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Phosphate adsorption characteristics of 'nanoclay' separated from an Indonesian volcanic tuff

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Abstract. *Research on Indonesia's natural nano materials is still limited. For environmental remediation application as an adsorbent, their adsorption characteristics and quality are particularly important to be assessed. From Indonesian volcanic tuff material, 'nanoclay' fraction of < 200 nm particle size was separated. The separated 'nanoclay' exhibits pH-dependent charge characteristics. Therefore, it could be used as an anionic adsorbent since its separation process was adjusted to proceed at pH < 4, resulted in a net positive charged 'nanoclay'. This study aims to compare phosphate adsorption characteristics of the separated 'nanoclay' based on Langmuir, Freundlich, Brunauer-Emmett-Teller (BET), and Dubinin-Radushkevich (D–R) iso-thermal models. The results showed that the application of Langmuir and D–R models produced adsorption capacity (qe parameter) of 461 (two-sites) and 440 mg P.g*$^{-1}$ *(heterogeneous-sites), respectively, while BET and Freundlich models produced adsorption at the first adsorptive layer (*q_{mono} *parameter) of 111,11 mg P.g*$^{-1}$ *(multi-layers) and adsorption constant (1/n parameter) of 0,28, respectively. The latter indicated that the assessed 'nanoclay' was a high-quality adsorbent (1/n value 0,10-0,50). Therefore, it could be utilized as adsorbent for the removal of anionic contaminants in eutrophic water systems. In this study, Langmuir Model revealed the best application performance compared to the other three adsorption models applied.*

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INTRODUCTION

A widely accepted definition for nanomaterials is that their particles have at least one dimension which is < 100 nm (Babick *et al*. 2016). Because of their nanoscale dimensions and large surface area/volume ratio, nanomaterials have properties that are very different from those of their bulk counterparts (Al-Dahhan *et al*. 2022; Barhoum *et al*. 2022). In soil science, the term clay refers to a class of materials, the particle size of which is < 2 mm in equivalent spherical diameter. The clay fraction would therefore include nanoclays, the particles of which are < 100 nm in diameter (Jacob *et al*. 2021).

Volcanic tuff is an extrusive igneous rock formed by the consolidation and lithification of volcanic products which have been ejected by an explosive volcanic eruption (Asniar *et al*. 2014; Pötzl *et al*. 2022). Java Island in Indonesia is dominated by volcanic ash soils. Weathering products of volcanic tuffs consist of allophane, imogolite, ferrihydrite, glass Volcan, opaline silica, labradorite, hypersthene, augite, hornblende, and Al/Fe humus complex, which are particularly important in the formation process of Andisols (Arifin *et al*. 2022; Takahashi 2020). Indonesia is located in the ring of fire areas and has 127 active volcanoes out of ~450 total volcanoes of the ring, resulting in widespread Andisols. The parent materials of Andisols in Java Island range from basic (calc-alkaline basaltic ash) in East Java to more acidic types (basalt-andesitic ash) in Central Java, and (andesitic tuffaceous ash) in West Java (Arifin *et al*. 2022; Ranst *et al*. 2004) and the estimated amounts of allophane (11 - 35%) in the fine earth increased from east to west. This trend holds true for the point of zero net charges (PZNC) and for pHo. Samples rich in allophane showed relatively high PZNC. The relatively high pHo values for the Central and West Java soils indicate the development of net positive variable charges at pH < pHo (Anda *et al*. 2021; Arifin *et al*. 2022; Ranst *et al*. 2002).

From volcanic tuff materials of Mount Salak, West Java, Indonesia, it could be separated ‘nanoclay’ fraction with a particle size of < 200 nm (Sudadi *et al*. 2019a, 2019b). Based on FTIR spectroscopy analysis, this ‘nanoclay’ was identified to contain allophane and imogolite (Sudadi *et al*. 2019a). These alumino-silicate XRD-amorphous minerals have specific characteristics, namely particle size at the nanometer scale, so that their specific surface areas are remarkably high and exhibit Si-OH (silanol), Fe-OH (ferrol), and Al-OH (aluminol) reactive surfaces with pH-dependent charge characteristic (Abidin *et al*. 2007; Yuan and Wada 2012). By adjusting the process of their separation to proceed at pH < 4,0, it could be obtained net positive charged ‘nanoclay’, while those negatively charged would be precipitated and vice versa when the process was conditioned to pH >10,0 (Calabi-Floody *et al*. 2009; Henmi and Wada 1976; Iravani *et al*. 2022). Therefore, the separated ‘nanoclay’ could be used as a natural adsorbent for the removal of anionic or cationic contaminants, depending on the pH of its separation process. Application of positively charged ‘nanoclay’ separated from an Indonesian volcanic tuff was reported effective for the removal of phosphate in a solution system (Sudadi *et al*. 2019a) and nitrate in palm oil mill effluent (Sudadi *et al*. 2019b).

Adsorption reaction is often used in the process of decontamination and the development of its engineering techniques and appropriate adsorbents for the removal of contaminants, particularly phosphate, in eutrophic waters, waste waters, and liquid wastes (Ravina *et al*. 2022; Yuan and Wu 2007). Adsorption capacity and quality of an adsorbent can be determined through isothermal adsorption modeling that have been developed by researchers to study the adsorption characteristics of sorbates at gas and solution phases on various adsorbents. The most frequently applied models to elaborate adsorption of single adsorbate were those of Langmuir, Freundlich, Brunauer-Emmett-Teller (BET), and Dubinin-Radushkevich (D–R) because of their simple and suitable mathematical equations and very well application performances (Ayawei *et al*. 2017; Hu and Zang 2019). Each of the models has its own specific application performances in terms of adsorption parameters obtained. Fitness of the modeling results can be indicated by the significance level of the R^2 values coefficient of determination of the linear equations obtained. Based on the background explained, this study aims to compare phosphate adsorption characteristics and quality of the net positive charged ‘nanoclay’ adsorbent separated from volcanic tuff based on Langmuir, Freundlich, BET, and D–R isothermal models.

METHODS

Separation of ‘nanoclay’

‘Nanoclay’ fraction was separated from a volcanic tuff bulk sample taken from the parent material layer (depth of 60 - 110 cm, *bvt*$_3$) of an Andisol profile at the foot slope (elevation 670 m asl) of Mount Salak, West Java, Indonesia (6º39’28” S; 106º43’52,2” E). Water content and textural class of the air-dried *bvt*$_3$ sample was determined according to gravimetric and Pipette methods, respectively. Then, the *bvt3* sample was sieved through a 250 mesh (< 53 μm) sieve, designated as *vt*$_3$ sample, and its water content was determined again. The chemical properties of *vt*$_3$ sample were analyzed for pH-H_2O, pH-KCl, pH-NaF, organic-C content, and Anion Exchange Capacity (AEC) using routine methods.

The ‘nanoclay’ was separated by applying US Patent No. US2010/0187474 A1 procedure originated to separate nanoclay from layered clay such as bentonite ore (Lo 2010), that was modified in this study with the addition of acid treatment using HCl. Into a glass container-60 L containing 1 kg air-dried basis volcanic tuff vt_3 sample, 30 L aqua dest was poured and gradually added with 12,5 mL 0,60 *N* HCl while stirring for conditioning the solution to reach a stable pH of < 4. Based on the Stokes’ law, the ‘nanoclay’ fraction of <200 nm particle size can be obtained at the top 10 cm part of the solution after sedimentation for at least 38 d (assumed that volcanic tuff particle density, water density, and water viscosity at room temperature were 2,4 $g.cm^{-3}$, 1 $g.cm^{-3}$, and $1{,}10^{-2}$ $g.cm^{-1}.d^{-1}$, respectively).

Then, the solution was stirred for 20 min and kept 38 d for hydration and dissolution reactions on the volcanic tuff to proceed that resulted in the dispersion of the dissolved positively charged ‘nanoclay’ fraction and gradual precipitation of the larger sized or heavier fractions to the base of the container due to gravitation. The sediment-free solution was subsequently decanted from the first into the second container and kept undisturbed for 4 d. Then, the top 10 cm part of the sediment-free solution in the second container was decanted into the third container and kept undisturbed for 7 d again to ascertain there was no precipitate formed anymore in the base of the container, and those dispersed in the solution was the net-positive charged ‘nanoclay’ fraction only. The solution was then concentrated by evaporating up to one-tenth of the initial volume to obtain ‘nanoclay’ suspension to be used later in the phosphate adsorption test.

Phosphate Adsorption Test

Batch experimentations were conducted to perform phosphate adsorption tests using twelve concentration series of inorganic phosphate solution prepared from KH_2PO_4 p.a. of 0, 5, 10, 20, 30, 40, 60, 80, 100, 140, 180, and 220 mg $P.L^{-1}$. In each batch, into polyethylene bottles-50 mL containing 5 mL ‘nanoclay’ suspension it was added 5 mL 0,10 *M* $CaCl_2$, as background electrolyte to obtain ionic strength of 0,03, series of P solution, and aqua dest up to a total volume of 50 mL and equilibrated for 48 h, where at the 0, 6th, 12th, 18th, 24th, 30th, 36th, 42th, and 48th h the suspensions were shaken horizontally for 30 min using a mechanical shaker. Then, the solutions were centrifugated at 2.500 rpm for 15 min and filtered. Aliquots obtained were used to determine P concentration colorimetrically by reacting 5 mL aliquot with 1 mL MR color reagent. The same procedure was applied to the standard solutions that were prepared with a series of 0; 0,10; 0,20; 0,40; 0,60; 0,80; and 1 mg $P.kg^{-1}$. Then, the solutions were homogenized using a stirrer, and the equilibrium P concentrations were determined using UV-Vis Spectrophotometer at 660 nm wavelength.

Data Analysis and Adsorption Modeling

Data obtained from the adsorption tests were subjected to phosphate adsorption modeling to get linear equations according to Langmuir, Freundlich, BET, and D–R isothermal adsorption models (Table 1).

Table 1 Isothermal adsorption models and equations according to Langmuir, Freundlich, Brunauer-Emmett-Teller, and Dubinin–Radushkevich

Model	**Equation**			
	Langmuir	**Freundlich**	**Brunauer-Emmett-Teller**	**Dubinin–Radushkevich**
Basic	$q = \frac{q_e\ K\ C_e}{1 + K\ C_e}$	$q = K_f\, C_e^{\frac{1}{n}}$	$\frac{q}{q_{mono}} = \frac{K}{\left(1 - \frac{C_e}{C_s}\right)\left[1 + \frac{C_e}{C_s}\ (K - 1)\right]} \frac{C_e}{C_s}$	$q = \ q_e \exp(-\beta\varepsilon^2)$
Linear	$\frac{C_e}{q} = \frac{1}{K\, q_e} + \frac{1}{q_e}\ C_e$	$\log\ (q) = \log\ (K_f) + \frac{1}{n}\ \log\ (C_e)$	$\frac{1}{q\left[\left(\frac{C_e}{C_s}\right)\ - 1\right]} = \frac{K - 1}{q_{mono}K}\left(\frac{C_e}{C_s}\right) + \frac{1}{q_{mono}K}$	$\ln q = \ln\ q_e - \beta\varepsilon^2$

Application of the Langmuir model results in adsorption maxima (qe) and adsorption energy (K) parameters (Islam *et al*. 2021), while Freundlich, BET, and D–R model results in empirical constant (1/n) and Freundlich constant (K_f) parameters (Kim and Kim 2020), adsorption capacity at the first adsorptive layer (q_{mono}) parameter (Vyawahare *et al*. 2022), adsorption maxima (qe) and transfer energy (E) parameters (Azouaou *et al*. 2010; Ragadhita and Nandiyanto 2021), respectively.

RESULTS AND DISCUSSION

Separated 'nanoclay'

The use of natural nanoclay materials as flocculant or adsorbent of contaminants such as phosphate in the process of waste waters purification was reported to be more effective, cost-effective, and environmentally friendly than synthetic flocculant (Mukasa Tebandeke *et al*. 2019; Yuan and Wu 2007). From volcanic tuff bulk samples (bvt_3), it could be obtained volcanic tuff samples that passed through 53 μm sieve (vt_3) equals 69,47 g vt_3.kg^{-1} bvt_3 and further separation yielded 'nanoclay' of < 200 nm particle size (nc_3) equals to 1.216 mg nc_3.g^{-1} vt_3 or 84,50 mg nc_3.kg^{-1} bvt_3 (Table 2).

Table 2 Separation yield of nanoclay fraction of < 200 nm particle size from volcanic tuff of Mt. Salak, West Java, Indonesia

Volcanic tuff bulk sample (bvt_3)		**Volcanic tuff sample passed through 53 μm sieve (vt_3)**			**Separated* nanoclay (nc_3)**		
Water content	**Weight (oven-dry basis)**	**Water content**	**Weight (oven-dry basis)**	**Proportion Weight of vt_3 to bvt_3**	**Weight (oven-dry basis)**	**Proportion Weight of nc_3 to vt_3**	**Proportion Weight of nc_3 to bvt_3**
%	**kg**	**%**	**g**	**g vt_3.kg^{-1} bvt_3**	**mg**	**mg nc_3.g^{-1} vt_3**	**mg nc_3.kg^{-1} bvt_3**
36,33	29,22	22,8	2.030	69,47			
	11,72		814,33	69,47	990,60	1.216	84,52

*By applying modified US Patent No. US2010/0187474 A1 procedure

Volcanic Tuff Characteristics

The physico-chemical characteristics of volcanic tuff vt_3 sample is given in Table 3, showing the pH NaF of vt_3 sample was > 10, indicating the volcanic tuff used in this study contained remarkable amount of allophane mineral. This mineral is rich in Al/Fe-OH groups. Fluor ion (F^-) from NaF reagent replaced OH^- from the Al/Fe-OH groups of the mineral through ligand exchange reaction resulted in a pH increase in the solution (Enang *et al*. 2019; Parfitt and Henmi 1980). The higher the content of allophane in the sample, the higher the increase of pH NaF in the solution (Yuliani *et al*. 2017). Meanwhile, its value of pH H_2O was higher than pH KCl resulting in ΔpH > 0, indicating the vt_3 sample possessed net negative variable charge (Tan 1998). However, the separation process of 'nanoclay' nc_3 from vt_3 in this study was by intention conditioned to proceed at pH < 4 to obtain net positive charged 'nanoclay' to be assessed as anionic adsorbent. This separation mechanism was also adopted by Calabi-Floody *et al*. (2011) in separating nanoclay fraction from an Andisol sample and followed as well in the procedure described in the US Patent No. US2010/0187474 A1 (Lo 2010) applied in this study.

As shown in Table 1, it could be separated 1.216 mg nc_3.g^{-1} vt_3. This value would only be meaningful if the adsorption capacity of the separated 'nanoclay' nc_3 is known. Then, since it was separated from volcanic tuff vt_3 sample that was characterized by remarkably high AEC and AECc (Table 2), it is becoming necessary and important to determine the more detailed characteristics of *nc*$_3$ in adsorbing anion, in the case of this study is phosphate, for the purpose to evaluate its quality as a natural adsorbent for the removal of anionic contaminants in eutrophic water systems.

Table 3 Physico-chemical characteristics of volcanic tuff sample of Mt. Salak, West Java, Indonesia passed through 53 µm sieve (*vt*$_3$)

Volcanic tuff bulk sample (*bvt*$_3$)			**Volcanic tuff sample passed through 53 µm sieve (*vt*$_3$)**							
Sand	Silt	Clay	Silt	Clay	pH H_2O (1:5)	pH KCl (1:5)	pH NaF	Org. C	AEC	AEC$_c$
	%		%					%	cmol(-).kg^{-1}	
64	20	16	55	45	5,52	4,75	11,95	0,76	6,95	15,44

‘Nanoclays’ Adsorption Characteristics

Data obtained from the phosphate adsorption tests were subjected to isothermal adsorption modeling according to Langmuir, Freundlich, Brunauer-Emmett-Teller (BET), and Dubinin-Radushkevich (D–R) equations to determine the ‘nanoclay’ *nc*$_3$ adsorption characteristics as well as its quality as an adsorbent. The results are given in Table 4 and Figure 1. Based on the coefficient of determinations of the best-fit equations obtained, it can be considered that the application of Langmuir model that resulted in the highest R^2 values was the most suitable for the purpose.

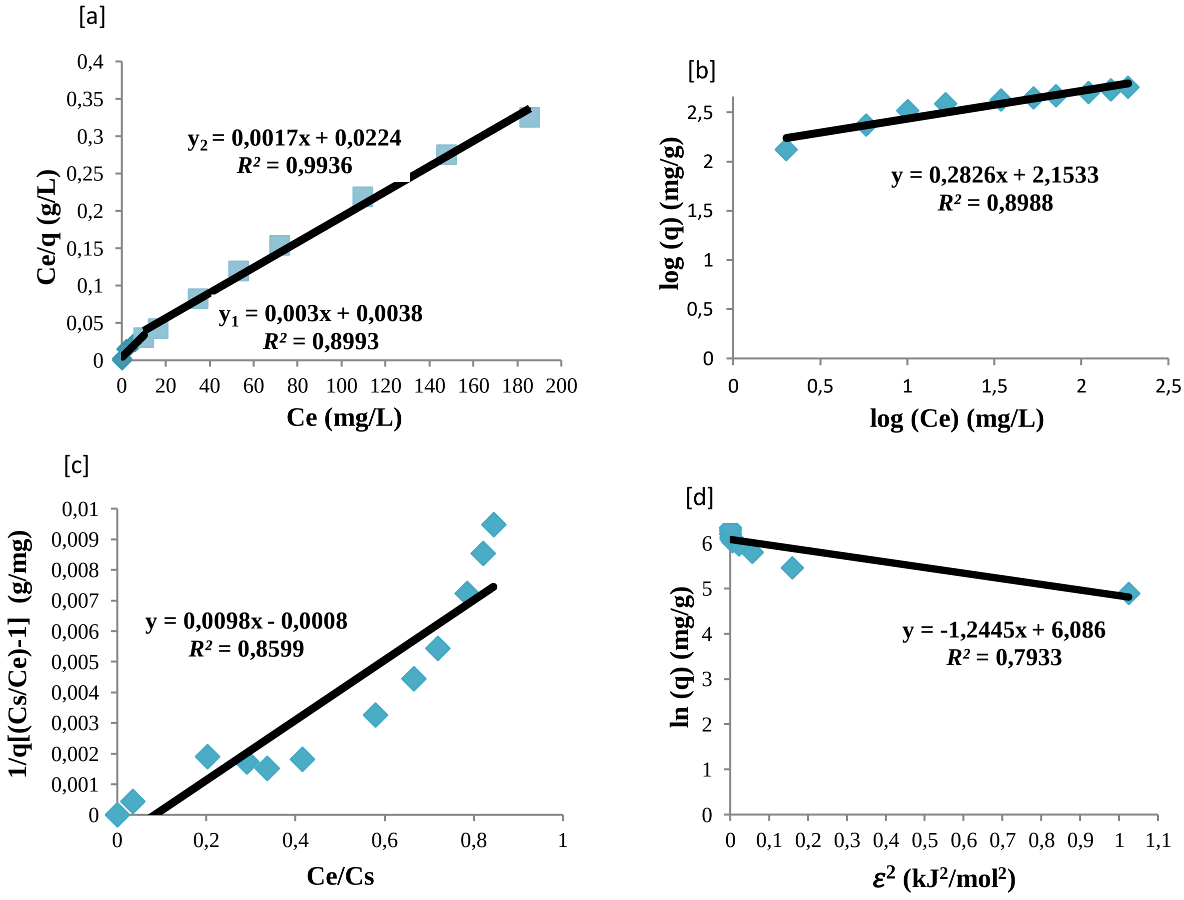

Figure 1 The linear curves and equations describing phosphate adsorption characteristics of the ‘nanoclay’ *nc*$_3$ according to the Langmuir [a], Freundlich [b], BET [c], and D-R [d] model

Table 4 shows differences in parameters of phosphate adsorption characteristics of the ‘nanoclay’ nc_3 amongst the four models applied. Langmuir model resulted in adsorption capacity or adsorption maxima (qe) and bonding energy (K) parameters of 460,78 mg.g^{-1} and 0,43 L.g^{-1}, respectively. This qe value is higher than those reported by Sudadi *et al.* (2019a), who using volcanic tuff material that was taken from the same site, but the ‘nanoclay’ was separated using a different procedure. They obtained qe of 117,54 mg.g^{-1}. This is most probably related to the finer ‘nanoclay’ fraction that could be separated in this study. The finer the particle size of the nanoclay, the higher its specific surface area and the more reactive it is as an adsorbent (Sudadi and Wijaya 2012; Tan 1998).

Table 4 The values of parameters of phosphate adsorption characteristics on the ‘nanoclay’ nc_3 according to the Langmuir, Freundlich, BET, and D-R model

Langmuir			**Freundlich**			**BET**			**D-R**		
R^2	**qe* mg.g^{-1}**	**K L.g^{-1}**	**R^2**	**K_f**	**1/n**	**R^2**	**q_{mono} mg.g^{-1}**	**K**	**R^2**	**qe mg.g^{-1}**	**E kJ.mol^{-1}**
0,95	460,78	0,43	0,90	142,33	0,28	0,86	111,11	–11,25	0,79	439,66	0,63

*Average of the Langmuir adsorption capacity parameter performing two adsorption sites: (qe1 + qe2)/2 (derived from Fig. 1[a])

Different from Langmuir, Freundlich model does not give information concerning adsorption capacity but parameters of Freundlich adsorption constant (K_f) and empirical constant (n). However, K_f relates to the bonding energy that affects, and thus can be used to interpret, the capacity of adsorption, while *n re*presents the intensity of adsorption. Applying Freundlich model, the ‘nanoclay’ nc_3 provided K_f and 1/n values of 142,33 and 0,28, respectively. The high value of K_f obtained attributed to the high adsorption capacity, while 1/n value that ranged from 0,10 to 0,50 indicated the separated ‘nanoclay’ nc_3 was performing an efficient or high-quality anionic adsorbent, particularly for phosphate, as assessed in this study. Furthermore, the range of 1/n value obtained in this study confirmed that the adsorption occurred on the heterogeneous surface of the adsorbent and no cooperative adsorption during the process or indicated normal adsorption. Meanwhile, the n value obtained that was greater than 1 informed the support of physical process in the adsorption (Kim and Kim 2020; Nandiyanto *et al.* 2020).

Whilst Langmuir and D-R model resulted in adsorption maxima (qe) of respectively 460,78 and 439,66 mg.g^{-1}, BET model provided adsorption capacity on the first adsorptive layer only (q_{mono}) of 111,11 mg.g^{-1}. Therefore, the q_{mono} obtained in this study was certainly lower than qe. However, the q_{mono} parameter provided by BET model is more accurate in describing adsorption characteristics of an adsorbent compared to those of Langmuir, Freundlich, and D–R model because in establishing the best-fit linear equation both the initial and final or equilibrium concentrations of the sorbate are incorporated in BET model (Brunauer *et al.* 1938; Vyawahare *et al.* 2022), while the other equations incorporate only the initial sorbate concentration.

Besides adsorption capacity (qe), the application of D–R model provides also E parameter, the energy required to transfer adsorbate from solution to adsorptive sites of adsorbent. The E parameter indicates the type of adsorption that occurred as well. In this study, the E value obtained was 0,63 kJ.mol^{-1}, which is < 8 kJ.mol^{-1}, also indicated that the phosphate adsorption occurred on the ‘nanoclay’ nc_3 was of physical adsorption type (Hu and Zhang 2019; Nandiyanto *et al.* 2020). This type of adsorption is reversible in nature and involves multilayered weak electrostatic interactions such as dipole-dipole and Van der Waals forces so that it makes it easy for the sorbate to desorb again into the solution (Al-Ghouti and Da’ana 2020). On the contrary, the chemical adsorption type involves covalent bonds with stronger monolayered sorbate-adsorbent interactions. Incorporating values of adsorption parameters obtained in this study, the basic equations for describing phosphate adsorption on the ‘nanoclay’ *nc₃* according to Langmuir, Freundlich, BET, and D–R model are given in Table 5.

Table 5 Basic isothermal equations describing phosphate adsorption on ‘nanoclay’ nc_3 according to Langmuir, Freundlich, BET, and D–R model

Basic adsorption equations according to the model of			
Langmuir	**Freundlich**	**Brunauer-Emmett-Teller**	**Dubinin–Radushkevich**
$q = \frac{199{,}37\ C_e}{1+0{,}43\ C_e}$	$q = 142{,}33\ {C_e}^{0{,}28}$	$q = \frac{-11{,}25}{\left(1-\frac{C_e}{C_s}\right)\left[1+\frac{C_e}{C_s}(-12{,}25)\right]}\frac{C_e}{C_s}\ 111{,}11$	$q = 439{,}66\ \exp(-1{,}2445\varepsilon^2)$

The implications derived from this study were, among others, that the ‘nanoclay’ separated from volcanic tuff of Indonesia could be used as a natural and high-quality adsorbent for the removal of anionic contaminants such as phosphates in eutrophic water systems. This is in accordance with Ayalew (2022) who stated that the development of clay-based composite materials is one of the upcoming directions to use effectively in water and wastewater treatment as adsorbent nano-materials.

Further research, however, are urgent to do to elaborate on the stability of the ‘nanoclay’ in term of its adsorption characteristics for various anionic contaminants in various water systems as well as to improve its separation and purification technique for obtaining a higher yield of a higher quality ‘nanoclay’ in more practical and cost-effective ways. Furthermore, besides its use as an adsorbent for environmental contamination control, the application of the ‘nanoclay’ for removing phosphates in eutrophic waters will form ‘nanoclay-phosphate’ flocs. The flocs formed will be of physical adsorption type as the case revealed in this study. Therefore, the flocs can be harvested later through sedimentation and reused as phosphate fertilizer on agricultural soils with pH > pHo.

CONCLUSION

Applying isothermal adsorption equations according to Langmuir, Freundlich, Brunauer-Emmett-Teller (BET), and Dubinin-Radushkevich (D–R) models, phosphate adsorption characterization of the ‘nanoclay’ separated from an Indonesian volcanic tuff resulted in different and specific adsorption parameters, namely Langmuir adsorption maxima or *qe* of 460,78 mg.g^{-1}, Freundlich adsorption constant or *1/n* of 0,28, BET adsorption on the first adsorptive layer or q_{mono} of 111,11 mg.g^{-1}, and D–R adsorption maxima or *qe* of 439,66 mg.g^{-1} and transfer energy or *E* of 0,63 kJ.mol^{-1}. These characteristics revealed that the nanoclay studied were remarkably potential to be developed as a high-quality natural adsorbent for anionic contaminants in water systems. Each of these adsorption models holds its own application limitations and advantages. The most suitable to characterize phosphate adsorption on the studied ‘nanoclay’ was the Langmuir model that resulted in linear equations with the highest coefficient of determination or R^2 values of > 0,90.

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