Local Si-allophane Rich Soil Adsorbent for Phosphate Removal From Synthetic Wastewater: Equilibrium, Kinetic, Thermodynamic and Co-ions Studies

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Abstract: A natural soil rich in allophane was tested as adsorbent for the removal of phosphate ions from aqueous solution. The soil was characterized using particle size distribution, EDS, FTIR, XRD, TGA, and Nitrogen adsorption-desorption analyses. The effects of contact time, pH, initial concentration, adsorbent dose, and temperature and co-ions on adsorption were performed. The soil is Si-allophane rich as Al:Si is 1.03. It has a BET surface area of 41.7112 m^2/g, total pore volume of 0.101018 cm^3/g and average pore width of 96.8741 Å with over 80% particles having sizes <100µm. Nearly 100% of the phosphate was removed in 5 minutes. There is a strong linear relationship between amount adsorbed and initial concentration due to the ability of the adsorbent to generate more adsorption sites with increase loading. About 1000 mg/g was adsorbed for 0.05 g of adsorbent. This high affinity is illustrated by Langmuir equilibrium constant (b) value of 2000 L/mg, the Jovanovic constant (K_J) of 0.002 and the $\Delta S°$ value of + 0.048 KJ/mol K. chloride and sulphate ions inhibits phosphate removal, but bicarbonate ions enhance phosphate removal. The phosphate removal is also enhanced with the simultaneous presence of cations and anions at low and elevated concentrations. The tested Si-rich allophane soil, which is cheap, locally available and needing no treatment is very effective in removing phosphate ions from wastewater.

Key-Words: - Allophane, Soil, Phosphate, Adsorption, Co-ions, Isotherms

1 Introduction

Though water has been described as the most important commodity for sustaining life, 1 in 9 people lack access to it worldwide [1, 2]. This water crisis has recently been reported as the number 4 global risk in terms of impact to society by the World Economic Forum [3]. The situation is not improving because the <1% of the total water on earth available for drinking, agriculture, industry, sanitation, food, etc. receives about 2 million tons of waste per day [4]. Polluted water is directly or indirectly responsible for 80% of all diseases, according to World Health Organization estimates [2]. The waste is mainly from anthropogenic activities such as agriculture, domestic and industries. One of the major pollutants discharged into water bodies from these wastes is phosphate. Phosphate enters the freshwater systems from both diffuse and point sources with global anthropogenic sources estimated at 1.5 Tg/yr [5]. The domestic sector is the major contributor with 54%, followed by agriculture (38%) and industry (8%) [5]. Particularly for the agricultural sector, cereal production contributes 31% of the phosphate load in freshwater sources followed by fruits, vegetables and oil crops contributing 15% each [5].

Phosphate is an essential element for growth of photosynthetic algae and other biological organisms in permissible limit [6, 7]. However, the phosphate presence beyond permissible limit contributes to the eutrophication process and impairment of water quality causing kidney damage and osteoporosis [6, 8]. The total concentration of phosphorus in uncontaminated waters is reported to be about 0.01 mg/L [8]. The fact that the domestic and agricultural sectors are the principal contributors to phosphate in water bodies is a major concern specifically for developing countries where management of urban and other wastes generated by various anthropogenic activities is a very critical challenge [8].

Because of the toxic effects of phosphate in water at elevated concentrations, many methods have been employed to remove it from contaminated water [7]. Removal by adsorption has been described as the best method because of its easy operation, potential efficiency, and ability to remove low and high levels of phosphate, high selectivity and low energy consumption [7]. Adsorption also depends strongly on the solid adsorbent in terms of its ability to bind the contaminant, availability and cost, regeneration and sludge generation and management. Some examples of adsorbents that have been used to bind phosphate from wastewater include dolomite, iron hydroxide eggshell waste, fly ash, ammonium functionalised mesoporous silica, goethite, aluminium oxide, chemically modified Aleppo pine saw dust, red mud, calcite iron oxide, iron oxide loaded activated carbon, biochar derived from peanut shell, iron hydroxide eggshell waste, boehmite, blast furnace slag, Albentonite, Fe-bentonite, bauxite, Fe–Al-bentonit, pyrrhotite, iron oxide, magnesium amorphous calcium carbonate and eggshell ash [7, 9]. The choice of adsorbent is therefore, strongly dependent initially on cost and management of resulting sludge from the treatment process. This is particularly important for developing countries with limited economic and technological capabilities. Cheap and locally available phosphate adsorbents would greatly enhance the phosphate removal from wastewater in a low cost process. One of such cheap adsorbent is soil rich in allophane. They are common in Japan, New Zealand, USA, Canada, Indonesia, Sweden, South America and Africa [10].

Parfitt (1990a) [11] defined allophane as “the name of a group of clay-size minerals with short-range order which contain silica, alumina and water in chemical combination’’. The Allophane (natural or synthetic) exist in three forms or types. The Al-rich soil allophanes with Al:Si ratio of ~2 , Si-rich soil allophanes with Al:Si ratio of ~1, and stream-deposit allophanes with Al:Si ratios of 0.9-1.8 [12]. The unit particles of allophane are made up of hollow aluminosilicate nanoballs having an outer diameter ranging from 3.5–5.0 nm [13]. Due to fact that they have small particle sizes, allophones have a large specific surface area. They equally have positive and negative charges [11] or simply carry electric charges resulting from the substitution of Al^{3+} and/or Si^{4+} by cations of lower valency, and the gain or loss of protons as the pH of the solution changes [13]. These properties give them the ability to be used as an adsorbent. Many studies have reported the very good adsorbent properties of natural and synthetic allophanes in adsorbing heavy metals (Cu, Cd, Pb, V, Cr, Fe, C, Mn) [14]. However, similar reported studies for phosphate are scanty in literature [13]. None of these studies reported the influence of co-ions in the adsorption process using natural or synthetic allophones. Natural or wastewater sources contain different types of electrolyte ions that can generate cations and anions (covering a wide range of concentrations) which can interfere with the adsorption process [15]. Particularly, our literature search has not revealed any published works on the adsorption characteristics of local Cameroonian natural allophane.

This paper therefore investigated the removal efficiency of phosphate from aqueous solution using local Cameroonian Si-rich allophane soil. The soil was characterized using particle size distribution, EDS, FTIR, XRD, TGA, and Nitrogen adsorption-desorption analyses. The effects of contact time, pH, initial concentration, adsorbent dose, and temperature, anions, and cations and anions mixture on adsorption were performed. The adsorption capacity, adsorbate-adsorbent interactions and the mechanism of adsorption were evaluated using eight isotherm models. Three kinetic models and thermodynamic studies were also used to calculate the kinetic and thermodynamic of the process. Si-allophane rich soil from Cameroon was used as adsorbent for phosphate removal from aqueous solution. This is about the first study in characterizing Cameroon allophane rich soil as adsorbent for phosphate adsorption.

2 Problem Formulation

2.1 Adsorbent Preparation

The soil was collected from the village of Fosimondi in the South West region of Cameroon along the Bamboutous highlands (coordinates N 05^{o} 37' 55,7"

E 009° 59' 28,2"). It was brought to the laboratory, washed several times with distilled water and dried at laboratory temperature of about 40°C for eight days. The dried particles were then ground to fine powder, stored in polyethylene bottles and used for further studies without further treatment.

2.2 Adsorbent Characterization

The particle size distribution of the soil adsorbent was analyzed using a Master Sizer 2000 (Malvern Instruments, UK). The elemental composition was determined by Energy-Dispersive Spectroscopy (EDS, Oxford Instruments plc., UK) while surface functional groups were determined using Fourier-transform infrared spectroscopy (FTIR) (FTIR, iS50 RAMAN, Thermo Scientific, USA) analysis. The peaks obtained were compared with those of sample soils reported in the literature for identification. The X-ray diffraction **(**XRD**)** technique was employed to determine the phase composition using the Philips/PANalytical X'Pert Pro-MPD Powder Diffractometer with Cu Kα radiation λ = 1.5418 Å (PANalytical, Almelo, The Netherlands). The differential scanning calorimetry-thermogravimetric (DSC-TGA) (SDT Q600 V20.9 Build 20, TGA-DTA, TA Instruments, USA) technique was used in the determination of different phase transformations involved with heating. Porosity and surface area characteristics were determined by gas adsorption using nitrogen adsorption-desorption at the liquid nitrogen temperature (- 195, 800°C) (Micromeritics tristar 3000 apparatus, USA).

2.3 Preparation of Synthetic Wastewater

A 1000 mg/L stock solution of HPO_4^{2-} was prepared by dissolving 1.479 g of Na_2HPO_4 (from Prolabo) in 1L of distilled water. Working solutions then were obtained by dilution of the stock solution.

Separate aqueous solutions of Cl^-, $SO_4^{2-}$and HCO_3^- with concentration of 0.01M, 0.171M and 1M for each species were prepared by dissolving the corresponding mass of their salts (NaCl, Na_2SO_4, and $NaHCO_3$) in demineralized water. Used salts were all of the analytical grades. These solutions and five commercial natural mineral water samples containing both cations and anions in varying concentrations were used to study the influence of co-ions.

2.4 Adsorption Experiments

All adsorption experiments were carried out on a batch scale using 250-mL stoppered Erlenmeyer flasks with 100 mL of working solution. For each test, a known mass of adsorbent was weighed into a 250 mL stoppered Erlenmeyer flask, and a phosphate solution of known concentration was added. Once other conditions (pH, temperature, etc.) of the process were adjusted, the flask, with its content, was then shaken at 150 rpm (on a Thermo Scientific Cimarec stirring hot plate, model: SP 131320-33) and phosphate solution samples withdrawn at regular time intervals and filtered on a Whatman filter paper N^0 1. The residual phosphate concentration was determined using molybdenum blue method [7, 16] on a UV/visible spectrophotometer (spectro 23RS, labo med.inc) at 854 nm. The quantity of phosphate adsorbed was calculated (q_e) and the percentage adsorbed (Re) were calculated using:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

$$R_e = \frac{(Co - Ce)}{Co} x\ 100$$

Where, C_0 and C_e (mg/L) are the initial and equilibrium concentrations; V (L) is the volume of solution, m (g) is the mass of allophane soil used; q_e (mg/g) is adsorption capacity and R_e (%) is percentage adsorbed.

The influence of contact time was studied by varying the time from 0 to 60 minutes. The working solution contained an initial phosphate concentration of 500 mg/L, 0.1g of adsorbent, pH of 6.8 and a temperature of 25°C.

Evaluation of the influence of initial concentration was studied by varying the phosphate initial concentration from 10 to 500 mg/L at a fixed adsorbent dose of 0.1g, pH of 6.8, temperature of 25°C and contact time of 10 minutes.

The influence of temperature was studied from 25-60 °C at fix initial phosphate concentration of 500 mg/L, 0.1 g adsorbent, pH of 6.8, and contact time of 10 minutes.

The influence of pH was evaluated by varying the pH from 2 to 10 at fix initial phosphate concentration of 500 mg/L, 0.1g of adsorbent, pH of 6.8, temperature of 25°C and contact time of 10 minutes. Similarly, the influence of adsorbent dose was evaluated by varying the mass of the soil adsorbent from 0.05 to 0.3g at fix initial phosphate concentration of 500 mg/L, pH of 6.8, temperature of 25°C and contact time of 10 minutes.

All pH adjustments were done using 0.1M solution of 0.1M NaOH and 0.1M HCl. pH measurements were measured using a Mettler Toledo Education line pH meter

The influence of co-ions was first done using Cl^-, $SO4^{2-}$ and HCO_3^- anions only with concentrations of 0M, 0.01M. 0.171M and 1M for each anion at fix initial phosphate concentration of 500 mg/L, 0.1 g adsorbent, pH of 6.8, and contact time of 10 minutes. Secondly, the study was done using five commercial natural mineral water samples containing both cations and anions in varying concentrations as summarized in Table 2. For each water sample, a fix initial phosphate concentration of 500 mg/L, 0.1 g adsorbent, pH of 6.8, and contact time of 10 minutes was used.

Table 1. Chemical properties of natural mineral water

Composition (mg/L)	**Mineral water samples** I	II	III	IV	V
Ca	45	14	10	32	30
mg	16.1	5.8	2	21	5.9
K	0.58	2	0	10	3.8
Na	1.02	4	4	1	0
HCO_3^-	268.4	2	13	217	134
Cl^-	0	0.03	15	1	1.3
NO_3^-	0	0.6	4	0	0
SO_4^{2-}	0	5	7	2	0
pH	7.2	7.4	6.9		7.1

The chi square statistics and standard deviation were employed to verify the correlation of obtained results from tested paramters. Chi square is a method used in statistics that calculates the difference between observed and expected data values. It is used to determine whether there is a statistically significant difference between the expected and observed data. A very small chi square test statistic means that observed data fits expected data extremely well. In other words, there is a relationship. A very large chi square test statistic means that the data does not fit very well. In other words, there isn't a relationship. The chi-square formula is given as:

$$\chi_c^2 = \sum \frac{(O_i - E_i)^2}{E_i}$$

O is observed value and E is expected value

The standard deviation is a statistic that measures the dispersion of a dataset relative to its mean and is calculated as the square root of the variance. If the data points are further from the mean, there is a higher deviation within the data set.

3 Problem Solution

3.1 Adsorbent Characteristics

The particle size distribution curve of the natural Cameroon allophane rich soil is presented in Fig. 2. This curve shows that over 80% of the particles are below 91 µm. Approximately, 8 % of these particles are < 2 µm, 38% < 20 µm and 72% from 2 μm to 91 μm. These findings are in agreement with those of Buurman et al. (1997) [17], who studied the Laser diffraction grain-size characteristics of the aggregate size of allophane in andisols of Costa Rica and concluded that the size of the allophane aggregates is between 2 and 20 µm, and it increases with the increasing allophane content. The fact that this soil is dominated by smaller particle sizes enables it to have a large surface area for adsorption.

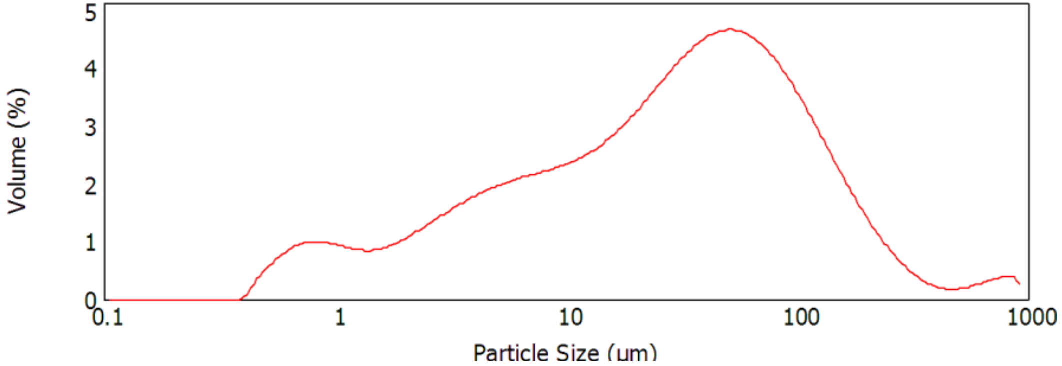

Fig. 1. Particle size distribution curve of allophane soil adsorbent

The EDX chemical composition of the allophone rich soil is shown in Fig. 2. The main elements are; C (13.8%), O (49.195%), Al (17.25%) Si (16.7425%), Fe (2.9225%) and Ti (0.35%). This gives the Al/Si ratio of 1.03 which is that of Si-rich allophone soils with Al: Si ratio of ~1 [12]. The results also confirm the fact that allophane soil is principally made up of silica and alumina [11].

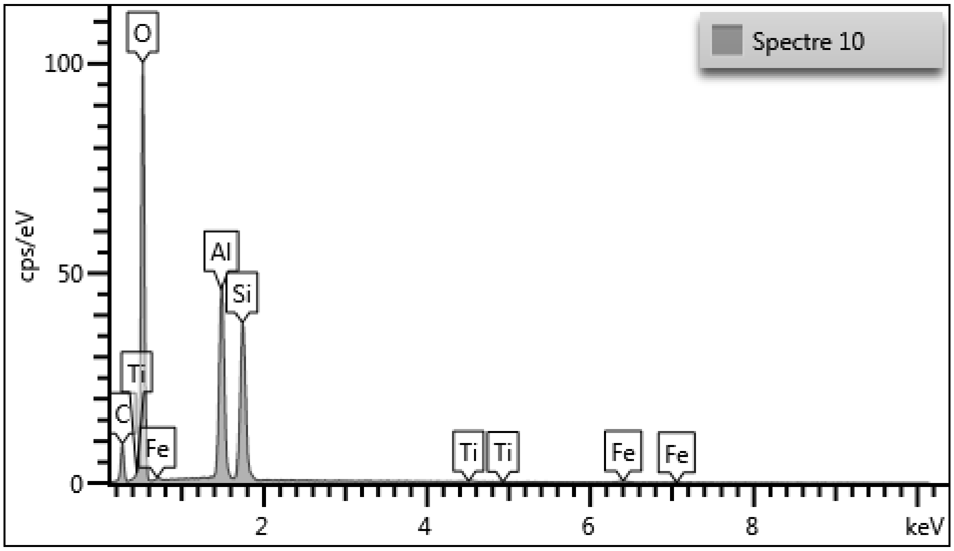

Fig. 2. Elemental composition of allophane soil adsorbent

The different functional groups present in the allophane soil were determined using FTIR analysis and the results are shown if Fig. 3. The two sharp peaks located at 3622.86 and 3695.07 cm^{-1} represent adsorbed water [10]. The bands at 100.05, 1028.99 and 1119.11 cm^{-1} are Si-O stretch of SiO4 groups [10, 12]. The intense band at 1028.99 cm^{-1} is peculiar for Si-rich allophone soil [12]. The groups occurring at 907.71, 793.52 and 748.39 cm^{-1} belong to Si–O–(Si) and Si–O–(Al), Al–O stretch of AlO_4 and T–O–T (TO_4; T=Si,Al) respectively [10]. The allophane crystal framework represented by the groups Al-O and Al-OH bonds appear at 522.87 and 460.28 cm^{-1} while the peak at 413.72 corresponds to O–Si–O (SiO_4) and Al–O–Al (AlO_6) groups [10, 12]. The dominance of the Al and Si surface groups as well as the intense water peaks confirms the EDX analysis and dominance of Al, Si and water in allophane rich soils.

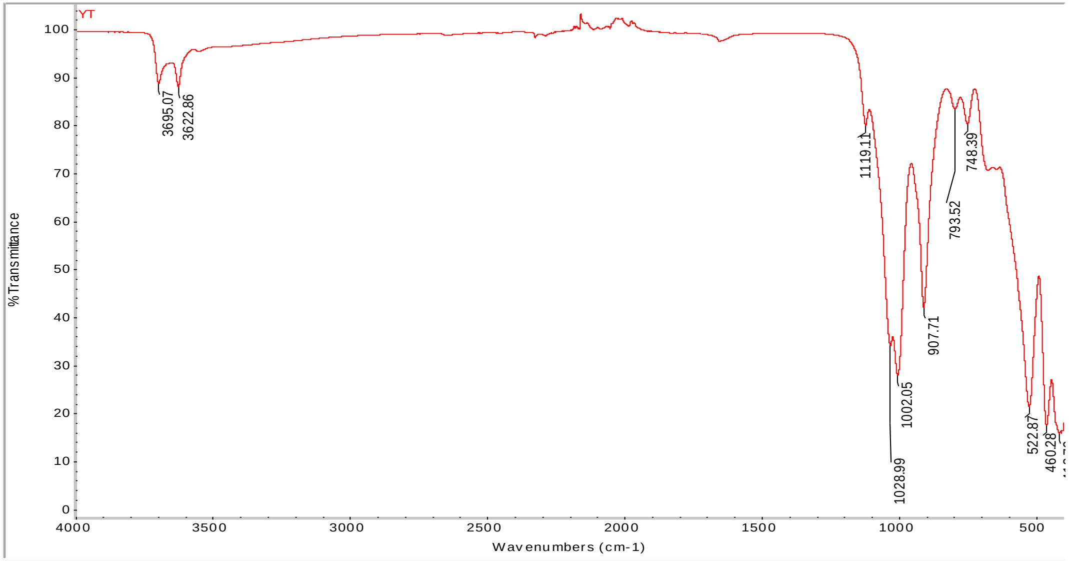

Fig. 3. FTIR spectrum of allophane soil adsorbent

The mineral phases present in the soil were determined by XRD and the results given in Fig.4. Three major peaks are observed from this diffractogram occurring at 2Ө = 12.012°, 20.82° and 24.78°.The peaks at 2Ө = 12.012° and 24.78° indicate the presence of the aluminosilicate plates, corresponding to the basal spacing of kaolinite $Si_2Al_2O_5(OH)_4$ while the peak at 2Ө = 20.82^0 corresponds to α-quartz SiO_2 [18]. Si-rich allophanes are also called defect kaolin allophane or halloysite-like allophane [12], thus, the aluminosilicate plates are allophane rich.

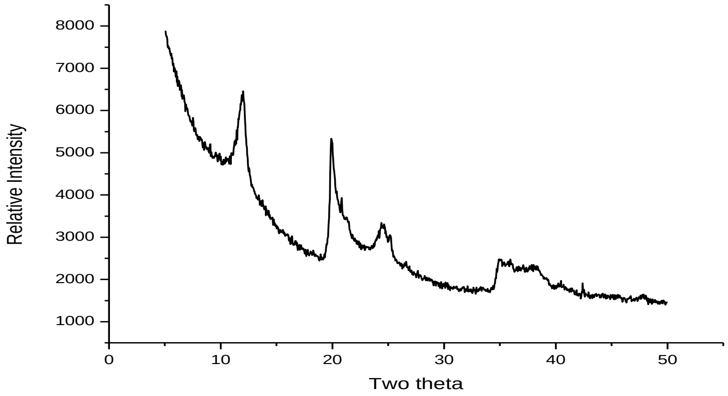

Fig. 4. XRD pattern of allophane soil adsorbent

The TGA curve (Fig. 5) shows three weight loss portions. The first weight loss occurs from 0 to 200°C (3%). The second weight loss occurs from 200-350°C (1%) while the third loss occurs from 300-850°C (12%). The first weight loss corresponds to the loss of physisorbed water while the second and third losses correspond to the dehydroxylation of coordinated and structural water respectively. Physisorbed water is loosely bound and very mobile so easily removed while the coordinated and structured water are strongly bound and linked and require higher temperatures for their removal [19]. While SiO_2 and $Si_2Al_2O_5(OH)_4$ are involved in first weight loss, losses from steps 2 and 3 are principally due to $Si_2Al_2O_5(OH)_4$ with much coordinated and structured water. The DSC shows three endothermic peaks occurring at 237°C, 433°C and 496°C, corresponding to loss of physisorbed water, and the dehydroxylation of coordinated and structural water respectively.

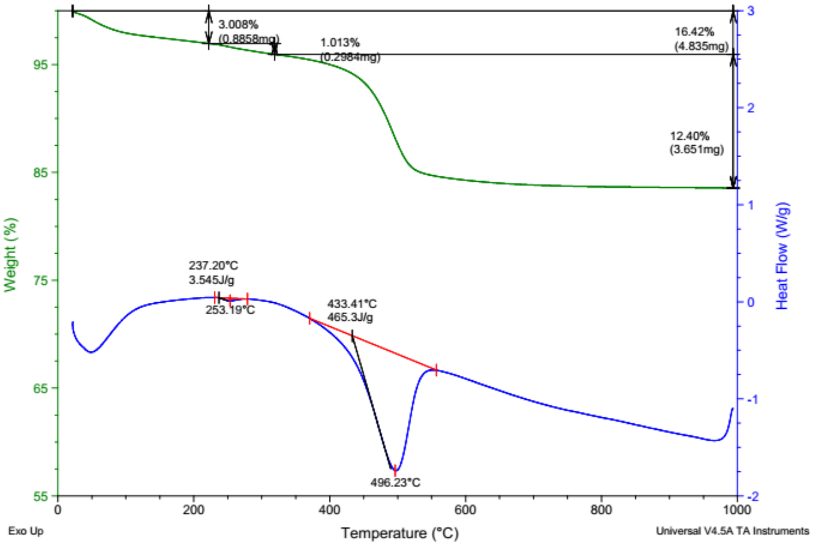

Fig. 5. TGA-DSC curves of allophane soil adsorbent

The N_2 adsorption-disruption of the soil depicted a type IV isotherm model on the basis of IUPAC recommendations [20] as depicted in Fig. 6. Mesopores dominate this isotherm model, though the micro and macro pores are also present. There is a significant number of micropores present as evident from a BET surface area of 41.7112 m²/g. BET theory is applied to obtain the specific surface area of microporous materials [20]. The material also has significant general porosity with a cumulative pore surface area of 32.851 m²/g, total pore volume of 0.101018 cm³/g and pore width of 96.8741 Å (Table 2).

Table 2. Textural properties of allophane soil adsorbent

Surface Area	
BET Surface Area (m²/g)	41.7112
Adsorption cumulative surface area of pores (m²/g)	32.851
Desorption cumulative surface area of pores (m²/g)	39.8643
Pore Volume	
Single point adsorption total pore volume of pores (cm³/g)	0.101018
Adsorption cumulative volume of pores (cm³/g)	0.132274
Desorption cumulative volume of pores (cm³/g)	0.135386
Pore Size	
Adsorption average pore width (Å)	96.8741
Adsorption average pore diameter (Å)	161.059
Desorption average pore diameter (Å)	135.847

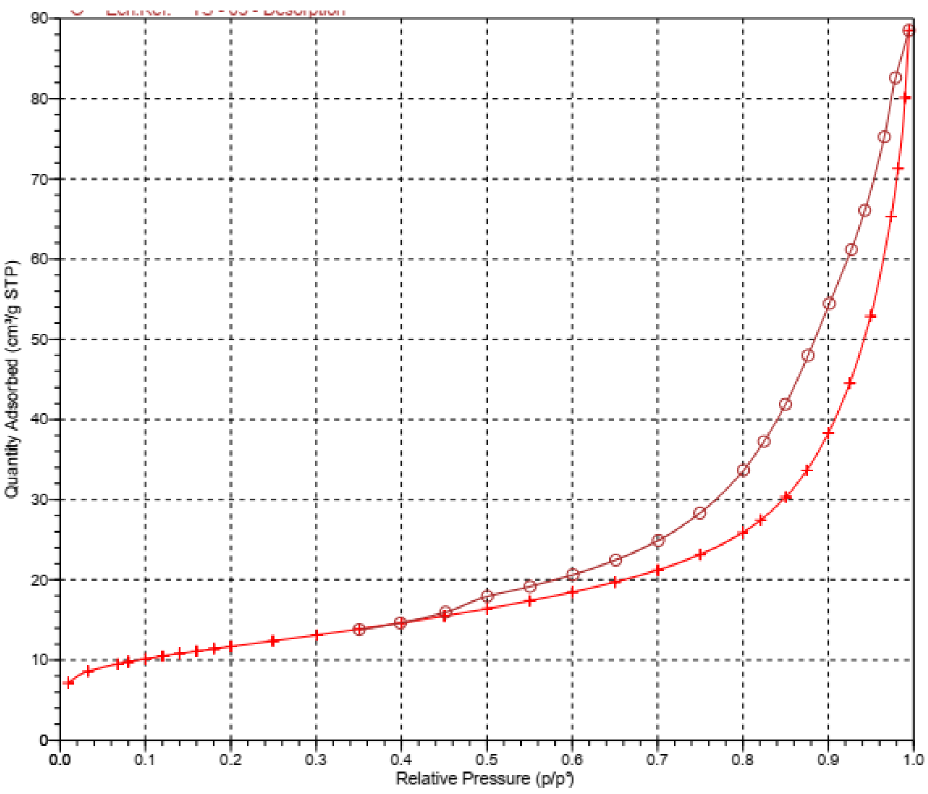

Fig. 6. Nitrogen adsorption-desorption isotherm of allophane soil adsorbent

3.2 Influence of contact time and adsorption kinetics

The results of the influence of contact time for phosphate adsorption on allophane soil (Fig. 7a) shows very rapid process within the first 5 minutes with over 99% removal (residual phosphate concentration of 1.12 mg/L). The nearly 100% adsorption obtained in 5 minutes, is due to smaller particle sizes with larger surface area of 41 m^2/g and enhanced porosity of the adsorbent as shown from textural results. Yuana and Wu (2007) [13] also obtained similar results using allophane nanoclay for the removal of phosphorus. This high adsorption is also due the high aluminium content of the soil adsorbent. Other studies have shown that the high phosphate adsorption on allophane soil has been directly attributed to its aluminium content [12, 21] because there is an alteration in the activity of aluminium in the soil with changes in pH compared to other constituents [22]. This alteration creates more sites for adsorption. Liu et al. (2006) [23] in their study concluded that allophanic soil has a greater P-retention capacity than pumic soil; hence, it is difficult for tree roots to mobilize P from an allophanic soil than from a pumice soil. The high adsorption by allophane soil was also reported by Taylor and Wilson (1979) [24] who obtained 85% of yeast removal using allophane in 30 minutes and 95% in 2 hours for their study on Yeast RNA adsorption by Allophane.

Kinetics analysis is used in assessing the rate of adsorption and the rate-limiting step of the transport mechanism, primarily used in the modelling, and design of the process [25]. Kinetic parameters were evaluated by modeling the data obtained from this study with Pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models whose model equations and linearized models are given in [26] .The calculated parameters are presented in Table 3. It is observed that only the pseudo-second-order model (Fig. 7b) describes phosphate adsorption on allophane soil with a correlation coefficient of 1 and strong correlation between calculated and experimental equilibrium amounts adsorbed. This implies that phosphate adsorption on allophane soil involves two-steps; migration of phosphate to soil surface followed by attachment [4]. The sorption of phosphate using both unrinsed and rinsed tamarind nut shell activated carbon (TNSAC) was also reported to be fitted with pseudo-second-order kinetic model only [27].

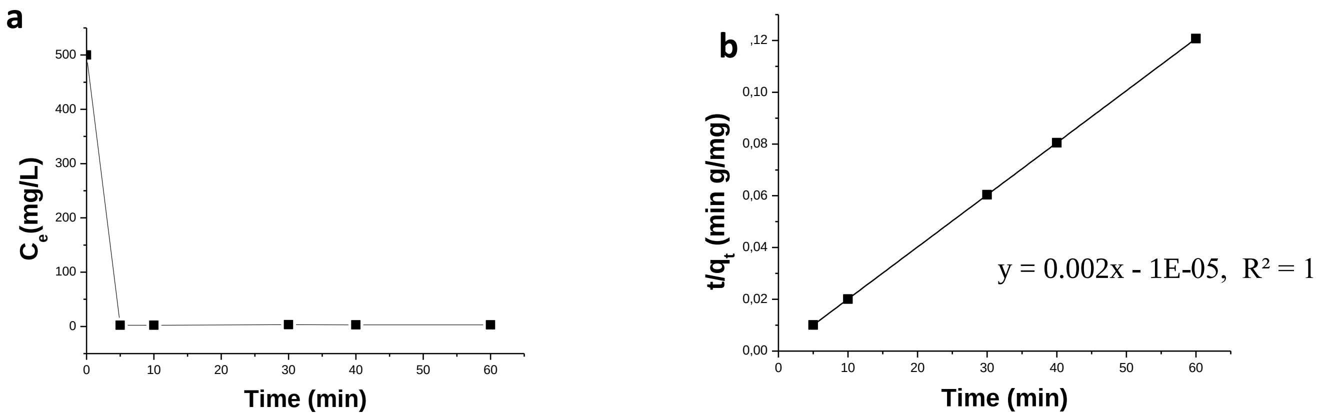

Fig. 7. **a** Influence of contact time **b** Linearized Pseudo-second order kinetic model towards PO_4^{3-} adsorption on allophane soil adsorbent

Table 3. Kinetic parameters for phosphate removal on Allophane soil adsorbent

Models	**Parameters**			
Pseudo-first-order	k_1(min)	qe, c (mg/g)	*q*e, ex (mg/g)	R^2
	-0.0081	0.899	497.66	0.1291
Pseudo-second-order	k_2(g/mg/min)	qe, c (mg/g)	*q*e, ex (mg/g)	R^2
	0.400	500	497.66	1.000
Weber–Morris	k_{id} (mg/g/min$^{1/2}$)	C (mg/g)	*q*e, ex (mg/g)	R^2
	0.136	497.96	497.66	0.5409

qe, c and *q*e, ex are respectively, calculated and experimental equilibrium amounts adsorbed

3.3 Influence of initial concentration and adsorption isotherms

The results of the effect of initial concentration obtained are shown in Fig. 8a. A very strong linear relation exists between the initial concentration and the amount adsorbed. A 100% adsorption is obtained at 10 mg/L initial concentration to 99.53% at 500 mg/L. This isotherm is the C isotherm model as described by Giles and Nakha (1962) [28]. According to them, the "conditions favouring the C curve appear to be i) a porous substrate with flexible molecules and regions of differing degrees of crystallinity ii) a solute with higher affinity for the substrate than the solvent has, and (c) a solute with better penetrating power, by virtue of condition (ii) and of molecular geometry, into the crystalline regions of the substrate." The authors equally reported that linearity indicates more adsorption sites are been created as more solute is being adsorbed. This is only possible when the solute has a higher affinity for the adsorbent molecules than the solvent has. The observed linear isotherm model indicates therefore, that the solute is penetrating regions inaccessible to the solvent, thus, the high phosphate adsorption.

The sorption equilibrium data obtained from the study was tested with Langmuir, Jovanovic, Freundlich, Dubinin–Radushkevich (D–R), Kiselev, Hill–de Boer, Harkin-Jura and Halsey isotherm models to evaluate the adsorption capacity; adsorbate-adsorbent interactions and the mechanism of adsorption. Their model equations and their linearized models are given in [20, 29], and the calculated parameters are summarized in Table 4.

The Langmuir model assumes adsorption onto monolayer surface with no interaction between adsorbed molecules [30]. The separation factor, R_L, which is considered as a more reliable indicator of the adsorption is defined by:

$$R_L = \frac{1}{1+bC_0}$$

Where, b (L/mg) is the Langmuir constant and C_0 (mg/L) the initial concentration of solute. For favorable adsorption, $0 < R_L < 1$; while $R_L > 1$, $R_L = 1$ and $R_L = 0$, respectively, describe unfavorable, linear and irreversible adsorption. As it can be seen from Table 4, the Langmuir model gave a good fit for phsosphate adsorption on local Cameroon allophane rich soil R^2 of 1, very high Langmuir equilibrium (b) value of 2000 L/mg and very low separation factor (R_L) of 9.99E-07. The high b and low R_L values confirm the very high affinity of the phosphate ions for the tested adsorbent, and thus, the ability of the adsorbent to easily adsorb the phosphate ion. This affinity is further confirmed by the high monolayer capacity value of 500 mg/g phosphate adsorbed by the adsorbent material. The good fit of the Langmuir isotherm model indicates that phosphate adsorption on the allophane soil occurred at monolayer coverage and involving homogenous sites. These homogenous sites can be confirmed by the particle size distribution curve of the soil adsorbent which showed the dominance of smaller particle sizes < 100 μm. Also, the FTIR analysis revealed the dominance of T-O groups on the surface (T = Si, Al). Theng et al. (1982) [21] also obtained similar results with allophane from the rhyolitic tephra, adsorbing 120 μmole/g phosphate at a solution concentration of 1 x 10^{-6} M.

Jovanovic model is also based on the same assumptions as those for the Langmuir model, but additionally predicts the possibility of some mechanical contacts between the adsorbate and adsorbent [20]. This mode also gave a correlation coefficient of 1 and with monolayer capacity of 500 mg/L as well (Table 4). The low value of Jovanovic constant (K_J) (0.002) shows that very little time of contact is necessary prior to adsorption with the addition of the adsorbent to phosphate solution, hence the high efficiency of the soil adsorbent for phosphate removal from aqueous solution.

Contrary to Langmuir and Jovanvic models, the Freundlich model describes multilayer removal adsorption on a on heterogeneous surface [30]. The adsorption intensity, *n*, is less than one by definition [31], hence the conformity of n value obtained in this study. The R^2 value of 0.9875 obtained by this model (Table 4) suggest adsorption on the soil adsorbent involved some hetergenous sites, though the homogenous sites dominate as revealed by Langmuir and Jovanvic isotherm models strong R^2 values. This result is justified by the different types of pores and surface groups of soil adsorbent, obtained from textural and FTIR analysis.

Dubinin-Radushkevich (D-R) model is generally applied to express adsorption mechanism with Gaussian energy distribution onto heterogeneous surfaces [31]. Its significance is to determine apparent adsorption energy, *E* (kJ/mol) which is given by:

$$E= 1/\sqrt{2\,K}$$

K is a constant related to the adsorption energy ($mol^2\ kJ^{-2}$)

If the value of E is between 8 and 16 kJ/mol, ion exchange is the main mechanism of the sorption process. If the value is lower than 8 kJ/mol, physical sorption is the main sorption mechanism and if the value is greater than 16 kJ/mol, it may be chemisorption [32]. Like Freundlich, D-R represented a less fit with $R^2 < 99\%$ (Table 4). The fact that $R^2 > 0.90\%$, suggest some heterogeneous sites are involved in the process. Adsorption energy value of 20.412 kJ/mol indicates phosphate adsorption on natural Cameroon allophane soil occurs by chemisorption. This explains the fact that tree roots are less able to mobilize soil P from an allophanic soils because the allophanic soil has a greater P-retention capacity, and a smaller concentration of plant available P [23]. Despite the chemisorption mechanism, the tested allophanic soil can create more adsorption sites as more of the solute is being adsorbed, due to its C isotherm model character.

The Kiselev adsorption isotherm equation also known as a localized monomolecular layer model [20]. k_1 represents Kiselev equilibrium constant (L/mg) while k_n represent constant of complex formation between adsorbed molecule. This model doesn't describe phosphate adsorption on allophane soil because of the very low R^2 value of 0.8611 (Table 4).

Hill–de Boer isotherm model assumes that there is mobile adsorption and lateral interaction among adsorbed molecules [20]. "A positive K_2 (energetic constant of the interaction between adsorbed molecules, $kJmol^{-1}$) means attraction between adsorbed species and a negative value means repulsion, that is the apparent affinity is increased with loading when there is attraction between adsorbed species, and it is decreased with loading when there is repulsion among the adsorbed species. When there is no interaction between adsorbed molecules (that is $K_2 = 0$)." The fact that a positive K_2 value of 0.002 $kJmol^{-1}$ (Table 4) was obtained means there is interaction between adsorbed species, indicating the apparent affinity of phosphate for allophane adsorbent increases with loading. This equally confirms the C isotherm model of the adsorbent. The high Hill–de Boer constant (K_1) value of 193.795 L/mg (Table 4) also confirms the high affinity of the phosphate ion for the allophane soil.

Harkin-Jura isotherm model assumes multilayer adsorption on an absorbents surface having heterogeneous pore distribution [20]. With an R^2 value of 0.9875 for this model (Table 4), it shows that the allophane soil adsorbent contains different pore types, confirming the results from textural analysis which showed this material to contain micro, meso and macro pores. The high coefficient of correlation for this model also suggests that multilayer phosphate adsorption occurs on the allophane soil adsorbent and a probable contributor to high phosphate adsorption on this material.

Halsey isotherm model equally assumes multilayer adsorption, but on a heterogeneous surface [20]. With an R^2 value of 0.9875 9 (Table 4), this model confirms multilayer adsorption of phosphate ion on allophane soil involving heterogeneous sites. The FTIR results indicated the presence of different groups such as Si-O, Si–O–(Si), Si–O–(Al), Al–O, T–O–T (TO_4; T=Si,Al) Al-O and Al-OH available for adsorption.

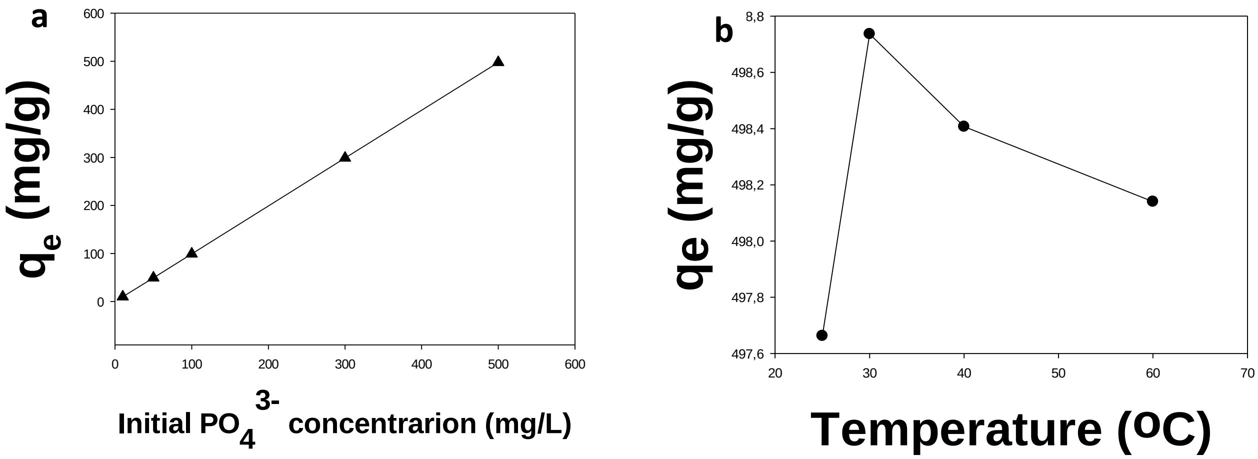

Fig. 8. **a** Influence of initial concentration (initial PO_4^{3-} concentration 10-500 mg/L, adsorbent dose 0.1g, pH 6.8, temperature of 25°C, contact time of 10 minutes) **b** Influence of temperature (initial PO_4^{3-} concentration 500 mg/L, 0.1 g adsorbent, pH 6.8, contact time 10 minutes) towards PO_4^{3-} adsorption on allophane soil adsorbent

Table 4. Isotherm models and parameters for phosphate removal on Allophane soil adsorbent

Isotherm Models/Parameters			
Freundlich/parameters			
K_F	n	R^2	
499.05	-833.333	0.9875	
Langmuir/parameters			
q_m	b	R^2	R_L
500	2000	1.000	9.99E-07
Jovanovic/parameters			
q_m	K_J	R^2	
500	0.002	1.000	
Dubinin Radushkevich/parameters			
X_m	K	R^2	E
498.90	-0.0012	0.945	20.412
Kiselev/parameters			
k_1	k_n	R^2	
3E+06	1.000	0.8611	
Hill–de Boer/parameters			
k_1	K_2	R^2	
193.795	0.005	0.9825	
Harkin-Jura/parameters			
A	B	R^2	
-1.11E+08	4.44E+02	0.9875	
Halsey/parameters			
$\ln K_H$	n_H	R^2	
5177.25	833.333	0.9875	

K_F = (mg/g)(L/mg)$^{1/n}$; $q_m = X_m$ = mg/g; b = k_1 = L/mg; K = mol^2 kJ$^{-2;}$ K_2 = E = kJmol^{-1}

3.4 Influence of temperature

Thermodynamic studies are carried out to determine if adsorption is spontaneous, exothermic or endothermic. Thus, thermodynamic parameters such enthalpy ΔH^0, entropy ΔS^0, and Gibbs free energy ΔG^0 were obtained from the following:

$$\Delta G^0 = -RTK$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

Where R is the ideal gas constant (kJ mol^{-1} K^{-1}) and T is the temperature (K). The enthalpy change (ΔH) and the entropy change (ΔS) are calculated from a plot of lnK versus 1/T.

K was calculated from $K = C_{ads}/C_e$

$$C_{ads} = C_o - C_e$$

Where K is the equilibrium constant, C_e is the residual concentration (mg/L) at temperature T, C_o is the initial concentration (mg/L), C_{ads} is the concentration of adsorbate in the adsorbent at equilibrium (mg/L) at temperature T.

Temperature variation from 25-60°C had no significant effect on phosphate adsorption using allophane rich soil adsorbent as shown in Fig. 8b.

The amount adsorbed at 25ºC was 497.66 mg/g. This amount increased to 498.74, 498.41 and 498.14 mg/g at 30, 40 and 60ºC respectively. The slight increase is also indicated by the calculated ΔG° values (Table 5) whose magnitude increased with increase temperature. Heating probably led to the creation of new active sites, resulting in the increase. Heating probably resulted in the acceleration of some originally slow adsorption steps, enhancing the mobility of adsorbate from the bulk solution towards the adsorbent surface [26]. This may also be a direct consequence of (a) opening up of structure of adsorbent beads (b) enhancing the mobility and extent of penetration within the adsorbent beads and (c) overcoming the activation energy barrier and enhancing the rate of intra-particle diffusion [26].The negative ΔG° values obtained, however, shows the process of phosphate adsorption on the tested allophane rich soil adsorbent is spontaneous and endothermic ($\Delta H^\circ > 0$) (Table 5) within the range of temperature studied. The positive value of entropy also indicates enhanced adsorption due to increased randomness at the solid-liquid interface.

Table 5. Thermodynamic parameters for phosphate removal on Allophane soil

Temperature (K)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol K)
298	-13,28	+ 0,212	+ 0,048
308	-15,06		
313	-14,95		
333	-15,48		

3.5 Influence of pH

From Fig. 9a, it is observed that pH has no effect on phosphate adsorption using allophane soil. The amounts adsorbed at pH 2, 4, 6, 7, 8 and 10 respectively, were 499.60, 499.50, 499.05, 499.68, 499.10 and 499.11 mg/g. Lopez-Hernandez and Burnham (1974) [22] studied the effect of pH on phosphate adsorption in soils and found out that the correlation between pH and phosphate retention was not significant for a group of mixed soils. They further concluded that phosphate adsorption isotherms obtained at different pH values and plotted using Langmuir and Temkin's representation approximate to linearity only in certain concentrations. Some other studies have reported that pH (2-11) has negligible effect on phosphorus adsorption [4, 33-36]. Allophane soil carries electric charges resulting from the gain or loss of protons as the pH of the solution changes [13]. This result shows that these charges are not significant to affect phosphate adsorption, suggesting smaller particle sizes and textural properties of the soil control this process.

3.6 Influence of adsorbent mass

The results of the influence of the mass of the allophane rich soil are given in Fig. 9b. It can be seen that about 1000 mg/g of phosphate is adsorbed with 0.05 g of allophane rich soil adsorbent. This amount decreased to about 166 mg/g for 0.3 g of adsorbent. At a higher adsorbent dosage, adsorption is very rapid due to increase surface area, thereby lowering the concentration of the adsorbate in solution. But as the concentration of adsorbate decreases in solution the number of adsorption sites on the adsorbent surface remains unsaturated. High adsorbent amount equally creates particle aggregation, resulting in a decrease in the total surface area and an increase in diffusional path length both of which contribute to decrease in amount adsorbed per unit mass [37].

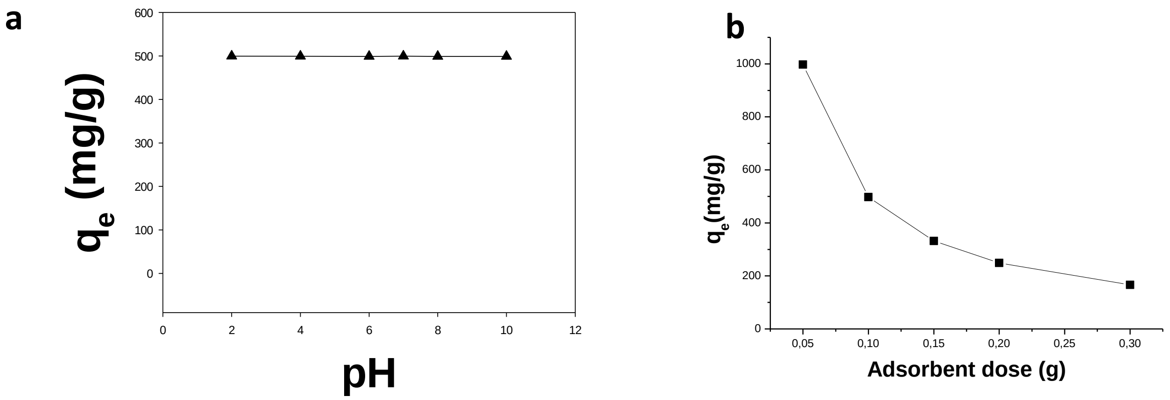

Fig. 9. **a** Influence of pH **b** Influence of adsorbent dose towards PO_4^{3-} adsorption on allophane soil adsorbent

3.7 Influence of co-ions

The effect of 0.01M, 0.171M and 1M of Cl^-, SO_4^{2-} and HCO_3^- on the adsorption of phosphate using allophane rich soil adsorbent is shown in Fig. 10. Equally, the effect of a mixture of cations and anions on the phosphate adsorption process is shown in Fig. 11.

From Fig. 10, the three anions have a small negative effect on phosphate adsorption with 0.01M, 0.171M and 1M of Cl^- and SO_4^{2-}. At 0.01M, 0.171M and 1M concentrations, respectively, the decreased was 0.11%, 0.16% and 0.18% for Cl^- and 0.17%, 0.20% and 0.24% for SO_4^{2-}. This trend shows that high tested anions concentrations present in wastewater will negatively impact phosphate removal process. The fact that the reduction is higher for SO_4^{2-} than for Cl^-, suggest the influence of the size of the molecule concern. This reduction may be due to the competition for adsorption sites by the anions and the phosphate ions. Taylor and Wilson (1979) [24] studied the influence of chloride, nitrate and sulphate presence on the adsorption of yeast RNA using allophane soil. They concluded that the nature of the anion electrolyte made no difference to the adsorption. The difference between these two studies is probably due to the nature of the adsorbate as yeast is an organic molecule.

This behaviour is the same with HCO_3^- with concentrations 0.01M and 0.171M. At HCO_3^-, concentration of 0.171M, almost zero phosphate was removed (spectrophotometer could not read due to intense blue colouration). However, at 1M HCO_3^- concentration, phosphate removal was maximum (100%). These results are similar to that of Chen et al. (2009) [38], who studied the effect of bicarbonate ion concentration on phosphate removal using xonotlite and concluded that high phosphate removal was achieved at high bicarbonate concentrations. Meaning the phosphate removal was slightly inhibited at low bicarbonate concentration. According to them, with increases in the bicarbonate concentration, the pH goes above 7.2 which apparently caused the formation of calcium phosphate precipitate, resulting in the enhancement of phosphate removal. Hence, they concluded that a relatively low bicarbonate ion concentration would not inhibit but somehow might promote the phosphate removal when the pH value is controlled at an appropriate level.

There are, however, conflicting experimental results on the effect of bicarbonate on phosphate removal based on whether there is precipitation of calcium carbonate or not [38-40]. In this study the sodium bicarbonate salt was used.

The influence of both anions and cations on phosphate removal using allophane soil adsorbent was tested using natural commercial mineral water samples containing Ca, Mg, K, Na, HCO_3^-, Cl^-, NO_3^-, SO_4^{2-} with pH ranging from 6.9 to 7.4 (Table 1). As shown in Fig. 11, phosphate removal was improved with the simultaneous presence of these anions and cations. This is probably due to phosphate precipitation by the different cations.

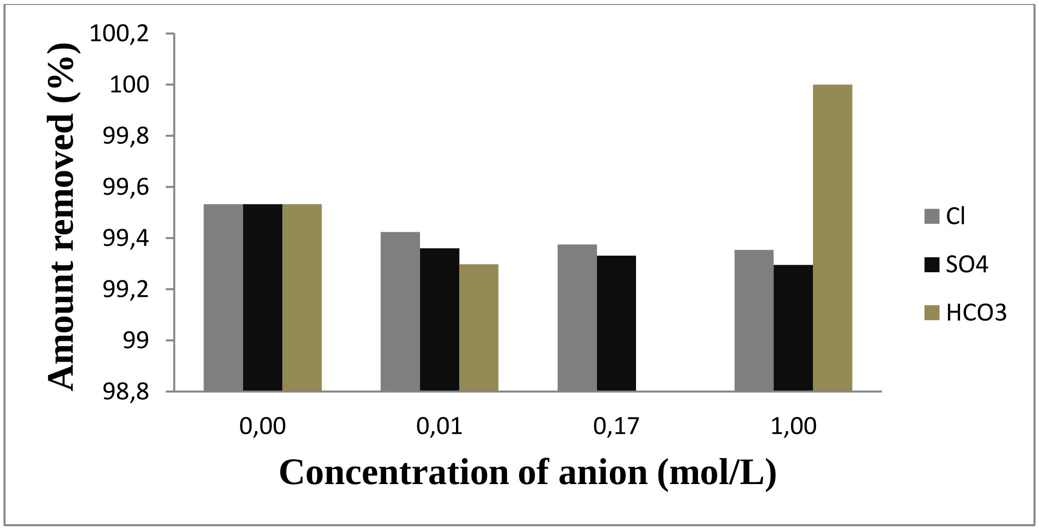

Fig. 10. Influence of Co-ions (anions) towards PO_4^{3-} adsorption on allophane soil adsorbent

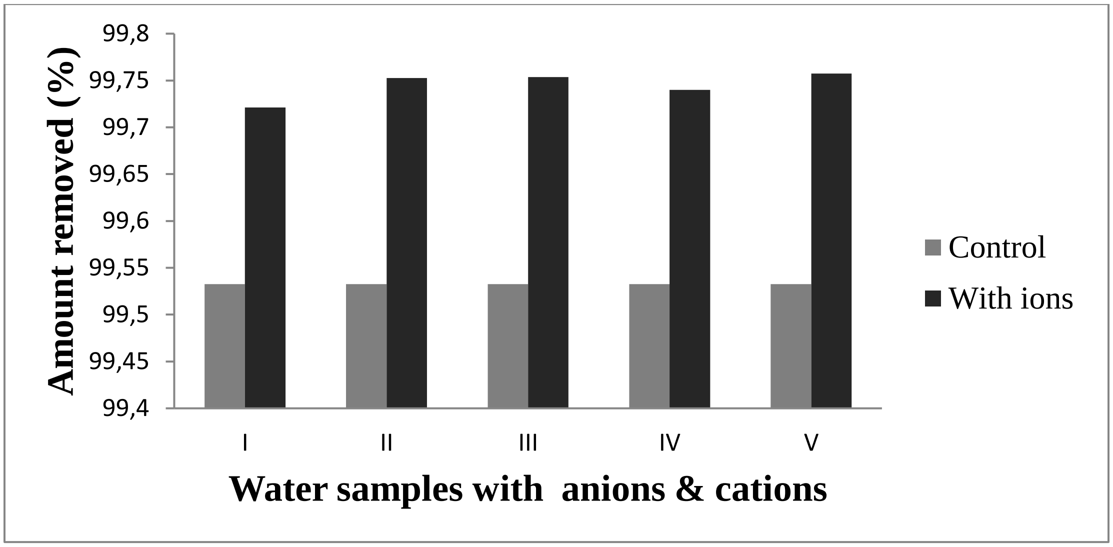

Fig. 11. Influence of Co-ions (anions & cations) towards PO_4^{3-} adsorption on allophane soil adsorbent

3.8 Statistical analysis

Statistical analysis models assist in measuring and calculatin the accuracy or confidence of investigated parameters [41] . Chi-square statistics was tested on all the parameters investigated on phosphate adsorption on allophane soil and the results are presented in Table 6. Very low values were obtained for contact time, temperature and influence of pH, implying a strong relationship between observed and calculated amounts adsorbed. The standard deviation values for these parameters were relatively low equally, indicating the accuracy of the obtained amounts adsorbed for these parameters. However, the influence of concentration and adsorbent dose showed a contrary behaviour. This is to be expected as different concentrations and different masses are involved as opposed to other parameters where they were constant. The presence of Cl^{-1}, SO_4^{2-} and cations and mixtures did not significantly affect phosphate adsorption with very low chi-square values but HCO_3^- had significant influence on this process (with 0% phosphate adsorbed at 0.17 HCO_3^- and 100% at 1M HCO_3^-) with large chi-square value. These statical analysis corrobates the results presented in Figs. 10 & 11.

Table 6. Chi-square analysis of influence of process parameters for phosphate removal on Allophane soil

Parameter	**Chi-square**	**Standard deviation**
Influence of contact time	0.003	0.354
Influence of initial concentration	1274.960	33439.891
Influence of temperature	0.004	0.154
Influence of pH	0.035	0.261
Influence of adsorbent dose	898.402	87350.377
Influence of co-ions (anions)		
Chloride	0.004	0.345
Sulphate	0.006	0.456
Bicarbonate	459.682	215.666
Influence of Co-ions (anions & cations)	0.011	0.066

4 Conclusion

A natural Si- rich allophane soil was used as adsorbent in this study for the removal of phosphate ions from aqueous solution. The results obtained showed that this soil has a high surface area and is very porous. It removed over 99% of phosphate in 5 minutes. The amount removed has a linear relationship with initial concentration. But pH and temperature showed a very negligible influence on the adsorption process. The removal process is however, strongly influenced by the quantity of the allophane soil adsorbent used. About 1000 mg/g of phosphate was removed with 0.05 g of adsorbent against 166 mg/g with 0.3 g. The different isotherm models tested showed that phosphate ions have a strong affinity for the allophane soil adsorbent using attractive mechanism. The presence of chloride and sulphate ions inhibits phosphate removal meanwhile bicarbonate ions enhances phosphate removal especially at higher concentration. The simultaneous presence of cations and anions at low and elevated concentrations promotes phosphate removal. The Si-rich allophanic soil can therefore, be used as an efficient low cost adsorbent in removing phosphate ions from wastewater. However, testing of this soil as adsorbent for other pollutants binding will be further investigated so that it can be applied in a real water treatment system owing to its availiability. Detailed instrumental analysis of mechanism of attachement of pollutant will be studied for the purpose of regeneration.

References:

[1] WHO, UNICEF, Joint Monitoring Programme, Progress on Drinking Water and Sanitation, 2017 *Update and MDG Assessment*, (2017). https://www.who.int/water_sanitation_health/publications/jmp-2017/en/.

[2] C. Tsamo, G.P. Kofa, L. Astaharam, Physico-chemical Characterization and Zero Valent Iron Treatment of Borehole Water of Maroua-Cameroon, *Journal of Environment and Ecology*, **10**, 16-27 (2019).

[3] WEF (World Economic Forum), The Global Risks Report 2019, *14th Edition*, (2019) . Available at http://wef.ch/risks2019

[4] C. Tsamo C, P.N. Djomou Djonga, J.M. Dangwang Dikdim, K. Kamga, Kinetic and Equilibrium Studies of Cr(VI), Cu(II) and Pb(II) Removal from Aqueous Solution Using Red Mud, a Low-Cost Adsorbent, *Arabian Journal for Science and Engineering*, **43,** 2353 (2018).

[5] M.M Mekonnen , A.Y. Hoekstra, Global anthropogenic phosphorus loads to freshwater and associated grey water footprints and water pollution levels: A high resolution global study, Water Resource Research, **54**, 34 (2018).

[6] A. L. Singh, A.K. Tripathi, A. Kumar, V.K. Singh, Nitrate and phosphate contamination in ground water of Varanasi, Uttar Pradesh. India, *Journal of Industrial Research & Technology*, **2,** 26-32 (2012).

[7] P.D. Djantio, C. Tsamo, M.R.S Topet, F.T. Matsinkou, B.B. Loura, Utilisation of waste from the production of millet derived local drink as adsorbent for phosphate removal from aqueous solution, Indian Chemical Enginerr, **61**, 309- 325 (2019).

[8] A.A. Adesuyi, V.C. Nnodu, K.L. Njoku, A. Jolaoso, Nitrate and Phosphate Pollution in Surface Water of Nwaja Creek, Port Harcourt, Niger Delta, Nigeria. *International Journal of Geology, Agriculture and Environmental Sciences*, **3,** 14-20 (2015).

[9] J. Torit, D. Phihusut , Phosphorus removal from wastewater using eggshell ash, Environtal Science and Pollution Research, **26**, 34101–34109 (2019). [10] M. Ristić, S. Krehula, S. Musić, Microstructural Properties of Natural Allophane/Gibbsite from a White Bauxite Deposit in Montenegro, *Croatica Chemica Acta*, ***91***, 65-70 (2018).

11.R.L. Parfitt, Allophane in New Zealand Australian Journal of Soil Research, **28**, 343-360 (1990a).

[12] R.L. Parfitt, Allophane and imogolite: role in soil biogeochemical processes, *Clay Mineral*, **44,**135-155 (2009).

[13] G. Yuana, L. Wu, Allophane nanoclay for the removal of phosphorus in water and wastewater. *Science and Technology of Advanced Materials*, **8**, 60–62 (2007).

[14] Pranoto, Suranto, H. Kristian, Sugiyarto, Ashadi, Javanese Volcanic Allophane Adsorbent as Heavy Metal Adsorberto Improve the Quality of Drinking Water in Surakarta, *Journal of Environment and Earth Science*, **3**, 48-56 (2013).

[15] M.R. Ghosh, S.P. Mishra, Effect of Co-ions on Cr(VI) and F- Adsorption by Thermally Treated

Bauxite (TTB), *Arabian Journal for Science and Engineering* , **42,** 4391-4400 (2017).

[16] T.A.H Nguyen, H.H. Ngo, W.S. Guo, J.L. Zhou, J. Wang, H. Liang, G. Li, Phosphorus Elimination From Aqueous Solution Using 'Zirconium Loaded Okara' as a Biosorbent, *Bioresource Technology*, **170,** 30- 37(2014).

[17] P. Buurman, K. de Boer, Th. Pape, Laser diffraction grain-size characteristics of Andisols in perhumid Costa Rica: the aggregate size of allophane. *Geoderma*, **78,**71-91 (1997)

[18] K. Flogeac, E. Guillon, M. Aplincour, E. Marceau, StievanoL, et al., Characterization of soil particles by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR) and transmission electron microscopy (TEM). Agron, *Sustainaible Development*, **25**, 345-353 (2005).

[19] A.K. Panda, B.G. Mishra, D.K. Mishra, R.K. Singh, Effect of sulphuric acid treatment on the physico-chemical characteristics of kaolin clay, *Colloids and Surfaces A: Physicochem. Eng Aspects* **363**, 98-104 (2010).

[20] C. Tsamo, P. Abba, D. Fotio, *T.A.V.* Vincent, W.F. Sales, One-, Two-, and Three-Parameter Isotherms, Kinetics, and Thermodynamic Evaluation of Co(II) Removal from Aqueous Solution Using Dead Neem Leaves, Int Journal of Chemical Engineering, **Volume 2019**, 1-14 (**2019b)** .

[21] B.K.G. Theng, M. Russell, G.J. Churchman, R.L. Parfitt, surface properties of allophane, halloysite, and imogolite, *Clays & Clay Minerals*, **30,** 143-149 (1982).

[22] D. Lopez-hernandez, C.P. Burnham, The effect of ph onphosphate adsorption in soils, *Journal of Soil Science*, **25**, 207-216 (1974).

[23] Q. Liu, P. Loganathan, M.J. Hedley, M.F. Skinner, Root processes influencing phosphorus availability in volcanic soils under young Pinus radiate plantations, *Canadian Journal of Forest Research*, **36**, 1913-1920 (2006)

[24] D.H. Taylor, A.T. Wilson, The adsorption of Yeast RNA by Allophane, *Clays & clay Minerals*, **27**, 261-268 (1979).

[25] R.P.S. Jeyakumar, V. Chandrasekaran, Adsorption of lead (II) ions by activated carbons prepared from marine green algae: equilibrium and kinetics studies. *International Journal of Industrial Chemistry*, **5**:1-9 (2014)

[26] C. Tsamo, I. Bachirou, I. Samomssa, T.B. Fougoung, Removal of Hexavalent Chromium from Aqueous Solution Using Unmodified Saw Dust: Batch and Column Studies, *Current J ournal of Applied Science and Technology*, **32**, 1-16 (2019a).

[27] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes. *Process Biochemistry*, **34**, 451-456 (1999).

[28] C.H. Giles, S.N. Nakha, A general treatment and classification of the solute adsorption isotherm, *Journal of Applied Chemistry*, **12**, 266 (1962).

[29] C. Tsamo, M. Assabe, J. Argue, S.O. Ihimbru, Discoloration of methylene blue and slaughter house wastewater using maize cob biochar produced using a constructed burning chamber: A comparative study, *Scientific African*, **3,** 1-13 (2019c).

[30] C. Tsamo, A. Palthahe, E.H. Miss Tjilha, G.T. Nyadjou Djabo, Evaluation of the Efficiency of Hydrochloric Acid Modified Red Mud in Removing Diclofenac from Aqueous Solution. *Journal of Pharmaceutical and Applied Chemistry*, **6,** 21-30 (2020).

[31] C. Tsamo, D. J. H. Tchouanyo, D.S. Meali, Treatment of red mud with distilled water to improve its efficiency to remove methylene blue from aqueous solution, *International Research Journal of Pure & Applied Chemistry*, **15**, 1-19 (2017).

[32] C. Tsamo, G.D. Kidwang, D.C. Dahaina, Removal of Rhodamine B from aqueous solution using silica extracted from rice husk, *SN Applied Sciences*, **2**, 256 (2020a).

[33] X. Xu, B. Gao, Q. Yue, Q. Zhong, Sorption of Phosphate Onto Giant Reed Based Adsorbent: FTIR, Raman Spectrum Analysis and Dynamic Sorption/Desorption Properties in Filter bed, *Bioresource Technology*, **102**, 5278-5282 (2011a).

[34] X. Xu, Y. Gao, B. Gao, X.Tan, Y.Q. Zhao, Q. Yue, Y. Wang, Characteristics of Diethylenetriamine–Crosslinked Cotton Stalk/Wheat Stalk and Their Biosorption Capacities for Phosphate. *Journal of Hazardous Matererials*, **192**, 1690–1696 (2011b).

[35] J. Zhang, W. Shan, J. Ge, Z. Shen, Y. Lei, W. Wang, Kinetic and Equilibrium Studies of Liquid-Phase Adsorption of Phosphate on Modified Sugarcane Bagasse, *Journal of Environmental Engineering*, **138**, 252-258 (2012).

[36] N.C. Selçuk, S. Kubilay, A. Savran, A.R. Kul, Kinetics and Thermodynamic Studies of Adsorption of Methylene Blue From Aqueous Solutions Onto Paliurus Spina-Christi Mill. Frutis and Seeds,*IOSR Journal of Applied Chemistry (IOSR-JAC)*, **10**, 53-63 (2017).

[37] S.S. Gupta, K.G. Bhattacharyya, Immobilization of Pb(II), Cd(II) and Ni(II) ions on kaolinite and montmorillonite surfaces from aqueous medium. *Journal of Environmental Management*, **87**, 46-58 (2008).

[38] X. Chen, H. Kong, D. Wu, X.Wang, Y. Lin, Phosphate removal and recovery through crystallization of hydroxyapatite using xonotlite as seed crystal, *Journal of Environmental Sciences*, **21**, 575-580 (2009).

[39] Y. Song, H. Hahn, E. Ho_mann, The effect of carbonate on the precipitation of calcium phosphate, *Environmental Technology*, **23**, 207-215 (2001).

[40] K. Moriyama, T. Kojima, Y. Minawa, S. Matsumoto, K. Nakamachi, Development of artificial seed crystal for crystallization of calcium phosphate. *Environmental Technology*, **22**, 1245-1252 (2001).

[41] N. Scheidt, Mo Adda, Framework of Confidence Values during Digital Forensic Investigation Processes, *WSEAS Transactions on Systems and Control*, **15**, 228-234 (2020)