Application of Modified Clinoptilolite as an Adsorbent Material in Activated Sludge Process

GP Seremo and John Kabuba[1]

***Abstract*—**This study aims to evaluate the modification of NH_4^+ and PO_4^{3+} for waste activated sludge reduction. Natural and modified clinoptilolites have been characterized using X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier-transformed infrared spectroscopy (FTIR). Important parameters such as adsorbent dosage, pH, and temperature were determined. The highest removal efficiency was obtained at absorbent dosage of 5g for both PO_4^{3+} and NH_4^+ removal, pH 5 for PO_4^{3+} removal and pH 8 for NH_4^+, and temperature of 70ºC for both PO_4^{3+} and NH_4^+ removal. Results show that NH_4^+ and PO_4^{3+} sorption on modified clinoptilolite is in good agreement with the pseudo-second kinetic model. NaOH modified clinoptilolite on ammonium fits well with Langmuir, Dubinin-Radushekevich, and Temkin with $R^2 > 0.972$. With regards to KOH modified clinoptilolite on phosphate fits well with Langmuir and Freundlich with the correlation coefficient approaching unity ($R^2 > 0.9$). The Gibbs energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were also determined. Modified clinoptilolite with NaOH and KOH could be considered appropriate for the removal of ammonium and phosphate from waste activated sludge.

***Keywords*—**Adsorption, Ammonium, Clinoptilolite, Phosphate, Sludge,

I. Introduction

Activated sludge process has been widely preferred for the treatment of municipal wastewater because of its good performance in the degradation of organic pollutants [1]. The activated process mainly alternates oxic and anoxic processes where oxidation of organic pollutants and ammonia takes place in the oxic chamber while denitrification takes place in the anoxic chamber [2]. Generation of excess waste activated sludge has been a major challenge facing application of activated sludge process in the treatment of municipal wastewater [3]. Sludge treatment and sludge disposal are the major challenge faced in waste activated sludge plant, since the environmental requirements of the emission of excess sludge during waste activated sludge process have been strengthened sludge treatment and disposal mostly rate as high as 50-65% of the process cost [4]. Thus, reasonable treatment and reducing waste activated sludge strategies are needed to minimize economical pollution. According to Alexandre et al., [5], waste activated sludge reduction is achieved through the following two methods (1) System changes – introducing technologies for reducing excess sludge production in waste activated sludge process, (2) Post treatment – reducing excess sludge disposed by waste activated sludge process. After waste activated sludge process, significant amounts of nutrients remain in the secondary effluent. Nutrients (Nitrogen and Phosphorus) pose possible risk to water pollution and might also lead to eutrophication if managed correctly, therefore it is necessary to introduce adsorption process to minimize waste activated sludge by removing nitrogen and phosphorus. However, the success of the adsorption process depends on the development of an efficient adsorbent. Clay minerals, zeolites, activated carbon, biomaterials have been broadly used as adsorbents for adsorption processes. Out of these adsorbents, the use of natural zeolites is well known for its large adsorption ratio surface area, high ion exchange capacity, high efficiency and also it is simple and more economical in terms of operation comparing to other adsorbents [6]. Natural zeolites are aluminosilicate minerals that can be found in sedimentary rocks formed by volcanoes. There are approximately 40 types of natural zeolites, although only few are commonly used such as clinoptilolites [7]. Clinoptilolites contains a special alumina tetrahedron structure which produces extreme amounts of negative charge. Therefore, has the strong adsorption of ammonium nitrogen (NH_4^+-N) [8], however it is not commonly used for phosphate adsorption due to the electrostatic repulsion. Changing the properties of natural clinoptilolites by chemical and thermal treatments improves the separation efficiency, currently the major methods of clinoptilolites modification to remove ammonium nitrogen and phosphate in waste activated sludge are inorganic salt, acid and alkali modification [6]. Since ammonium and phosphate are one of the most predominant forms of inorganic nitrogen and phosphorus present in waste activated sludge, in this project waste activated sludge from waste activated sludge process will be reduced by adsorbing ammonium nitrogen and phosphate using modified clinoptilolite as an adsorbent material.

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II. Materials and Methods

A. Review Preparation of synthetic wastewater and clinoptilolite

All the reagents and chemicals used in the present work were of analytical grade (98-99%) and were acquired from

Sigma- Aldrich Company. The solutions were prepared using high-purity deionized water.

Clinoptilolite used in this work was obtained from a mining company from South Africa. Waste activated sludge was sourced from a local wastewater treatment plant in Vereeniging, South Africa and was stored prior for the experiments. pH was adjusted using HCl (1M) and NaOH (1M). Modification of clinoptilolites was done using sodium hydroxide (NaOH) and potassium hydroxide (KOH).

Natural clinoptilolite was washed in deionized water to eliminate impurities and dried at 60°C for 24 hours, afterwards the sample was crushed and sieved at an average particle size of 1000-3000µm. The modification process was as follows: 50g of natural clinoptilolite was added to 100 mL of sodium hydroxide (NaOH), after which the mixture was stirred at 185 rpm, 80°C for 8 hours and dried at 100°C for 24 hours. Finally, the modified sample was heated at 5°C/min to 540°C for calcination for 5 hours, for first modification. For second modification 50g of natural clinoptilolite was added to 100 mL of potassium hydroxide (KOH), and the mixture was also stirred at 185 rpm, 80°C for 8 hours and dried at 100°C for 24 hours. Finally, the modified sample was heated at 5°C/min to 540°C for calcination for 5 hours.

B. Adsorption experiment

Batch experiments was conducted in a conical flask (250 mL). The removal of ammonia nitrogen and phosphate from waste activated sludge by natural and modified clinoptilolites was performed in a shaking incubator at 150 rmp, 25°C for 4hrs. 50 g of modified clinoptilolites was put in two conical flasks containing, flask 1-ammonium nitrogen solution and flask 2- phosphate solution.

The amount of ammonia nitrogen (NH_4^+-N) removed from waste activated sludge was calculated using Equation (1):

$$Q = \frac{(Co - Ce)V}{W} \quad (1)$$

where Q = Total adsorption ($mg.g^{-1}$); Co = Initial concentration (mg. L^{-1}); Ce = Equilibrium concentration (mg. L^{-1}); V= Solution volume (L) ; W= Absorption weight (g)

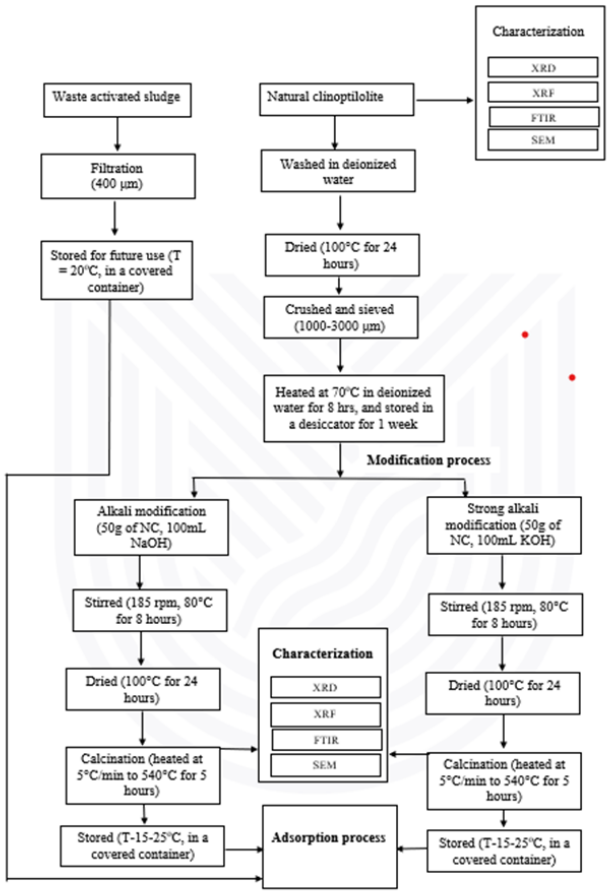

Fig. 1 Mapping nonlinear data to a higher dimensional feature space

III. Results and Discussion

TABLE I
CHEMICAL COMPOSITION OF NATURAL AND MODIFIED CLINOPTILOLITE

	Clinoptilolites		
Metal oxide in (%)	Natural	Modified with NaOH	Modified with KOH
SiO_2	76.41	13.39	70.59
Al_2O_3	12.81	4.54	12.44
K_2O	5.27	0.76	6.86
Fe_2O_3	2.63	27.78	3.42
Na_2O	0.00	2.52	2.32
CaO	1.93	31.7	2.33
MgO	0.47	8.08	0.86
Ratio Si/Al	**5.96**	**2.95**	**5.67**

Table I presents the XRF result of natural and modified clinoptilolites with potassium hydroxide and sodium hydroxide. The chemical composition of natural clinoptilolite has changed through alkali modifications, it is observed that after NaOH treatment, Na_2O have increased from 0.00 to 2.52 wt%, thus NaOH modified clinoptilolite has higher NH_4^+ ion-exchange capacity than natural and KOH modified clinoptilolites. Fe_2O_3, CaO and MgO have also increased. This results also signifies a great amount of silicon and slight amount of aluminium removal from natural clinoptilolite, a great amount of silicon removal is caused by OH¬ in the alkali

solution which is influenced by the Si/Al ratio, can selective dissolution the amorphous silicon. Since clinoptilolite is negatively charged, it attacks the OH¬ and aluminium will preserve the 4 neighbouring silicon atoms [8] signifying the effect of desilication and dealumination. Prior to KOH treatment, the incorporation of exchangeable potassium ions to natural clinoptilolite occurred during modification process hence the K_2O content increased after the sample was treated with KOH from 5.27 to 6.86 wt%. Fe_2O_3, CaO and MgO have also increased after KOH modification SiO_2/Al_2O_3 ratio slightly decreased due to the slight removal of silicon and aluminium from natural clinoptilolite.

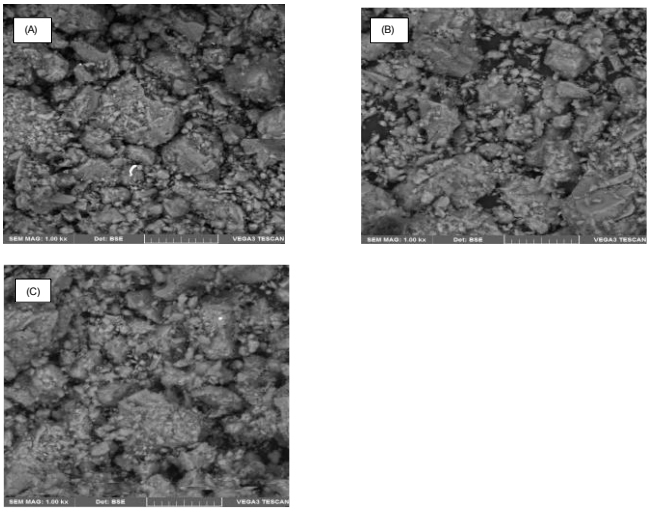

Fig. 2 Scanning electron microscope (SEM) image of: (A) Natural clinoptilolite, (B) modified clinoptilolite with NaOH and (C) modified clinoptilolite with KOH

The SEM results was used to examine the morphology and microstructure of natural and modified clinoptilolites. Fig. 2 indicates the surface of a natural clinoptilolite, with a small porosity and unruly surface area. After NaOH treatment, great pores among the particles could be seen due to the removal of excess amount of silica dissolved, as indicated from the XRF results NaOH dissolved a large amount of silica which resulted in desilication and increased the pore volume. Fig. 2C represents the SEM image of KOH modified clinoptilolite, treating clinoptilolite using KOH did not significantly change the surface structure of natural clinoptilolite, the sample still shows an unruly surface area with small porosity.

A. Effect of adsorbent dosage

Adsorbent dosage is an important parameter since it affects the capacity of modified adsorbent at the initial concentration. In this study, the adsorbent dosage was studied at the rage of 2, 4, 8, and 10 g and pH, initial concentration, and temperature were kept constant at pH 7, 600 mg/L and 25˚C. The investigational data is demonstrated in Fig. 3. Fig. 3(A) shows that the phosphate removal capacity improved with adsorbent dosage, it improved from 163.24 to 209.36 mg/g which indicates a dependence adsorption upon the availability of binding sites for phosphate. On the other hand, unmodified sample had a very small removal capacity, however its removal capacity improved with increased adsorbent dosage of natural clinoptilolite, proving that natural clinoptilolite couldn't adsorb phosphate completely due to its small adsorption ability caused by the electrostatic repulsion.

Fig. 3(B) indicates that the ammonium removal capacity increased with adsorbent dosage. The removal efficiency of ammonium also improved from 128.24 to 139.98 mg/g. Fig. 3(B) also shows that the modification of natural clinoptilolite increased the ammonium removal capacity. Additionally, natural clinoptilolite removal capacity increases with increasing dosage, proving that natural clinoptilolite also has a strong capacity of adsorbing ammonium.

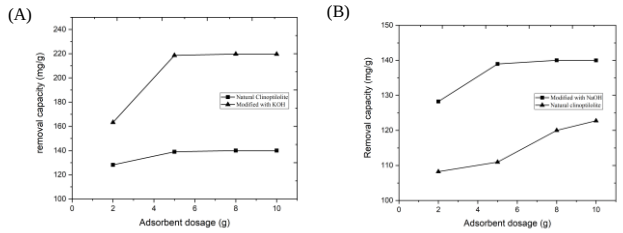

Fig. 3 Effect of adsorbent dosage (A) on phosphate removal and (B) ammonium removal (pH =7, initial concentration = 600 mg/L, and Temperature = 25ºC)

B. Effect of pH

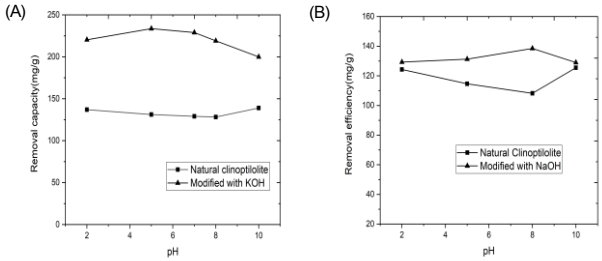

Fig. 4 Effect of pH (A) on phosphate removal and (B) ammonium removal (Adsorption dosage = 2 g, initial concentration = 600 mg/L, and Temperature = 25ºC)

pH is a crucial variable in adsorption process, because the physio-chemical properties of adsorbent and the type of process is affected the pH [9]. The adsorption of nutrients was investigated at pH range of 2, 4, 8, and 10 and the adsorbent dosage, initial concentration, and temperature were kept constant at 2g, 600 mg/L and 25˚C.

Fig. 4(A) shows the results obtained from the batch experiments, and the highest phosphate removal is between pH 5 and 7 with modified sample, which is also higher than the natural clinoptilolite. It is observed that the removal capacity of phosphate did not change significantly over the pH value from 5-8, all above 225 mg/g.

The removal capacity of natural clinoptilolite increased with increasing pH from acidic to alkaline range while KOH modified sample removal capacity decreased with increasing

pH. For modified sample, pH 8 is where the least harm is done to the structure and property of the adsorbent. Additionally, Tu et al., [10] has mentioned that the affinity of adsorbent for anions mainly depends on the anion's valence and size. The higher the valence and the smaller the hydrated ionic radius, the stronger is the adsorption.

Phosphate may be signified in four different chemical forms when the pH value fluctuates, when pH < 2, PO_4^{3-} exists as H_3PO_4, pH between 3 and 6.5, PO_4^{3-} exists as H_2PO_4, pH from 7.5-12, PO_4^{3-} exists as HPO_4^{2-} , and pH > 12, PO_4^{3-} is portrayed in the form of PO_4^{3-}, hence the modified removal sample is decreases with the increasing pH [10]. Figure 4.5(B) indicate the results obtained from the batch experiments; the highest ammonium removed is at pH 8 with a modified sample. The removal capacity of natural clinoptilolite increases at pH 2-8, this behaviour might be due to the decrease in hydrogen ion solution related, therefore the completion H ions with NH_4^+ ions for adsorption exchanging sites onto clinoptilolite [11]. At pH 8 the removal capacity of NH_4^+ started to decrease with increasing pH until when pH = 10. According to [11], this behaviour is probably due to the fact that at pH values above 8 partially dissolution of the natural clinoptilolite occurs, and it is also likely that NH_4^+ is converted into NH_3. Since NH_3 is neutral it does not exchange with metals in the adsorbent and causes the removal capacity to decrease [9].

C. Effect of temperature

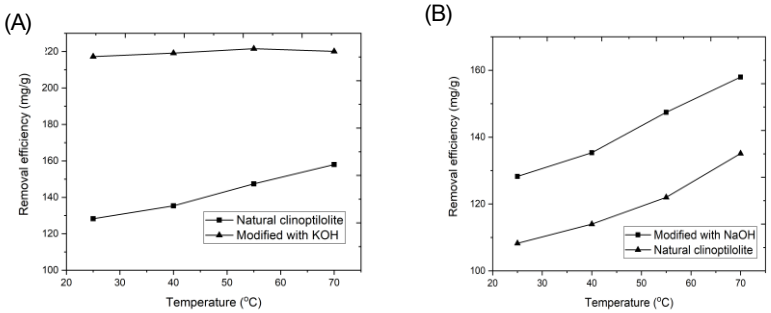

Fig. 5 Effect of Temperature (A) on phosphate removal and (B) ammonium removal (Adsorption dosage = 2g, initial concentration = 600 mg/L, and pH = 7)

The effect of temperature on the character of phosphate adsorption onto natural and modified clinoptilolite was also checked. Temperature was varied from 25 to 70°C and adsorbent dosage, initial concentration, and pH were kept constant at 2 g, 600 mg/L and pH 7. The investigational data is demonstrated in Fig. 5.

Fig. 5(A) shows the phosphate removal capacity of natural and KOH modified clinoptilolite. Both the removal capacity of natural and modified clinoptilolite increases with increasing temperature, however the modified sample changed its behaviour, it might be due to precipitation reaction held the major possession instead of inion exchange [10]. It is also observed that modifying clinoptilolite with KOH increases the removal capacity. The highest removal capacity is at the highest temperature (70°C) with 135.09 mg/g [11]. reported that it is caused by the movement of ions in the solution and higher possibility of collision between PO_4^{3-} ions and adsorption sites. In regards with PO_4^{3-} removal using natural clinoptilolite, removal capacity also increases with increasing temperature, Tu et al. [10] confirmed that it is due to the clinoptilolite particles diffusion rate though the external boundary layer and in the internal pores was increased, since the attractive forces between clinoptilolite surface and ions were made weak. Fig. 5 (B) indicates the ammonium removal capacity using natural and modified clinoptilolite, the highest removal capacity is at temperature is at 70°C and 157.98 mg/g on a modified sample. Additionally, both results show the removal capacity increases with increasing temperature. The reason being due to the availability of chemical adsorption sites during the ion exchange, the attractive forces of between the NH_4^+ and adsorbent sites became strong hence the removal efficiency increased with increasing temperature.

D. Adsorption isotherms

Adsorption isotherms are important for the description of how ammonium and phosphate concentration will interact with natural and modified clinoptilolite as an adsorbent. Adsorption capacity of NaOH modified clinoptilolite on ammonium and KOH modified clinoptilolite on phosphate was examined by equilibrium adsorption isotherm study. In order to achieve that, it is essential to create the most suitable correlation for the equilibrium curve. A perfect mathematical description of equilibrium adsorption capacity is crucial for comparing adsorption behaviour for various adsorbent systems and predicting the adsorption parameters [13]. In this study, numerous isotherm models are used for analysing the experimental data, namely: Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich

Langmuir model is frequently utilized for solute adsorption from liquid solutions, it also assumes a monolayer adsorption onto homogeneous surface at fixed localized sites by identical energies of adsorption [14]. On the other hand, Freundlich, Tempkin and Dubinin–Radushkevich specify that adsorption process is mostly characterised by the heterogeneous multilayer formed by the adsorbed species. Additionally, these four models also considers that there are possible interactions between the adsorbed species driven by Van der Waal forces [15]. The mathematical expressions of Langmuir, Freundlich, Dubinin-Radushkevich model and Temkin models

respectively). Isotherm parameters are summarised in Table II

TABLE II
ISOTHERM PARAMETERS FOR NH_4^+ AND PO_4^{3-} ADSORPTION

Langmuir				
	q_m (mg/g)	K_L (L/mg)	R_L	R^2
Ammonium	602.409	0.414	0.024	0.972
Phosphate	199.203	0.831	0.004	0.984
Freundlich				
	1/n	K_L(mol^2/J^2)	R^2	
Ammonium	0.86606	0.476464	0.847	
Phosphate	0.76493	0.706675	0.957	
Dubinin-Radushekevich				
	q_m(mg/g)	B(mol$^{2/2}$)	ε	R^2
Ammonium	240.912	0.0017	17.252	0.953
Phosphate	562.719	0.00158	17.789	0.893
Temkin				
	B_T(J/mo)	K_L(L/m)	R^2	
Ammonium	370.047	0.019	0.964	
Phosphate	432.759	0.016176	0.832	

According to the coefficient of determination (R^2) the models indicate that the experimental data of NaOH modified clinoptilolite on ammonium fits well with Langmuir, Dubinin-Radushekevich, Temkin with the correlation coefficient approaching unity ($R^2 > 0.9$). Based on the Langmuir model, the uptake capacity is 602.409 mg/g and for Dubinin-Radushekevich the uptake capacity is 240.912 mg/g, respectively.

With regards to KOH modified clinoptilolite on phosphate could be well fitted in by Langmuir and Freundlich with the coefficient of determination approaching unity ($R^2 > 0.9$). Additionally, it is also worth noticing that for PO_4^{3-}, Langmuir model offered a better description ($R^2 \geq 0.984$), which indicates a monolayer adsorption. R_L value shows that nature of the process to be either linear ($R_L = 1$), unfavourable ($R_L > 1$), favourable ($0 < R_L < 1$) and irreversible ($R_L = 0$). Phosphate adsorption onto modified clinoptilolite is favourable, as presented in Table II

E. Adsorption kinetic models

The pseudo-first-order, pseudo-second-order, and intra-particle diffusion models were employed for investigating conditions to evaluate the efficiency of NaOH and KOH modified clinoptilolite in reducing ammonium and phosphate from waste activated sludge. The coefficient of determination (R^2) of pseudo second order was highest for both ammonium ($R^2 > 0.99363$) and phosphate ($R^2 > 0.999$), these results indicate that the pseudo second order models were more suitable to define the adsorption process of both NH_4^+ and PO_4^{3-}.

TABLE III
KINETIC PARAMETERS FOR NH_4^+ AND PO_4^{3-} ADSORPTION

Model type	Parameters	Ammonium (NH_4^+)	Phosphate (PO_4^{3-})
Pseudo first order	R^2	0.942	0.884
	q_e (mg/g)	250.934	22.079
	K_1(1/min)	-0.0049	-0.0026
Pseudo second order	R^2	0.9936	0.999
	q_e (mg/g)	9592.244	38.023
	K_2(g/mg.min)	0.0176	0.393
Intra-particle diffusion	R^2	0.967	0.965
	K_{diff}	69190.48	131624.4
	C	20.635	3.079

A. Adsorption thermodynamics

TABLE IV
THERMODYNAMIC PARAMETERS FOR NH^{4+} AND PO_4^{3-} ADSORPTION

	T(K)	LnK_L	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)
Ammonium	298	0.287	0.710	14.200	50.212
	328	0.925	2.523		
	338	0.914	2.569		
Phosphate	298	0.137	0.339	22.096	0.752
	313	0.548	1.426		
	328	0.953	2.599		

The thermodynamics studies were conducted to reveal the nature of adsorption of ammonium and phosphate from waste activated sludge using modified clinoptilolite as an adsorbent. With regards to ammonium adsorption, the thermodynamic parameters were conducted at temperatures of 298, 328, and 338K. For the removal of phosphate, 298, 313, and 228K were employed by using the equation 2.10, 2.11 and 2.12.

where ΔG° = change in Gibbs energy in kJ/mol., ΔH°= change in enthalpy in kJ/mol., ΔS°= change in entropy in kJ/mol. K

Enthalpy (ΔH°) and entropy (ΔS°) were evaluated from a straight line graph, obtained by the intercept and slope of the plot of lnK_L and 1/T. Table IV indicates the values of T, K_L, ΔG°, ΔH°, and ΔS°.

The negative value of ΔG° was found for both NH_4^+ and PO_4^{3-} indicates that the removal processes were spontaneous, therefore no energy input to the system was needed. Additionally, the removal processes were also considered physisorption as both ΔG° values were less than 18 kJ/mol. A positive ΔH° was obtained for both processes, which indicates that the removal processes were endothermic. Furthermore, entropy was found to be positive for both processes, suggesting an increase in solid–liquid interfacial disorder and a decrease in orderliness during adsorption by modified synthetic zeolites and it also shows the randomness behaviour of modified adsorbents. These results correspond to the ammonium results obtained from [16]. With regards to

phosphate removal, the results correspond with the results obtained from [17].

IV. Conclusion

Activated sludge using modified clinoptilolite as an adsorbent was examined, the experimental results confirmed that modification of clinoptilolite with NaOH is a potential material for the removal of ammonium and KOH is a potential material for the removal of phosphate from waste activated sludge. Furthermore, it has been concluded that: XRF, XRD, FTIR, and SEM studies revealed that chemical modification took place and improved clinoptilolite adsorption capacity, they also revealed that NaOH modification increased the total pore volume and surface area, and therefore increased the amount of adsorption activity centre to promote removal of NH_4^+ from waste activated sludge. The adsorption capacity of ammonium and phosphate was to controlled by the adsorbent dosage, pH, and temperature. The correlation coefficient R^2 reveals that the experimental data of NaOH modified clinoptilolite on ammonium fits well with Langmuir, Dubinin-Radushekevich, and Temkin, with regards to KOH modified clinoptilolite on phosphate could be well fitted in by Langmuir and Freundlich. The pseudo second order models were more suitable to define the adsorption process of both NH_4^+ and PO_4^{3-}. The thermodynamics studies showed that removal processes were for both ammonium and phosphate were spontaneous and endothermic reaction.

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