INDONESIAN NANOCLAYS FOR THE REMOVAL OF NITRATE IN LIQUID WASTE CONTAINING PALM OIL MILL EFFLUENT

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ABSTRACT

Land application of liquid waste containing palm oil mill effluent (LW-POME) as soil ameliorant can cause water contamination due to its high content of nitrate if improperly treated. Indonesia is rich with volcanic tuff materials that contain variable charged soil clay minerals. This study was aimed at extracting nanoclays (fraction sized <200 nm) from volcanic tuffs of Mt. Salak, West Java, Indonesia, and evaluate their potential use as adsorbent of nitrate in LW-POME. By applying dispersion, ultrasonication, centrifugation, and dialysis separation techniques, it could be extracted positively charged nanoclays nc3 and nc4 from the respectively tuff materials tv3 and tv4. Their potential use as natural adsorbent of nitrate as anionic contaminant was evaluated using Langmuir isothermal adsorption model. After 48 h equilibration, it could be extracted 4.33 mg nc3/g tv3 and 7.73 mg nc4/g tv4 with nitrate adsorption maxima of 48.3 and 40 mg/g for nc3 and nc4, respectively. The removal of nitrate in the LW-POME from 62 to 20 mg/L as to comply with the Indonesian liquid waste quality standard required 29.81 mg nc3/L or 39.34 mg nc4/L. The extracted nanoclays were considered prospective to be utilized as natural adsorbent for nitrate removal in LW-POME.

Keywords: anionic contaminant, natural adsorbent, nitrate adsorption, volcanic tuff

INTRODUCTION

Palm oil mill-effluent (POME) is a byproduct of the final production of crude palm oil and kernel palm oil processes from fresh fruit bunches in the mill. It is mainly generated from the processes of sterilization, hydro-cyclone, and clarification as condensate, drain-off, and sludge, respectively (Igwe and Onyegbado, 2007; Wu et al., 2010). After treated in ponding systems, it is commonly recycled by oil palm plantation companies in Indonesia and Malaysia as soil ameliorant by way of land application practice (Amelia et al., 2017; Kamyab et al., 2018). However, application of this practice for long-term period can generate negative environmental impacts, one of which is nitrate contamination in waters of the surrounding plantation area.

Soils and soil parent materials are potential source of natural adsorbent for the removal of anionic contaminants such as phosphate, fluorate, and arsenate in waters, wastewater, and liquid waste (Gitari and Mudzielwan, 2015; Sudadi et al., 2019; Wambu et al., 2015). From volcanic tuff materials, that are abundant in Indonesia, it can be extracted fraction with physical dimension of <200 nm (Kaufold et al., 2010; Shukla et al., 2013; Sudadi et al., 2019). These nanoclays pose a pH-dependent charge characteristic (Kaufold et al., 2010). Being treated or modified in acid condition, the nanoclays perform positive charge characteristic and
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hence can be utilized as natural adsorbent for the removal of anionic contaminants (Shukla et al., 2013).

This study was aimed at to extract nanoclays from volcanic tuff materials of Mt. Salak, Indonesia, and to evaluate their potential use as natural adsorbent for the removal of nitrate in liquid waste containing palm oil mill effluent. Subsequently in this paper, the latter is abbreviated as LW-POME.

METHOD

Tools and Materials
The tools used in this study consist of glasswares, 240-mesh sieve, digital analytical balance, oven, ultrasonic, centrifuge, pH-meter, spray bottle, EC-meter, Kjeldahl apparatus, and UV-Vis spectrophotometer. For data analysis, we applied Microsoft Office Excell and SAS statistical softwares.

The tuff materials used in this study (tv3 and tv4) were collected from the 3rd (87-135 cm depth) and 4th (>135 cm depth) layers of an Andisol profile at the slope (670 m asl) of Mt. Salak located in Sukajadi Village, Tamansari Subdistrict, Bogor Regency, West Java (6° 39’ 28” S and 106° 43’ 52.2” E) in March 2017. The sample of LW-POME was collected from a palm oil plantation mill in Rokan Hulu Regency, Riau in July 2017. The experiment was conducted in March to July 2017 at the Soil Chemistry and Fertility Laboratory, Department of Soil Science and Land Resource, Faculty of Agriculture, IPB University.

Extraction of Nanoclay Fraction
Briefly, by dispersing in acid condition, followed with ultrasonication, centrifugation, and purification using membrane dialysis technique, it can be extracted nanoclay fraction from volcanic tuff materials. This procedure refers to Henmi and Wada (1976) that was modified by Calabi-Floody et al. (2009; 2011) with the addition of ultrasonication step.

Detail of the procedure is described as follows. Water content of the air dried 240 mesh sieved-tuff materials (tv3 and tv4) were first determined using gravimetric procedure. Initial chemical analysis of tv3 and tv4 was conducted for pH H2O, pH NaF, and organic-C content. Then, 10 g of tv3 and tv4 were separately put into 2 cylinders-1L, added each with aquadest up to 1 L total volume, conditioned into pH 4.0 by addition of 4.5 mL 0.21 N HCl, ultrasonicated at sonic wave of 20 kHz for 15 min, and sedimented for 20 h. Afterwards, the top 10 cm solutions (around 200 mL each), which were considered to contain nanoclay fractions with positive charge characteristic, were transferred using plastic pipe into beaker glass-1000 mL. This step was conducted 8 times, using in total 84.41 g air-dried tv3 and tv4 each, until around 1600 mL of the top 10 cm solutions each were obtained. The solutions were then flocculated using 100 mL N NaCl and resedimented for another 20 h. The top clear solutions were then decanted and the flocculated fractions of around 160 mL each were kept for the next steps.

The 160 mL flocculated fractions of tv3 and tv4 from the previous step were redispersed at pH 4.0 and then transferred each separately into 4 centrifuge bottles-40 mL. The volume or height of the solutions in all bottles were made equal by addition of aquadest in order to obtain optimal centrifugations at 3500 rpm for 4 x 30 min. After the fourth centrifugation, it can be differentiated of about 1 cm top clear solution part, which was considered as the excess NaCl from the flocculation step, with the suspension and solid parts below it. The top clear solution part was decanted, whilst the suspension and solid parts, which were considered as to contain the extracted nanoclay fraction, were transferred into beaker glass-500 mL.
The suspension was directly transferred into the other beaker glass, while the solids were dissolved first with aquadest by means of spray bottle. Then, the accumulated suspensions in beaker glass were further purified from the excess NaCl by performing membrane-dialysis technique. At the dialysis step, an amount of nanoclay suspension was put into dialysis membrane of about 4 cm length and tied at both ends at about 1 cm position using strings and then soaked with drift position in beaker glass containing 1000 mL aquadest. During this step, aquadest in the beaker glass was changed regularly with the fresh one until an equilibrium condition was attained, in which the concentration of ions inside the membrane was equal to those in aquadest outside the membrane or when the electrical conductivity (EC) of aquadest in the beaker glass was almost equal to that of pure aquadest (0.5-0.8 µS/cm), indicating that nanoclay suspension inside the membrane was already free from the excess NaCl and therefore assumed to contain only positively charged reactive nanoclays. The EC determination was done using EC-meter.

The next step was determination of the extracted nanoclay concentration in the suspension. Each suspension, i.e. originated from tv3 and tv4, was transferred from the corresponding membranes into 2 volumetric flasks-500 mL separately and made up the volume by addition of aquadest. Up to this step, nanoclay nc3 and nc4 originated respectively from tv3 and tv4 materials were already obtained and ready for use for the LW-POME nitrate adsorption batch experiment.

The concentrations of nanoclays nc3 and nc4 in each 500 mL suspensions in the corresponding volumetric flasks were determined gravimetrically with 3 replications by pipetting 10 mL of each suspension into oven plates and oven-dried at 105°C for 24 h or until their constant weights were obtained. Then, percentage of the respectively dry weight of nc3 and nc4 per unit dry weight of tv3 and tv4 were calculated.

**Nitrate Adsorption Test**

Briefly, nitrate adsorption test was carried out by referring to the Langmuir isothermal adsorption model. The test was performed by conducting batch experiment to obtain adsorption maxima (b value) of LW-POME nitrate onto the extracted nanoclays at 4 equilibration times, i.e. 12, 24, 48, and 72 h, each with 3 replications.

The batch experiments consisted of 2x4 sets of 6 polyethylene tubes. Twenty four tubes were contained with 0, 2.5, 5, 10, 15, and 20 mL suspension containing nanoclay nc3 and the other 24 tubes with those of nc4, respectively, added each with 20 mL LW-POME, 5 mL 0.01 N CaCl2 as background electrolyte, and aquadest up to a total volume of 50 mL. Then, the tubes were equilibrated for 12, 24, 48, or 72 h by way of agitation for 30 min using mechanical end-to-end shaker at time 0, 6, and 12 h for the first set; at time 0, 6, 12, 18, and 24 h for the second set; at time 0, 6, 12, 24, 30, 36, 42, and 48 h for the third set, and at time 0, 6, 12, 18, 24, 30, 36, 42, 48, and 72 h for the fourth set. After these equilibrations, the suspensions were centrifugated and filtered for the determination of nitrate concentration in the aliquot using Kjeldahl method.

The general Langmuir isothermal adsorption model, x/m = kbC / 1+kC, can be converted into a linear equation C/x/m = 1/b + 1/kb C, where x/m stands for the amount of nitrate adsorbed per unit weight of nanoclay (mg/g), i.e. the difference between the added nitrate concentration (20 mL LW-POME containing 62 mg nitrate/L added into the 50 mL solution series containing nanoclay suspensions from 0 to 20 mL) and nitrate concentration at equilibrium state (C, mg/L). The data obtained were then simulated using the linear Langmuir equation to obtain b
values (adsorption maxima, mg/g). The b value was calculated based on the intercept of the curve (1/b value of the resulted linear regression equation C/x/m = 1/b + 1/kb C).

Data Analysis

The linear Langmuir equations were determined using Microsoft Excell software. Statistical analysis to determine mean difference significance amongst the adsorption maximas (b values) of nitrate contained in LW-POME into the nanoclays nc3 and nc4 at 12, 24, 48, and 72 h equilibration times were performed by applying t-test using SAS software.

RESULTS AND DISCUSSION

Extracted Nanoclays

Volcanic tuff material is a pyroclastic substance originated from volcano eruption that is already solidified and lithified due to association with water. Andisols in the sampling location of volcanic tuffs used in this study were developed from andesitic volcanic parent materials of Mt. Salak (Van Ranst et al., 2002). Weathering results of the acidic volcanic tuff material forms, among others, nanoclay fraction which contains nanocrystalline aluminosilicate minerals nanoball allophane (diameter of 3.5-5 nm) and nanotube imogolite (diameter of 1-3 nm) that poses pH-dependent charge characteristic (Abidin et al., 2007). In acid condition, it behaves positive charge, while in alkaline condition it behaves negative charge. The positive charge is originated from protonation of hydroxil groups at the silanol (Si-OH), aluminol (Al-OH), and ferol (Fe-OH) reactive surfaces so that anion can be adsorbed. Whilst the negative charge is originated from deprotonation of hydroxil groups at the same reactive surfaces so that cation can be attracted (Abidin et al., 2007; Calabi-floody et al., 2009, 2011; Tan, 1998).

Table 1 shows that the volcanic tuff materials tv3 were characterized with lower pH H2O and pH NaF but higher organic-C content than those of tv4. As to contain aluminosilicate minerals, nanoclay fractions poses OH terminals at each of its silanol (Si-OH), aluminol (Al-OH), and ferol (Fe-OH) reactive surfaces. In the course of pH NaF determination, ion F from NaF replaced hydroxide ion (OH-) at those reactive surfaces and released it to the soil solution so that increased the pH value. Hence, the higher the pH NaF value of the solution obtained, the higher the concentration of the extracted nanoclays could be expected (Tan, 1998). As shown in Table 2, from 84.42 g tv3 it could be extracted 0.28 g nanoclay fraction nc3 that equals to 4.33 mg nc3/g tv3, whilst from 84.42 g tv4 it could be extracted 0.48 g nanoclay fraction nc4 that equals to 7.73 mg nc4/g tv4. Concentration of the nanoclays that could be extracted from tv4 was higher than that of tv3 which was in accordance with the higher pH NaF of tv4 than that of tv3. Furthermore, the higher organic-C content in tv3 made it more difficult to extract nanoclay fraction from tv3 as compared to tv4 because of the aggregation effect of organic matter (Tan, 1998).

Nitrate Adsorption Characteristic of Extracted Nanoclays

Table 2 shows that the nitrate adsorption maxima (b value) of nc3 were higher than those of nc4 at all of the four equilibration time tested (12, 24, 48, and 72 h). Therefore, nc3 was considered more prospective than nc4 to be utilized as adsorbent for the removal of anionic contaminant such as nitrate contained in the tested LW-POME.

The b value or adsorption maxima of an adsorbent is, among others, affected by its particle size. Therefore, results of this study indicated that there was a difference in particle size between nc3 and nc4. This is probably due to the difference in
crystallization state. Position of tv3 layer in the soil profile was closer to the parent material than that of tv4. The closer the layer position to the parent material, the lower the weathering and crystallization level of the formed minerals (Tan, 1998).

**Effects of Equilibration Time**

Results of the t-test (Table 3) show that nitrate adsorption maxima of the extracted nanoclay nc3 and nc4 after equilibrated for 12 h were not significantly different with those of 24 h, whilst those of 48 h were significantly higher than those of 24 for both and of 72 h for nc4. This indicated that increasing equilibration up to 72 h did not result in higher nitrate adsorption significantly. Therefore, the most effective equilibration for application of the extracted nanoclays as adsorbent of nitrate was 48 h. Using the same extracted nanoclays that were tested to adsorb phosphate in a eutrophic water, the most effective equilibration time obtained was also 48 h as to compared to those of 12 and 24 h (Sudadi et al., 2019).

**Nanoclays Required to Reduce Nitrate as to Comply with the Wastewater Quality Standard**

For the intention to utilize the extracted nanoclays as adsorbent of nitrate in the management of liquid waste or contaminated waters, then it is necessary to calculate the required amount of the nanoclays to reduce the contamination level as to comply with the liquid waste quality standard that apply. The quality

### Table 1. Properties of the volcanic tuff materials of Mt. Salak, West Java, Indonesia

| Sample Code | Depth of sampling (cm) | pH H2O 1:5 | pH NaF 1:5 | Organic-C (%) |
|-------------|------------------------|------------|------------|---------------|
| tv3         | 87-135                 | 5.13       | 11.08      | 0.99          |
| tv4         | 135+                   | 5.58       | 11.35      | 0.09          |

### Table 2. Extracted nanoclays from the volcanic tuff materials of Mt. Salak, West Java, Indonesia

| Volcanic tuff material | Air dry weight | Water content | Dry weight | Dry weight |
|------------------------|----------------|---------------|------------|------------|
|                        | g              | %             | g          | mg         | mg/g tv    |
| tv3                    | 84.42          | 30.80         | 64.53      | nc3        | 0.28       | 4.33       |
| tv4                    | 84.42          | 37.36         | 61.45      | nc4        | 0.48       | 7.73       |

### Table 3. Nitrate adsorption maxima of the extracted nanoclays from volcanic tuff materials of Mt. Salak, West Java, Indonesia

| Extracted nanoclays | Equilibration time | Average value of nitrate adsorption maxima |
|---------------------|--------------------|--------------------------------------------|
|                     | 12 h               | 24 h                                      | 48 h                           | 72 h  |
| nc3                 | 25.06<sup>a</sup> | 32.25<sup>abc</sup>                       | 48.30<sup>d</sup>              | 26.59<sup>ab</sup>             |
| nc4                 | 21.40<sup>q</sup> | 25.97<sup>qr</sup>                        | 40.00<sup>s</sup>              | 10.68<sup>p</sup>              |

Note: “Means in the same row with different italic letter differ significantly (p<0.05)”
standard of nitrate concentration in liquid waste or effluent of oil palm mill of category I according to the Ministry of Environment Regulation, Republic of Indonesia No.5 year 2014 is 20 mg nitrate/L.

Weight of the extracted nanoclays required to reduce nitrate concentration in the LW-POME to 20 mg nitrate/L was determined by means of linear regression analysis of the relationship between the applied weight of nanoclay (mg) as X-axis and the resulted nitrate concentration (mg/L) after 48 h equilibration as Y-axis. Then, the obtained X value perpendicular to the intersection point of the regression curves ($Y_{nc3} = -1.25X + 57.27$ (r = 0.983, $p<0.01$) and $Y_{nc4} = -0.908X + 55.73$ (r = 0.977, $p<0.01$) with the horizontal line at $Y = 20$ mg nitrate/L showed the required weight of the extracted nanoclays for the purpose.

The required weight of nc$_3$ (29.81 mg/L) for the purpose to reduce nitrate concentration in the LW-POME from 62 to 20 mg/L was lower than that of nc$_4$ (39.34 mg/L). This was related to the higher value of adsorption maxima of nc$_3$ than that of nc$_4$ (Table 3). However, the extracted amount of nc$_3$ per unit weight of the corresponding tuff material was lower than that of nc$_4$ (Table 2). Consequently, to obtain an equal application efficacy of the extracted nanoclays as adsorbent of nitrate, the required amount of tv$_3$ would be higher than that of tv$_4$ or vice-versa. Similar result was obtained from application of the same nanoclays as adsorbent of phosphate in eutrophic water (Sudadi et al., 2019).

CONCLUSION

After 48 h equilibration, it could be extracted 4.33 mg nc$_3$/g tv$_3$ and 7.73 mg nc$_4$/g tv$_4$. The nitrate adsorption maxima of nc$_3$ was higher than that of nc$_4$. The removal of nitrate in the LW-POME from 62 mg/L to 20 mg/L as to comply with the quality standard of nitrate concentration in liquid waste of oil palm mill of category I according to the Ministry of Environment Regulation No.5/2014 required 29.81 mg nc$_3$/L or 39.34 mg nc$_4$/L. The extracted nanoclays were prospective to be utilized as adsorbent for nitrate removal in LW-POME.

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