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ISOTHERM AND THERMODYNAMIC ADSORPTION STUDIES OF NITRATE, PHOSPHATE AND AMMONIUM ONTOBENEFICIATED KAOLIN CLAY FROM KUTIGI, NIGER STATE, NIGERIA

[1](**Ogundipe Felix O**., *Federal Ministry of Water Resources, Abuja, Nigeria*)
Corresponding Author: ***ogundipefelixo@yahoo.com***

[2](**Saidu Muhammed,** *Department of Civil Engineering, Federal University of Technology, Minna, Nigeria*)

[3](**Abdulkareem, Ambali S**., *Department of Chemical Engineering, Federal University of Technology, Minna, Nigeria*)

[4](**Busari, Afis O.,** *Department of Civil Engineering, Federal University of Technology, Minna, Nigeria*)

ABSTRACT : *This study describes adsorption capacity of Beneficiated Kaolin Clay (BKC) from Kutigi, Niger State, Nigeria in removing Nitrate, Phosphate, Ammonium from domestic wastewater. Effects of temperature, contact time, and adsorbent dosage of the removal process were investigated. Langmuir and Freundlich isotherms were applied to experimental data and the goodness of their fit for adsorption was compared. Enthalpy (ΔH), Gibb's free energy (ΔG) and entropy of adsorptions (ΔS) were done to ascertain the exothermic or endothermic nature of the treatment process. The results show that the adsorption of nitrate, phosphate and ammonium onto the beneficiated kaolin clay from Kutigi, Niger State followed Langmuir and Freundlich isotherm models. The results confirmed that the beneficiated kaolin clay illustrated higher adsorption capacities and can be used for the adsorptive removal of nitrate, phosphate, ammonium from domestic wastewater.*

.***KEYWORDS:*** *Adsorption, Kaolin Clay, Phosphate, Nitrate, Ammonium, Domestic Wastewater, Kutigi.*

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I. INTRODUCTION

Wastewater and its nutrient contents are used for crop production. This offers substantial advantage to the farming societies. However, wastewater can also impose negative impacts on communities and ecosystems. Farmers are affected by direct contact with wastewater, and its use in agriculture has adverse effect on public health by eating agricultural produce planted with wastewater (Odigie, 2014). Nitrate (NO32-) and phosphate (PO43-) as nutrients contained in domestic wastewater are significant sources of water pollution. Eutrophication which is due to excessive amounts of nutrients contributes to the reduction of dissolved oxygen (Okereke et al, 2016) in freshwater. Nitrate is a risk to human health and a possible cause of infant methemoglobinemia (Takahiro & Ryoko, 2014). Nitrate, ammonium and phosphate trigger algae bloom in rivers, lakes, estuaries, and oceans. These nutrients have harmful effects on aquatic life, human health, and the environment. Domestic sewage, agriculture, and industries are sources of nitrate, ammonium and phosphate. Domestic sewage is the major source nitrate, ammonium and phosphate in Nigeria and for this reason, these nutrients are to be removed before they are finally discharged into the environment.

The removal of nitrate, phosphate and ammonium from domestic wastewater should be considered as an emerging worldwide concern because of the eutrophication in natural water. Having realised the dangers inherent in indiscriminate discharge of domestic wastewater and in a bid to protect the environment from pollution arising from domestic wastewater discharge, kaolin clay from Kutigi in Niger State was beneficiated at nano scale to remove nitrate, phosphate, ammonium from the domestic wastewater. Kaolin clay is classified as potential solid mineral in Niger State (NBS, 2017). There is deposit of kaolin clay in 13 local government areas of the state namely, Agaie, Bida, Bosso, Edati, Gbako, Katcha, Lapai, Lavun, Mashegu, Mokwa, Paikoro, Shiroro and Wushishi (RMRDC, 2018). Human society has been using clays and clay minerals since the stone age, primarily because clay minerals are common at the earth's surface and are widely utilized for agriculture (soils), ceramics (Auta and Hameed, 2013), environmental applications (Murray, 2000), absorbents(Saikiaet al, 2003) and wastewater treatment(Chun et al, 2013). Clay materials have been increasingly paid attention because their sheet-like structures provide high specific surface area (Dhaval & Painter, 2017) for wastewater treatment through adsorption processes. Adsorption is a widely used method for the treatment of industrial wastewater containing colour, heavy metals, inorganic and organic impurities (Rakhi et al, 2016). Adsorption is found to be one of the effective methods for removal of toxic heavy metals from industrial waste effluents (Amandeep & Sangeeta, 2017). Adoption method appears to be more suitable for domestic wastewater treatment because of its advantages in simplicity of operation, low cost and without sludge formation compared to other separation processes. In this study, the ability of beneficiated kaolin clay to remove phosphate, nitrate and ammonium was studied. The adsorption capacity of phosphate, nitrate and ammonium were examined using the adsorption isotherm technique. The Freundlich and Langmuir isotherms along with thermodynamic equations were used to fit the equilibrium data.

II. MATERIALS AND METHODS

The preparation of chemicals and materials involved are discussed in this chapter. Adsorption experiments were carried out at the National Water Quality Reference Laboratory, Minna, Niger State. The characterisation of the beneficiated kaolin was done at the University of South Africa, Johannesburg in conjunction with Federal University of Technology Minna, Nigeria. The major materials used for this research work were kaolin clay collected from its deposit in Kutigi, Niger State, Nigeria and domestic wastewater collected from Shiroro hydro-power station's office building.

A. BENEFICIATED KAOLIN CLAY

200g of raw kaolin clay lumps were put in 4 Litres Beakers with 4 Litres of distilled water added. This represents 5 % w/w kaolin clay slurry in distilled water. The Beaker was stirred for 1 hour using Heildolph RGL500 High viscosity stirrer at control speed of 40 revolutions per minute for adequate dispersion of the kaolin clay particles in distilled water.Acid activation was done by treating the beneficiated kaolin clay with 0.5M of HCl to remove carbonate and washed by 10% Hydrogen Peroxide (H_2O_2) to oxide organic matter (Bachiri*et al*, 2014) and the resulting mixture was allowed to swell in distilled water for 22hrs 57mins as calculated by Stoke's Law using equation 1.

$$u_s = \frac{g(\rho_p - \rho_w) d_p^2}{18\mu} \qquad 1$$

Where ρ_p = particle density, kg/m^3 (Kaolin clay particle = 1600kg/m^3), μ= liquid viscosity, kg/m.s (distilled water = 8.90 × 10^{-4} Pa·s), ρ_w = density of water, kg/m^3 (997kg/m^3), u_s= Particle settling velocity, m/s, d_p = diameter of particle (m), g = acceleration due to gravity, m/s^2(9.81m/s^2), t = Settling Time, R = particle size (radius) of clay, assumed to be spherical (1µm = 1 X 10^{-6}m), h = Settling Height of Fluid (12cm = 0.12m),The resultant slurries were thereafter dried in a laboratory oven at a temperature of 105^{o}C until the water evaporated and the samples weight became constant. Grinding of the dried samples was done using a laboratory porcelain pestle and mortar. The grinded kaolin clay samples were stored in laboratory sterile 100 ml plastic bottle for characterisation and for further studies. The percentage yield (Y) was calculated using equation 2.

$$Y = \frac{Mass\ of\ Beneficiated\ Kaolin\ Clay\ Produced}{Mass\ of\ Raw\ Kaolin\ Clay}\ x\ 100\% \qquad 2$$

B. CHARACTERISATION

The structural changes in the beneficiated kaolin clay were analysed as explained in Table 1.

Table 1: Characterisation of Beneficiated Kaolin Clay

S/N	Test Equipment	Uses	Location
1	X-Ray Diffractometer (XRD), Emma 0141, GCB SCIENTIFIC EQUIPMENT	Determination of mineral phases and compounds in materials. Study of crystal structure of the mineral phases and compounds in materials	University of South Africa (UNISA), Johannesburg, South Africa
2	Dispersive X – Ray Fluorescence (XRF) Machine, EDXRF-3600B, OXFORD INSTRUMENT	Chemical analyses of materials	University of South Africa (UNISA), Johannesburg, South Africa
3	High Resolution Transmission Electron Microscope (HRTEM), TECNAI G2, FEI Netherlands	Determination of Microstructure and particle size of materials	University of South Africa (UNISA), Johannesburg, South Africa
4	BET Nitrogen Absorption Analyser, TriStar II 3020, MICROMETRICS, USA	Surface area and pore size	University of South Africa (UNISA), Johannesburg, South Africa
5	UV – Spectrometer, UV – 1800 SHMADZU, Japan	Determination of purity and concentration of a solution	Centre for Genetic Engineering and Biotechnology, FUT Minna

C. ADSORPTION ISOTHERMS STUDIES

The adsorption capacity of the beneficiated kaolin clay to remove nitrate, phosphate, ammonium from the wastewater was tested using both Langmuir isotherms and Freundlich models. 25 g of the beneficiated kaolin clay were mixed with 100ml of the desired concentrations of the domestic wastewater at 30 ^oC in a temperature-controlled water bath with constant shaking. The samples were withdrawn after 30 minutes, and treated effluents were separated from the adsorbent using Whatman filter paper.

- **Effect of Contact Time:** The effect of contact time on the adsorption of nitrate, phosphate, ammonium onto beneficiated kaolin clay was studied at contact time of 10, 20, 30, 40, 50 and 60 minutes using an adsorbent dosage of 25g/100 ml of wastewater at a temperature of 29.5^{o}C and pH of 6.9.
- **Effect of Dosage:** The effects of adsorbent dosage of beneficiated kaolin clay on the removal of nitrate, phosphate, ammonium from wastewater was studied at adsorbent dosages of 5 – 30g at constant pH 6.9, temperature of 29.4^{o}C and contact time of 30 minutes.
- **Effect of Temperature*:*** The effect of temperatures on the adsorption of nitrate, phosphate, ammonium onto beneficiated kaolin clay was studied at temperature of 30, 40, 50, 60, 70 and 80^{o}C using an adsorbent dosage of 25g/100 ml of wastewater at a temperature of 29.5^{o}C and pH of 6.9.
- At the end of the experiment on contact time, dosage and temperature, the treated sample was filtered, and the filtrates were used for nitrate, phosphate and ammonium concentration determination.

D. LANGMUIR ADSORPTION ISOTHERM

Langmuir isotherm was employed to evaluate the multilayer adsorption at a relatively large distance from the surface of the adsorbents. The model represents one of the first theoretical treatments of non-linear adsorption and suggests that uptake occurs on a homogenous surface by monolayer adsorption without interaction between adsorbed molecules. The rate change of concentration due to adsorption equals to the rate of concentration due to desorption. As a result, the Langmuir isotherm is as expressed in equation 3.

$$\frac{Ce}{q_e} = \frac{1}{Q_o b} + \frac{Ce}{Qo} \qquad 3$$

Where Ce=Equilibrium concentration (mg/l),q_e =Amount adsorbed at equilibrium time (mg/g), Q_o=Langmuir constants derived from the slope, b =Langmuir constants derived from the intercept, The values of the Langmuir constants were calculated from the intercept and slope of the plot of $\frac{Ce}{q_e}$ versus Ce.The dimensionless separation factor expressed on favourable adsorption nature was calculated from equation 4.

$$\boldsymbol{R_L} = \frac{\mathbf{1}}{(\mathbf{1} + \boldsymbol{bC_i})} \qquad 4$$

WhereC_i =Initial concentration of the wastewater (mg/l), b =Langmuir constant (l/mg), R_L= indicate the type of isotherm as shown in Table 2.

Table 2: Isotherm Type

R_L Value	Type of Isotherm
R_L> 1	Unfavourable
R_L = 1	Linear
R_L< 1	Favourable
R_L = 0	Irreversible

E. FREUNDLICH ADSORPTION ISOTHERM

The Freundlich isotherm is an empirical relationship which often gives a more satisfactory model of experimental data. The Freundlich model can be applied onto heterogeneous surface involving multilayer adsorption. (Ikhazuangbe et al, 2017).
Freundlich isotherm is expressed in 5 and 6.

$$K_f C_e^{\frac{1}{n}} \qquad 5$$

However, the linearized Freundlich adsorption isotherm can be expressed in the form of:

$$Log\ q_e = Log\ (K_f + \frac{1}{n} Log\ C_e \qquad 6$$

Where C_e =Equilibrium concentration, q_e =Adsorption capacity at equilibrium stage, K_f and n=Freundlich constants which incorporates all factors affecting the adsorption process (adsorption capacity and intensity).Values of K_f and n were obtained from the intercept and slope of a plot of adsorption capacity (q_e) against equilibrium concentration (C_e). Both parameters K_f and n affect the adsorption isotherm. The larger the K_f and n values, the higher the adsorption capacity. Moreover, the magnitude of the exponent n gives an indication of the favourability of the adsorption process (Ikhazuangbe et al, 2017). When the value of n is greater than unity (1< n < 10) that means adsorption process is favourable (Bashir et al, 2013).

F. THERMODYNAMIC STUDIES

The determination of the basic thermodynamic parameters: enthalpy of adsorption (ΔH), Gibb's free energy of adsorption (ΔG) and entropy of adsorption (ΔS), is important as it allows to estimate if the process is favourable or not from thermodynamic point of view, to assess the spontaneity of the system and to ascertain the exothermic or endothermic nature of the process. An adsorption process is generally considered as physical if $\Delta H^\circ < 84$ kJ mol–1 and as chemical when ΔH° lies between 84 and 420 kJ mol–1. The thermodynamic parameters of the adsorption process were determined from the experimental data obtained at various temperatures using equations 7 and 9 (Bashir et al, 2013; Ikhazuangbe et al, 2017; Al-Kadhi, 2019).

$$\Delta G = -RTlnK_d \quad (6)$$
$$K_d = \frac{q_e}{C_e} \quad (7)$$
$$lnK_d = \frac{\Delta So}{R} - \frac{\Delta Ho}{RT} \quad (8)$$
$$\Delta Go = \Delta Ho - T\Delta So \quad (9)$$

Where K_d = Distribution coefficient for the adsorption ,q_e= Amount of contaminants adsorbed on the adsorbent per litre of wastewater at equilibrium, Ce=Equilibrium concentration (mg/L) of the contaminants in wastewater, T= Absolute temperature, R=Gas constant, ΔGo=Gibbs free energy change, ΔHo=Enthalpy change, ΔSo=Entropy change. The values of enthalpy change (ΔHo) and entropy change (ΔSo) were obtained from the slope and intercept of lnKd versus 1/T plots.

III. RESULTS AND DISCUSSION

The results of the experiments at different contact times, dosage of the adsorbents and temperatures are presented in this chapter. The adsorption isotherm and kinetic parameters of the process, effects of contact times, adsorbents dosage and temperatures efficiencies were evaluated and discussed.

A. CHARACTERISATION

The characterisation results of the beneficiated clay showed in Table 3 confirmed the formation of the beneficiated kaolin clay adsorbent at nanoscale.

Table 3: Characterisation of Beneficiated Kaolin Clay

Adsorbent	**Results**						
	d–Spacing (nm)	**Crystallite Size (nm)**	**SiO_2/Al_2O_3 Ratio**	**BET Surface Area ($m^2.g^{-1}$)**	**Single Point Adsorption Total Volume of Pores (cm^3/g)**	**Adsorption Average Pore Diameter (nm)**	**Desorption Average Pore Diameter (nm)**
Beneficiated Kaolin Clay	3.532	28.114	1.35	14.5126	0.003740	1.0309	14.9174

B. WASTEWATER ANALYSIS

Domestic wastewater collected was analysed to determine the initial concentration of nitrate, phosphate, ammonium in the wastewater before treatment. The obtained analytical results for the nitrate, phosphate and ammonium were found to be 230 mg/L, 11.8 mg/L, 37.2 mg/L and 133 mg/L respectively. These listed values were far above the maximum permissible level set by NESREA (2011).

C. LANGMUIR ISOTHERM

Tables 4 showed the Langmuir model isotherm for the determination of Q_o and b**.** From the slopes and intercepts of the plots of $\frac{Ce}{q_e}$ versus Ce for the removal of nitrate, phosphate, ammonium in wastewater, the model showed the multilayer adsorption patterns and the fitting to the heterosporous nature of beneficiated kaolin clay. It was evident that the linear correlation coefficients (R^2) for the beneficiated kaolin clay in the removal of nitrate, phosphate, ammonium were all greater than 0.90. This showed that the experimental data moderately fit Langmuir adsorption isotherm. The calculated R_L values for nitrate, phosphate, and ammonium gave an indication of the favourability of the adsorption process and type of the isotherm which is R_L< 1 as shown in the Table 4.The results show that beneficiated kaolin clay corresponded to the Langmuir model.

Table 4: Langmuir Adsorption Isotherm Constants for Beneficiated Kaolin Clay

Parameters	Intercept = 1/Qob	Slope = 1/Qo	Qo	b	R_L	R^2
Nitrate	0.1275	0.0013	769.2308	0.010196	0.296236	0.9613
Phosphate	0.0646	0.0405	24.69136	0.626935	0.119078	0.9899
Ammonium	0.0772	0.0103	97.08738	0.13342	0.167695	0.9444

D. FREUNDLICH ADSORPTION ISOTHERM

Tables 5 showed the Freundlich model isotherm values of K_f and n obtained from the intercept and slope of a plot of adsorption capacity (q_e) against equilibrium concentration (C_e). Both parameters K_f and n affect the adsorption isotherm. The larger the K_f and n values, the higher the adsorption capacity. From the plot of adsorption capacity (q_e) against equilibrium concentration (C_e) for the removal of nitrate, phosphate and ammonium in wastewater, the model showed the multilayer adsorption patterns and the fitting to the heterosporous nature of beneficiated kaolin clay. It was evident that the linear correlation coefficients (R^2) for beneficiated kaolin clay in the removal of nitrate, phosphate, ammonium were greater than 0.90. This showed that the experimental data moderately fit Freundlich adsorption isotherm. The larger the K_f and n values, the higher the adsorption capacity. Furthermore, the magnitude of the exponent n gave an indication of the favourability of the adsorption process. When the value of n is greater than unity (1< n < 10), the adsorption process is favourable. The calculated n values for nitrate, phosphate, ammonium gave an indication of the favourability of the adsorption process as shown in the Table 5.The slopes and R^2 were present in Table 5. The plot exhibited linearity and good correlation coefficient. The values of R^2 were very close to unit, showing a strong agreement with the Freundlich isotherm.

Table 5: Freundlich Adsorption Isotherm Constants for Beneficiated Kaolin Clay

Parameter	Slope = 1/n	n	K	R2	
Nitrate	1.3139	0.6354	1.573812	20.60155	0.9879
Phosphate	0.978	0.4235	2.361275	9.506048	0.9015
Ammonium	1.2494	0.4707	2.124495	17.75824	0.9890

E. THERMODYNAMIC STUDIES

The determination of the basic thermodynamic parameters: enthalpy of adsorption (ΔH), Gibb's free energy of adsorption (ΔG) and entropy of adsorption (ΔS) were done to assess the spontaneity of the system and to ascertain the exothermic or endothermic nature of the treatment process. The values of enthalpy change (ΔH^o) and entropy change (ΔS^o) as presented in Table 6 were obtained from the slope and intercept of $\ln K_d$ versus 1/T plots. The values of $\Delta H^o$and ΔS^o were found to be positive. The positive values of ΔH^o showed that the adsorption processes of the beneficiated kaolin clay were endothermic in nature. The negative values of ΔG^o indicated the adsorption of nitrate, phosphate, ammonium onto beneficiated kaolin clay adsorbent is spontaneous and exothermic over the study range of temperatures (Abbas *et al.*, 2020).The reduction of Gibbs free energy with increase in temperature indicated a driving force that led to higher adsorption capacity. At elevated temperature, adsorption process increased because of increase in randomness and non-spontaneity of the process. The thermodynamic study suggested chemical adsorption due to strong interface where the sorbates adhered on the surfaces of the adsorbents through strong forces forming chemical bonds.

Table 6: Thermodynamic Parameters of TotalIron, Cadmium, Lead, Copper, Manganese, Arsenic, Mercury Silver and Zinc, using Beneficiated Kaolin Clay

Parameters	Intercept = ΔS°/R	Slope = -ΔH°/R	R^2	R ($Jmol^{-1}K^{-1}$)	ΔS°	ΔH°	ΔG°					
							303	313	323	333	343	353
Nitrate	12.823	-2856.7	0.9306	8.3145	107	23752	-8553	-9619	-10685	-11751	-12818	-13884
Phosphate	14.071	-2678.2	0.9363	8.3145	117	22268	-13181	-14351	-15521	-16691	-17861	-19031
Ammonium	13.569	-2706.4	0.9354	8.3145	113	22502	-11682	-12810	-13938	-15067	-16195	-17323

F. EFFECT OF CONTACT TIME

The effect of contact time on the adsorption of nitrate, phosphate and ammonium contaminants onto the beneficiated kaolin clay was studied at contact time of 10, 20, 30, 40, 50 and 60 minutes using an adsorbent dosage of 25g/100 ml of wastewater at a temperature of 29.5°C and pH of 6.9. The response of contact time on the removal of nitrate, phosphate and ammonium is presented in Figures 1. The observation revealed that an increase in the fraction of nitrate, phosphate and ammonium adsorbed occurred with corresponding increase in the contact time as shown in Fig.1. It was observed that rapid adsorption rates were obtained between the contact time of 10 – 40 minutes at various contact time. The increase in contact time from 10 min gradually reduced the concentration of nitrate, phosphate and ammonium contaminants till 40 min contact time. The rate of adsorption equals the rate of desorption on reaching the equilibrium, therefore slow or no uptake of nitrate, phosphate and ammonium was observed between 40 min – 60 min contact time. The slow uptake and the no increase in percentage removal with further increase in contact time were due to saturation of the surface of the adsorbent with pollutants.

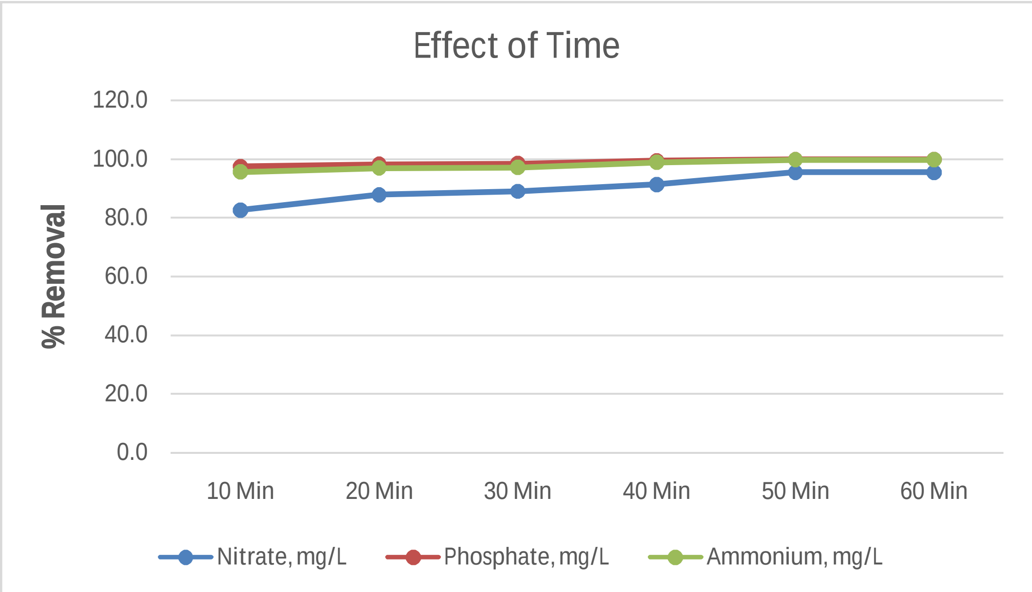

Fig. 1: Effect of Contact Time

G. EFFECT OF DOSAGE

It was observed that the removal of the nitrate, phosphate and ammonium pollutants followed similar trends as presented in Fig.2. At a lower dosage, the rate of adsorption was influenced by inter ionic competition and at higher dosage, the adsorption process was observed to increase. This is because of an increase in the availability of the active binding sites and large surface areas of the adsorbents. This could also be inferred to be due to the availability of vast exchangeable sites for adsorption. The higher the adsorbent dosages used in the treatment, the higher the removal efficiencies of the pollutants from the wastewater by the adsorbents. At higher dosages, the adsorption increased due to the availability of more active binding exchangeable sites for adsorption of the target pollutants (Abukhadra and Mohamed, 2019). Therefore, the adsorbent dosage is a paramount parameter responsible for the adsorption of pollutants by the adsorbent.

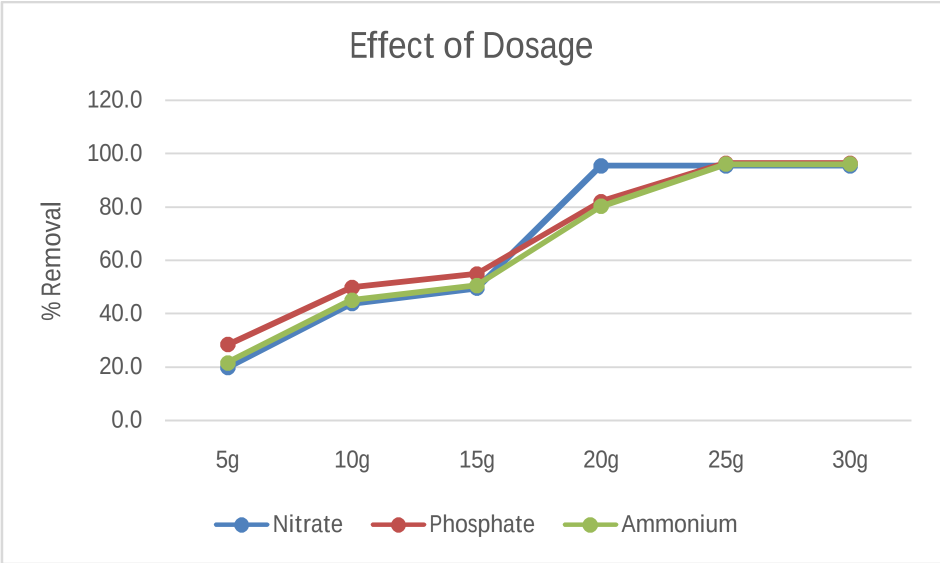

Fig. 2: Effect of Dosage

H. EFFECT OF TEMPERATURE

The effect of temperatures on the adsorption of nitrate, phosphate and ammonium was studied at temperature of 30, 40, 50, 60, 70 and 80^{o}C using an adsorbent dosage of 25g/100 ml of wastewater at a temperature of 29.5^{o}C and pH of 6.9. The effect of temperature on the removal of nitrate, phosphate and ammonium was presented in Fig.3. The observation revealed that an increase in the fraction of the nitrate, phosphate and ammonium adsorbed occurred with corresponding increase in the temperature as shown in Fig.3. The increase in temperature from 30^{o}C gradually increased nitrate, phosphate and ammonium adsorption. The rate of adsorption equals the rate of desorption at equilibrium; therefore, slow uptake of pollutants was observed from 60^{o}C to 80^{o}C. The slow uptake and the slight or no increase in percentage removal with further increase in temperature might be due to saturation of the surface area of the adsorbent with nitrate, phosphate and ammonium pollutants.

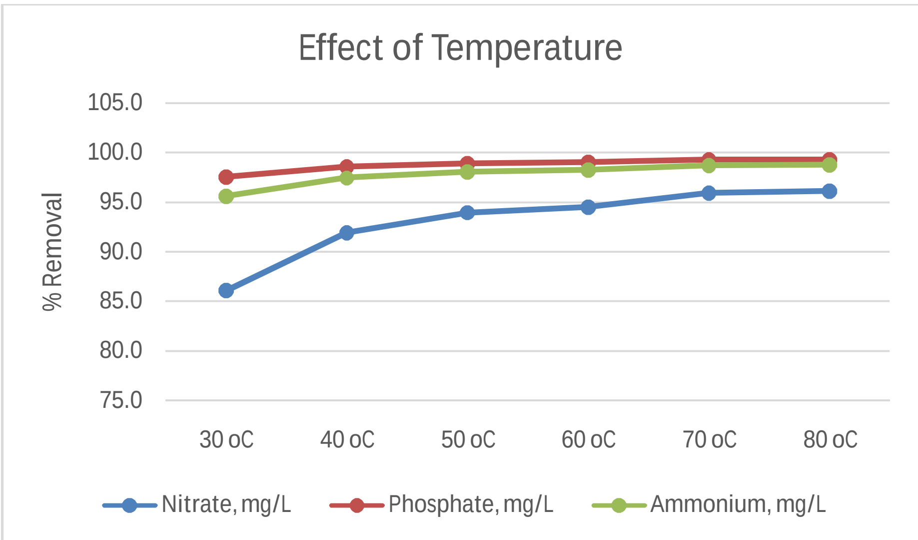

Fig.3: Effect of Temperature

IV. CONCLUSION

Removal of nitrate, phosphate, ammonium from domestic wastewater was possible using the beneficiated kaolin clay from Kutigi, Niger State, Nigeria. Both the Langmuir and Freundlich isotherms models provided the good fits to predict the adsorption of nitrate, phosphate, ammonium onto the beneficiated kaolin clay. The values of ΔH^o and ΔS^o were found to be positive. The positive values of ΔH^o showed that the adsorption processes of the beneficiated kaolin clay were endothermic in nature. The results confirmed that the beneficiated kaolin clay illustrated higher adsorption capacities and can be used for the adsorptive removal of nitrate, phosphate, ammonium from domestic wastewater.

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