

# AGROTEKNOLOGI

Volume 13, Nomor 02, Desember 2019

<b>ANALISIS PENENTUAN LOKASI PENGEMBANGAN KLASSTER INDUSTRI BERBASIS SINGKONG DI KABUPATEN JEMBER</b>	98-107
Emi Kurniawati, Yuli Wibowo, Ida Bagus Suryaningrat	
<b>KARAKTERISTIK MUTU BUBUK OKARA HASIL KERAGAMAN PERLAKUAN HIDROTERMAL DAN SUHU PENDINGINAN</b>	108-117
Iwan Taruna	
<b>KARAKTERISTIK PERMEN <i>JELLY</i> JANTUNG BUAH NANAS DENGAN VARIASI KONSENTRASI KARAGENAN DAN SUHU PEMANASAN</b>	118-130
Giyarto Giyarto, Sony Suwasono, Putri Oktavilia Surya	
<b>POTENSI LIMBAH KULIT RAMBUTAN (<i>Nephelium lappaceum</i>) SEBAGAI MINUMAN SEDUHAN HERBAL</b>	131-136
Denny Anggara, Meassy Shawitry Harijanja, Alvika Musfitasari, Martha Marselinha, Fransiskus Xaverius Arif Wahyudianto, Andrian Fernandes	
<b>PROPORSI MOCAF DAN TEPUNG LARUT DENGAN PENAMBAHAN MALTODEKSTRIN PADA PENGOLAHAN <i>COOKIES</i></b>	137-147
Indra Agustanugraha Pramadi, Fungsi Sri Rejeki, Tri Rahayuningsih, Endang Retno Wedowati	
<b>AKSELERASI PRODUKSI MOROMI MENGGUNAKAN INOKULUM <i>Pediococcus halophilus</i> FNCC 0033 DAN <i>Zygosacharomices rouxii</i> FNCC 3008</b>	148-155
Jay Jayus, Etika Hanif Rosyidawati, Bambang Herry Purnomo	
<b>MORFOGENESIS DAN INDUKSI KALUS TIN (<i>Ficus carica</i> L.) PADA MEDIA MURASHIGE DAN SKOOG (MS) DENGAN PENAMBAHAN <i>BENZYLAMINOPURINE</i></b>	156-163
Pangesti Nugrahani, Didik Utomo Pribadi	
<b><i>INDONESIAN NANOCLAYS FOR THE REMOVAL OF NITRATE IN LIQUID WASTE CONTAINING PALM OIL MILL EFFLUENT</i></b>	164-170
Untung Sudadi, Syaiful Anwar, Rendy Aggriawan, Tengku Afrizal	
<b>SISTEM PRODUKSI DAN PENGOLAHAN KOPI BERKELANJUTAN: <i>STATE OF THE ART</i></b>	171-179
Rachman Jaya, Yusriana Yusriana, Rizky Ardiansyah	
<b>PRODUK ENKAPSULASI ASAP CAIR SEKAM PADI DAN APLIKASINYA UNTUK MENGAWETKAN TAHU PUTIH</b>	180-194
Ana Andiana, Nur Aini, Karseno Karseno	
<b>DETERMINASI DIVERSIFIKASI VERTIKAL PRODUK OLAHAN JAMBU MERAH</b>	195-202
Marina Ekawati, Yuli Wibowo, Kiky Chily Arum Dalu, Nurhayati Nurhayati	

Diterbitkan oleh:

Fakultas Teknologi Pertanian Universitas Jember

Bekerjasama dengan:

Perhimpunan Ahli Teknologi Pangan Indonesia (PATPI)

Perhimpunan Teknik Pertanian Indonesia (PERTETA)

Asosiasi Profesi Teknologi Agroindustri (APTA)

# Jurnal AGROTEKNOLOGI

Volume 13 Nomor 02, Desember 2019

p-ISSN 1978-1555; e-ISSN 2502-4906

Jurnal Agroteknologi (J-AGT)  
Publikasi Ilmiah Fakultas Teknologi Pertanian (FTP)  
Universitas Jember (UNEJ)

#### Visi:

Menjadi terbitan berkala ilmiah skala nasional yang mempublikasikan hasil penelitian bidang teknologi pertanian yaitu teknologi hasil pertanian, keteknikan pertanian, dan teknologi industri pertanian.

#### Misi:

1. Menyebarluaskan hasil penelitian dosen dan peneliti fungsional dari berbagai perguruan tinggi dan badan litbang pertanian, litbang kesehatan, litbang perindustrian dan yang sejenis di Indonesia
2. Mengkomunikasikan hasil penelitian, ulasan ilmiah dalam bentuk komunikasi singkat, dan atau paket industri bidang teknologi pertanian: teknologi hasil pertanian, keteknikan pertanian, dan teknologi industri pertanian.

#### Ruang Lingkup

Jurnal Agroteknologi terbit dua nomor per volume, dan mempublikasikan hasil penelitian dalam bidang ilmu dan teknologi pertanian yang mencakup teknologi hasil pertanian, keteknikan pertanian, dan industri pertanian. Selain itu, juga dimungkinkan membahas ulasan ilmiah, resensi buku, komunikasi singkat, dan paket industri agroteknologi.

#### Diterbitkan oleh:

Fakultas Teknologi Pertanian Universitas Jember

Bekerjasama dengan:

Perhimpunan Ahli Teknologi Pangan Indonesia (PATPI)

Perhimpunan Teknik Pertanian Indonesia (PERTETA)

Asosiasi Profesi Teknologi Agroindustri (APTA)

Ketua Dewan Redaksi:

Dr. Nurhayati, S.TP, M.Si

Dewan Redaksi (Penyunting):

Prof. Dr. Indarto., S.TP, DEA.

Dr. Puspita Sari S.TP., M.Ph

Dr. Ir. Iwan Taruna, M.Eng.

Dr. Ir. Sih Yuwanti, M.P.

Dr. Dedy Wirawan Soediby, S.TP, M.Si

Dr. Ir. Soni Sisbudi Harsono, M.Eng, M.Phil

Ir. Giyarto, M.Sc

Dr. Elida Novita, S.TP, MT

Desain dan Photographer:  
Rufiani Nadzirah, S.TP, M.Sc

#### Sekretariat:

Dr. Ir. Herlina, MP  
Astriani, S.TP, M.Biotek

#### Mitra Bebestari:

Dr. Yuli Wibowo,

(Manajemen Agroindustri, UNEJ)

Dr. Didah Nur Farida, S.TP, M.Si

(Teknologi Pangan, IPB)

Dr. Maria Belgis, S.TP, M.P.

(Teknologi Pangan, UNEJ)

Dr. Ir. Bambang Marhaenanto, M.Eng.

(Elektrifikasi dan Energi, UNEJ)

Dr. Ida Bagus Suryaningrat, S.TP, M.M.

(Manajemen Agroindustri, UNEJ)

Ir. Umi Purwandari, M.App.Sc, Ph.D.

(Teknologi Pangan, Universitas Trunojoyo Madura)

Dr. Dedin Finatsiyatul Rosida, S.TP, M.Kes.

(Teknologi Pangan, UPN Veteran Jawa Timur)

Dr. Nur Aini, S.TP, M.P.

(Teknologi Pangan, Unsoed)

Dr. Triana Lindriati, ST, M.P.

(Teknik Kimia dan Pangan, UNEJ)

Dr. Ir. Tri Dewanti Widyarningsih, M.Kes.

(Nutrisi dan Teknologi Pangan, UB)

Prof. Dr. Yuli Witono S.TP, M.P.

(Biokimia Pangan, UNEJ)

#### Alamat Redaksi:

Sekretariat Jurnal Agroteknologi (J-AGT)

Fakultas Teknologi Pertanian

Universitas Jember

Jl. Kalimantan No. 37 Kampus Tegalboto

Jember 68121, Fax/Telp. 0331-321784

E-mail : j\_agrotek.ftp@unej.ac.id

#### Kontributor

Menerima naskah dari staf pengajar, peneliti, pemerhati, mahasiswa, dan praktisi di bidang agroteknologi. Harga langganan per tahun (2 nomor) Rp. 200.000,00. Pembayaran melalui transfer ke Rekening BRI an. Nurhayati Cabang Jember No. Rek. 0021-01-071127-50-6. Konfirmasi transfer dapat dilakukan dengan mengirimkan bukti transfer ke j\_agrotek.ftp@unej.ac.id

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

Untung Sudadi<sup>1)\*</sup>, Syaiful Anwar<sup>1)</sup>, Rendy Anggriawan<sup>2)</sup>, Tengku Afrizal<sup>3)</sup>

<sup>1)</sup>Department of Soil Science and Land Resource, Faculty of Agriculture, IPB University

Jl. Meranti, Campus IPB Dramaga, Bogor 16680, Indonesia

<sup>2)</sup>Department of Agrotechnology, Faculty of Agriculture, Muhammadiyah University of Jember

Jl. Karimata 49, Jember 68121, Indonesia

<sup>3)</sup>Alumni of Land Resource Management Study Program, Department of Soil Science and Land

Resource, Faculty of Agriculture, IPB University

Jl. Meranti, Campus IPB Dramaga, Bogor 16680, Indonesia

\*Corresponding author: untungsudadi@yahoo.com

### 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 to extract 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 nc<sub>3</sub> and nc<sub>4</sub> from the respectively tuff materials tv<sub>3</sub> and tv<sub>4</sub>. 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 nc<sub>3</sub>/g tv<sub>3</sub> and 7.73 mg nc<sub>4</sub>/g tv<sub>4</sub> with nitrate adsorption maxima of 48.3 and 40 mg/g for nc<sub>3</sub> and nc<sub>4</sub>, 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 nc<sub>3</sub>/L or 39.34 mg nc<sub>4</sub>/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, fluoride, 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

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 (tv<sub>3</sub> and tv<sub>4</sub>) were collected from the 3<sup>rd</sup> (87-135 cm depth) and 4<sup>th</sup> (>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 (tv<sub>3</sub> and tv<sub>4</sub>) were first determined using gravimetric procedure. Initial chemical analysis of tv<sub>3</sub> and tv<sub>4</sub> was conducted for pH H<sub>2</sub>O, pH NaF, and organic-C content. Then, 10 g of tv<sub>3</sub> and tv<sub>4</sub> 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 tv<sub>3</sub> and tv<sub>4</sub> 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 tv<sub>3</sub> and tv<sub>4</sub> 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 mean 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  $\mu\text{S}/\text{cm}$ ), 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 were done using EC-meter.

The next step was determination of the extracted nanoclay concentration in the suspension. Each suspension, i.e. originated from tv<sub>3</sub> and tv<sub>4</sub>, 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 nc<sub>3</sub> and nc<sub>4</sub> originated respectively from tv<sub>3</sub> and tv<sub>4</sub> materials were already obtained and ready for use for the LW-POME nitrate adsorption batch-experiment.

The concentrations of nanoclays nc<sub>3</sub> and nc<sub>4</sub> 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 nc<sub>3</sub> and nc<sub>4</sub> per unit dry weight of tv<sub>3</sub> and tv<sub>4</sub> 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, dan 20 mL suspension containing nanoclay nc<sub>3</sub> and the other 24 tubes with those of nc<sub>4</sub>, respectively, added each with 20 mL LW-POME, 5 mL 0.01 N CaCl<sub>2</sub> 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, 18, 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 nc<sub>3</sub> and nc<sub>4</sub> 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 hydroxyl 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 hydroxyl 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 tv<sub>3</sub> were characterized with lower pH H<sub>2</sub>O and pH NaF but higher organic-C content than those of tv<sub>4</sub>. As to contain aluminosilicate minerals, nanoclay fractions poses OH<sup>-</sup> 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<sup>-</sup> from NaF replaced hydroxide ion (OH<sup>-</sup>) 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 tv<sub>3</sub> it could be extracted 0.28 g nanoclay fraction nc<sub>3</sub> that equals to 4.33 mg nc<sub>3</sub>/g tv<sub>3</sub>, whilst from 84.42 g tv<sub>4</sub> it could be extracted 0.48 g nanoclay fraction nc<sub>4</sub> that equals to 7.73 mg nc<sub>4</sub>/g tv<sub>4</sub>. Concentration of the nanoclays that could be extracted from tv<sub>4</sub> was higher than that of tv<sub>3</sub> which was in accordance with the higher pH NaF of tv<sub>4</sub> than that of tv<sub>3</sub>. Furthermore, the higher organic-C content in tv<sub>3</sub> made it more difficult to extract nanoclay fraction from tv<sub>3</sub> as compared to tv<sub>4</sub> 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 nc<sub>3</sub> were higher than those of nc<sub>4</sub> at all of the four equilibration time tested (12, 24, 48, and 72 h). Therefore, nc<sub>3</sub> was considered more prospective than nc<sub>4</sub> 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 nc<sub>3</sub> and nc<sub>4</sub>. This is probably due to the difference in

crystallization state. Position of tv<sub>3</sub> layer in the soil profile was closer to the parent material than that of tv<sub>4</sub>. 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 nc<sub>3</sub> and nc<sub>4</sub> 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 nc<sub>4</sub>. 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 H <sub>2</sub> O 1:5	pH NaF 1:5	Organic-C (%)
tv <sub>3</sub>	87-135	5.13	11.08	0.99
tv <sub>4</sub>	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			Extracted nanoclays		
	Air dry weight	Water content	Dry weight	Dry weight		
	g	%	g	mg	mg/g tv	
tv <sub>3</sub>	84.42	30.80	64.53	nc <sub>3</sub>	0.28	4.33
tv <sub>4</sub>	84.42	37.36	61.45	nc <sub>4</sub>	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	Average value of nitrate adsorption maxima			
	Equilibration time			
	12 h	24 h	48 h	72 h
	mg/g			
nc <sub>3</sub>	25.06 <sub>a</sub>	32.25 <sub>abc</sub>	48.30 <sub>d</sub>	26.59 <sub>ab</sub>
nc <sub>4</sub>	21.40 <sub>q</sub>	25.97 <sub>qr</sub>	40.00 <sub>s</sub>	10.68 <sub>p</sub>

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.

## REFERENCES

- Abidin, Z., Matsue, N., Henmi, T. 2007. Differential formation of allophane and imogolite: Experimental and molecular orbital study. *J. Computer-Aided Mater Des.*, 14: 5-8.
- Amelia, J.R., Suprihatin, S., Indrasti, N.S., Hasanudin, U., Murakami, R., Fujie, K. 2017. Effects of treated palm oil mill effluent application on the soil microbial community structure and oil palm plantation productivity. *J. Water Environ. Tech.*, 15 (3): 77-85.
- Calabi-Floody, M., Theng, B.K.G., Preyes, P., Mora, M.L. 2009. Natural nanoclays: Applications and future trends – a Chilean perspective. *Clay Miner.*, 44: 161-176.
- Calabi-Floody, M., Bendall, J.S., Jara, A.A., Welland, M.E., Theng, B.K.G., Rumpel, C., Mora, M.L. 2011. Nanoclays from an Andisol: Extraction, properties and carbon stabilization. *Geoderma*, 161: 159-167.
- Gitari, M.W., Mudzielwana, R. 2018. Mineralogical and chemical characteristics of raw and modified clays and their application in arsenic and fluoride removal: Review, current topics in the utilization of clay in industrial and medical applications. *Mansoor Zoveidavianpoor, IntechOpen*. [DOI: 10.5772/intechopen.74474].
- Henmi, T., Wada, K. 1976. Morphology and composition of allophane. *Amer. Mineralogist*, 61: 379-390.
- Igwe, J.C., Onyegbado, C.C. 2007. A review of palm oil mill effluent (Pome) water treatment. *Global J. Environ. Res.*, 1 (2): 54-62.



- Kamyab, H., Chelliapan, S., Md Din, M.F., Rezania, S., Khademi, T., Kumar, A. 2018. Palm oil mill effluent as an environmental pollutant, *Palm Oil*, Viduranga Waisundara, IntechOpen, [DOI: 10.5772/intechopen.75811].
- Kaufold, S.D., Abidin, Z., Henmi, T., Matsue, N., Eichinger, L., Kaufold, A., Jahn, R. 2010. Allophane compared with other sorbent minerals for the removal of fluoride from water with particular focus on a mineable Ecuadorian allophane. *Appl. Clay Sci.*, 50: 25-33.
- Ministry of Environment Regulation. 2014. Republic of Indonesia Number 05 year 2014 Concerning the Quality Standards of Wastewaters. 85 p. (in Indonesian).
- Shukla, E.A., Johan, E., Abidin, Z.A., Henmi, T., Matsue, N. 2013. A comparative study of arsenate and phosphate adsorption on nano-ball allophane. *Clay Sci.*, 17: 83-91.
- Sudadi, U., Anggriawan, R., Anwar, S. 2019. Application of nanoclays from volcanic tuff of Salak Mountain, Indonesia as a natural adsorbent of anionic contaminants: Phosphate in water environment (in Indonesian). *JPSL*, 9 (4): 1032-1040. [DOI:10.29244/jpsl.9.4.1032-1040].
- Tan, K.H. 1998. *Principles of Soil Chemistry*. 3<sup>rd</sup> Ed, Revised and Expanded. Marcel Dekker Inc., New York, USA.
- Van Ranst, E., Utami, S.R., Shamshuddin, J. 2002. Andisols on volcanic ash from Java Island, Indonesia: Physico-chemical properties and classification. *Soil Sci.*, 167 (1): 68-79.
- Wambu, E.W., Ambusso, W., Onindo, C.O., Muthakia, G.K. 2015. Review of fluoride removal from water by adsorption using soil adsorbents – An evaluation of the status. *J. Water Reuse Desalination*, 8 (1). [DOI: 10.2166/wrd.2015.073].
- Wu, T.Y., Mohammad, A.W., Md. Jahim, J., Anuar, N. 2010. Pollution control technologies for the treatment of palm oil mill effluent (POME) through end-of-pipe processes. *J. Environ. Manag.*, 91: 1467-1490.