and endanger the life of aquatic biota due to ammonia toxicity. Nitrogen in water can be found in the form of ammonia, ammonium, nitrite, nitrate, and molecular nitrogen in the form of gas (Sawyer, 2003). In conditions in the field, the compounds of nitrogen naturally occur in wastewater. For example organic nitrogen in the waters comes from nitrogen fixation and the decay process of dead living things. Ammonia comes from the hydrolysis of organic nitrogen, decay of organic material, and metabolic waste from aquatic biota.

Conclusion

Palm oil mill will give impacts for environment caused by waste material such as nitrogen in rubber factory wastewater. Rubber factory wastewater in anaerobic ponds contains Nitrogen 106 mg / L, and at the aerobic pond 13 mg / L. Natural bentonite and activated bentonite can reduce 81% and 8% nitrogen from anaerobic ponds. Activated bentonite more efficient than natural bentonite for removal nitrogen at anaerobic ponds, it caused by surface area and pores of activated bentonite better than natural bentonite.

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