THE EFFECT OF SYNTHESIZED NPK LOADED SURFACTANT MODIFIED ZEOLITE A BASED FERTILIZER IN TOMATO *(Lycopersycum esclentum)* CULTIVATION

Salako. O.[1], *Kovo, A.S.[1], Abdulkareem, A.S.[1], Yusuf, S.T.[2], Afolabi, E.A.[1] and Auta, M.[1]

[1]Department of Chemical Engineering, Federal University of Technology, Minna

[2]Department of Crop Production, Federal University of Technology, Minna

*corresponding author: Kovo@futminna.edu.ng, 08094059107

ABSTRACT

The surface of zeolite A synthesised from Ahoko kaolin was optimally modified by quaternary ammonium compound, HDTMA and used as fertilizer carrier. Characterization techniques such as FTIR and BET were used to characterise the zeolite A and modified zeolite A samples. Zeolite A's maximum adsorption capacity of 7.55mg/g was obtained with initial concentration of 162.6 mmol/L, contact time of 16 h, and temperature of 25 ^oC. The initial HDTMA concentration was the most significant term that influenced the adsorption capacity of zeolite A. The interactive effect that contributed significantly to the maximum adsorption capacity (6.27 mg/g) of the zeolite occurred with initial HDTMA concentration (243.80 mmol/L) and adsorption temperature of 25.21^oC as predicted by the Design Expert software version 7 used for the work. The surfactant modification of the surface of zeolite A reversed the negative charges on the framework to positive and allowed the adsorption of oxyanions such as nitrates and phosphates. The results indicated a reduction in the BET surface area of HDTMA modified zeolite A from 65 to 46.72 m^2/g and 62.27 m^2/g for phosphate loaded zeolite A and nitrate loaded zeolite A based fertilizers respectively. Conventional NPK 15:15:15 and the NPK loaded zeolite A based fertilizer were applied on tomato crop. The result of a higher leaf count (growth parameter) of zeolite A based fertilizer with mean (54.2) compared with NPK 15:15:15 with mean (25.7) at 11 WAT indicated the slow release property and nutrient retention of zeolite A based fertilizer. The zeolite A based fertilizer treated plants had a higher fruit yield with mean (84.69) compared with NPK 15:15:15 fertilizer with mean (69.34).

Keywords: Zeolite A, Surfactant Modified Zeolite A, Optimization, Zeolite A based slow release fertilizer, Plant growth, fruit yield.

INTRODUCTION

The application of excessive high soluble inorganic fertilizers has resulted to agronomic and pollution problems (Rahman and Zhang, 2018). Zeolite based slow release fertilizers signify an endeavour to answer the drawback of low nutrient retention capacity and nutrient leaching which causes low crop yields and soil contamination. Zeolites are hydrated crystalline aluminosilicates of alkali and alkaline earth cations with 3 – dimensional framework channelled by pores and channels (Notario del Pino *et al*., 1995). The negative charge framework of zeolites creates the prospect for surface modification of zeolites by functional groups such as cationic surfactants. This surface functionalization of zeolites improves its activity in the sorption of anionic species (Thirunavukkarasu and Subramanion, 2014). Baniswal *et al*. (2006) reported the use of modified synthetic zeolite in environmental applications especially for the adsorption of anionic nutrients such as phosphate, nitrate and nitrite. Surfactant modified zeolites (SMZ) have been known for high sorption capacity for phosphates, nitrates, sulphates, and chromates (Li *et al*., 1988). Studies on zeolites are increasing because of their high cation exchange capacity which subsequently increases the fertility of the soil. They are also used as inexpensive carriers of plant nutrients because of their slow release property (Ramesh *et al*., 2015). Baniswal *et al*. (2006) observed that the phosphorous released from fertilizer loaded SMZ was available even after 1080 h of continuous percolation whereas phosphorous release from KH_2PO_4 was exhausted in 264 h. The result suggests that SMZ could be used as carriers for slow release fertilizers (SRF) to control phosphate release.

Jakkula *et al*. (2011) reported that synthetic phillipsite had a high affinity for ammonium ion when it was used as a soil amendment compared to natural phillipsite.

Synthetic phillipsite could be a potential slow release fertilizer due to its high selectivity and high affinity for ammonium ion.

Li (2003) also reported using surfactant-modified zeolite (SMZ) as fertilizer carrier to control nitrate release. Results indicated that the adsorption of nitrate by SMZ increased as the HDTMA loading on SMZ increased. The result further showed that 30 – 40 % of adsorbed nitrate still remained on SMZ after 100 pore volumes of distilled water was used to desorb the nitrate from SMZ. The result indicate that slow release of nitrate is achievable.

Li and Zhang (2010) reported the practicality of using SMZ as fertilizer additives to control sulphate release in batch and column leaching experiments. Batch results indicated an almost instantaneous and partially reversible sulphate release while 70 % and 85 % of the loaded sulphate was still remaining on SMZ modified to 150 % and 200 % external cation exchange capacity (ECEC) respectively. The initial sulphate concentration of leachate was reduced by a factor of three.

Tomato is grown in low fertile soils in Nigeria because of continuous cropping with no added inputs to enhance soil fertility (Mofuka *et al*., 2007). FAO (2012) reported the yield level of tomato in Nigeria with a mean of 3.91 t ha^{-1} in comparison to producing countries like Ethiopia and Niger Republic with a mean yield of 7.11 t ha^{-1}. Past researches on the effect of NPK zeolite based SRF on plant growth, fruit yield and soil nutrient efficiency on tomato crops focused only on the natural forms of zeolite, natural zeolite use as soil amendment and the use of one variable at a time (OVAT) experimental design in the synthesis of zeolite from kaolin. However, this paper reports the optimized surfactant modified zeolite A synthesis from kaolin and the effects of NPK loaded zeolite A based SRF on tomato growth and fruit yield.

MATERIALS AND METHODS

Preparation of hexa-decytrimethyl ammonium bromide (HDTMA) modified zeolite

Zeolite A was produced from Ahoko kaolin through a process of metakaolization, gel formation and zeolitization by hydrothermal method as reported by Salako *et al*. (2017). The surfactant modified zeolite A samples were prepared according to a procedure described by Schick *et al*. (2010) by treating 5 g of raw zeolite A by 25 mL of 25 – 299 mmol/L surfactant (HDTMA) solution at temperature between 60 to 120 ºC for a period of 8 to 24 h using a central composite design. The mixture was continuously stirred at 150 rpm to achieve equilibrium. After filtration, the sample was washed with 50ml distilled water to remove the excess HDTMA and it was thereafter dried at 70 ºC overnight. Table 1 shows the experimental design matrix for the adsorption of HDTMA on zeolite A.

Table 1: Experimental design matrix of the adsorption of HDTMA on zeolite A

Std	HDTMA conc mmol/ kg	Temperature ºC	Contact time (h)	Adsorption Capacity (q) mg /kg
1	81.3	25	8	3.75
2	243.9	25	8	5.95
3	81.3	65	8	0.5
4	243.9	65	8	2
5	81.3	25	24	0.5
6	243.9	25	24	5.25
7	81.3	65	24	0.35
8	243.9	65	24	2
9	25.87	47.5	16	1.95
10	299.33	47.5	16	5.85
11	162.6	25	16	7.55
12	162.6	85.34	16	1.3

Std	HDTMA conc mmol/ kg	Temperature ºC	Contact time (h)	Adsorption Capacity (q) mg /kg
13	162.6	47.5	2.55	0
14	162.6	47.5	29.45	0.6
15	162.6	47.5	16	1.1
16	162.6	47.5	16	0.7
17	162.6	47.5	16	1.35
18	162.6	47.5	16	0.6
19	162.6	47.5	16	1
20	162.6	47.5	16	1.25

The central composite design which is significant for its five factor levels is a tool in Response Surface Methodology obtained from Design Expert software version 7, Stat-Ease Incorporation, Minneapolis, USA. The experimental matrix was generated from three independent variables comprising of concentration of HDTMA, adsorption temperature and contact time to give a total of 20 experimental runs in a standard order as shown in Table 1. Response surface methodology is a statistical approach used to maximize the adsorption process by optimization of operational variables. The interactive effects of the adsorption process were also determined by this statistical technique.

Phosphate and nitrate loading on surfactant modified zeolite A

KH_2PO_4 was used as the reagent to carry out ion exchange for phosphate on surfactant modified zeolite A. 25 mL of KH_2PO_4 solution was added to 5 g of surfactant modified zeolite A and stirred continuously at 150 rpm in a conical flask for 16 h at room temperature as also reported by Jakkula *et al*. (2011). 1 mole of ammonium nitrate solution was added to 5 g for of HDTMA modified zeolite A in a 250 ml conical stoppered flask. The mixture was placed in a mechanical shaker and agitated at 150 rpm for 16 h. Each of the solutions was filtered and washed with 50 ml of distilled water to wash off the excess soluble nutrients loaded on the extra lattice framework and dried at temperature of 40 ºC for 24 h (Zhaohu *et al*., 2013). The phosphate and nitrate loaded zeolite A were blended to give the NPK loaded zeolite A based slow release fertilizer.

Samples of zeolite A and HDTMA modified zeolite A were analysed with the Perkin Elmer 100 Fourier Transform Infra-red (FTIR) Spectrometer model "Spectrum Two" to identify functional groups. 0.005 g of each sample was placed directly under the FTIR probe and scanned. Spectra corresponding to each individual sample were collected after the peaks were smoothened.

The zeolite A and the modified zeolite A samples for the Brunnauer, Emmett and Teller (BET) analysis were degassed under vacuum at 250 ºC for 3 h to remove any residual moisture. They were then placed in a sample holder for the adsorption of nitrogen gas on the surface of the solid at 77 K. Surface areas were estimated using the multipoint BET fit at relative pressures < 0.1.

Evaluation of the effects of zeolite A based slow release fertilizer application on growth and fruit yield of tomato (*Lycopersycum esculentum*) in pot experiment.

A pot experiment was conducted to evaluate the efficacy of the synthesized zeolite A based fertilizer on the growth and fruit yield of two cultivars of tomato (Roma VF and UC82B). Treatment consists of four levels each of the synthesized zeolite A based fertilizer, and NPK 15:15:15 fertilizer laid out in completely randomized design (CRD) with three replications. Soil samples were initially collected from a depth of 0 - 20 cm, processed and subjected to physico-chemical analysis. The tomato seeds were initially sown in germination trays and later transplanted into pots 3 week after sowing the seeds. Application of the synthesized zeolite A based fertilizers and NPK 15:15:15 at four levels of treatment (Soil alone 0 % as control, 0.66 g, 1.33 g, 2.66 g which is equivalent to 0, 150, 300 and 600 kg/ha) took place 5 weeks after transplanting. At 6 weeks after transplanting (6 WAT), data were recorded on growth parameters viz; number of leaves, plant height, number of fruits and fruit yield on a weekly basis. At crop maturity and following the ripening of the tomato fruit, harvesting were carried out and fruit yields on treatment basis were determined accordingly.

All data generated through the experiment were subjected to statistical analysis engaging statistical analysis software (SAS). The means were separated by Duncan's Multiple Range Test (DMRT) at 5 % level of probability.

RESULTS AND DISCUSSION

Analysis of zeolite A and HDTMA modified zeolite A. The Fourier transform infra-red spectroscopy (FTIR) was employed to understand the interaction between the zeolite and the cationic surfactant. The spectrum of the synthesized zeolites in Figures 1 and 2 showed vibrational bands with different types of functional groups present. The overall spectrum of FTIR is divided into two general regions: 4000 –1300 cm^{-1} (the functional group region) and 1300 – 400 cm^{-1} (the fingerprint region). The frequency assignment approach was used for the interpretation of the spectrum. The FTIR spectrum demonstrated that HDTMA had completely adsorbed on zeolite A surface as observed from HDTMA-Modified zeolite A in Figure 2. The absorption bands near 3488 cm^{-1} represent OH groups for the surfaces of zeolite A and HDTMA-modified zeolite A. This showed that zeolites are hydrated materials. The OH group in Figure 2 also suggests that HDTMA only adsorbs on partial surface of the zeolites. The weak absorbance of the signal near 1000 cm^{-1} for the zeolite A and HDTMA modified zeolite A in Figures 1 and 2 indicate the presence of asymmetric stretching vibration modes of internal T-O bonds in TO_4 tetrahedral (T = Si and Al) on the surface. The strong absorbance signal near 1000 cm^{-1} for the HDTMA modified zeolite A is considered as the CN group on the zeolite surface. The absorbance of the HDTMA modified zeolite located in the region below 1000 cm^{-1} might have resulted from the alkyl groups of HDTMA on the zeolite surface. It is important to note that HDTMA molecules adsorb on the external surface of the zeolite and do not react completely with all the surface hydroxyl groups because HDTMA molecules are too big to enter the internal pores of zeolite A. The net effect leads to HDTMA modified zeolite A having the positive charge on the external surface and also the negative charge on the internal pore surface.

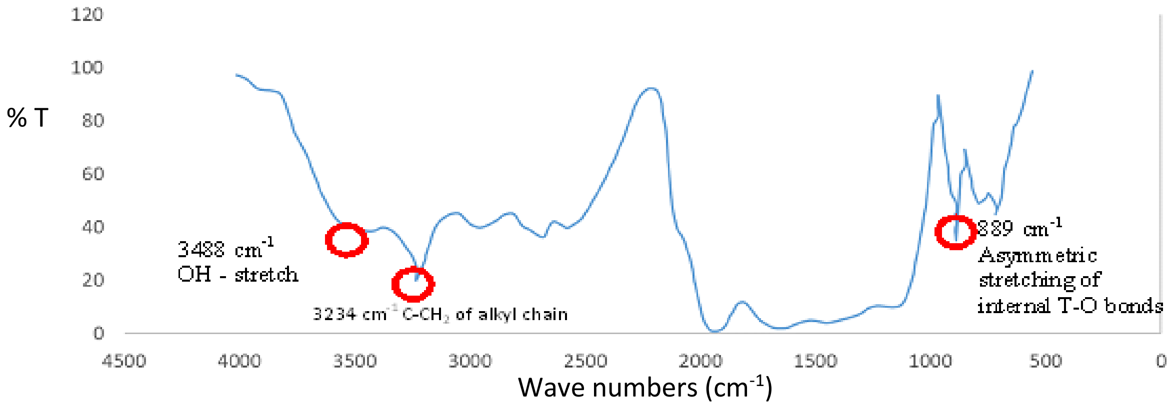


Figure 1: FTIR spectrum of the synthesized zeolite A

The bands observed at 3488 cm^{-1} and 2978 cm^{-1} in Figure 2 were attributed to symmetrical stretching vibration of C-CH_2 of alkyl chain while the band around 1404 cm^{-1} was assigned to the trimethylammonium quaternary group vibration C-$N(CH_3)_3$ (Aroke and El-Nafaty, 2014; Maina, 2016). These spectra bands could be correlated with antisymmetric and symmetric C-H stretching of the methylene group. The extra peaks suggest that the HDTMA surfactant successfully modified the zeolite surface. There was no change in band positions after modification in Zeolite A and this showed that the basic zeolite structure was kept unchanged (Aseidu, 2016).

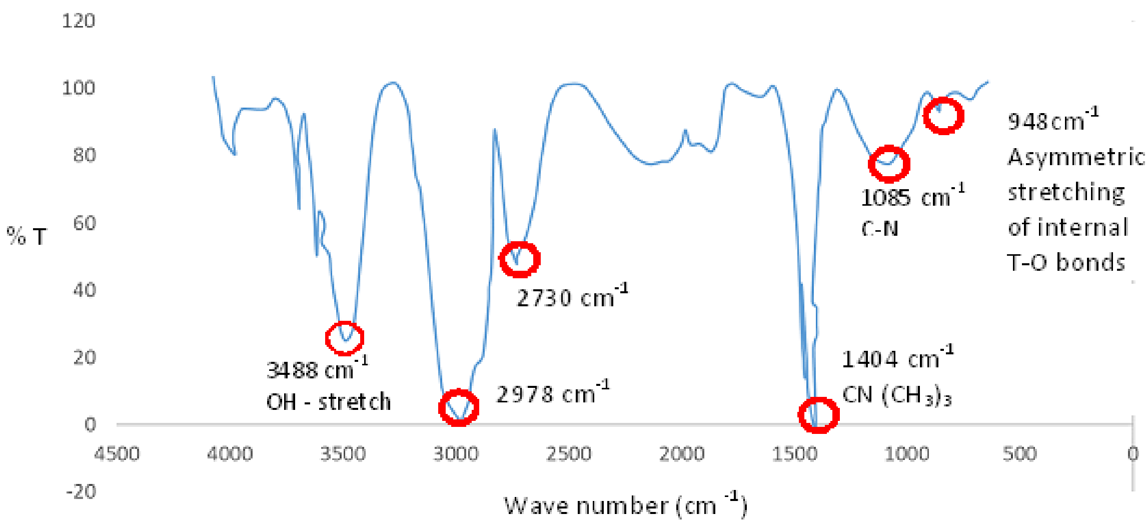


Figure 2: FTIR spectra of the HDTMA modified Zeolite A

Textural analysis by Nitrogen adsorption

Surface areas, pore volumes and pore sizes are important characteristics responsible for the description of the adsorption process in zeolites. The BET surface area analysis was performed on the synthesized zeolite A and its modification as shown in Table 2. It was observed that the specific surface areas of zeolite A reduced with HDTMA modification. Subsequent loading of phosphate ions (KH_2PO_4) and nitrate ions (NH_4NO_3) on the HDTMA-zeolite A modification reduced the surface areas further. This result is similar to the trend observed by Fungaro and Magdalena (2014) that the modified zeolites show lower total BET surface area than the unmodified zeolite. The authors further reported that the addition of the external surface area and micropore surface area gave the total BET surface area. The internal area of the zeolites was blocked and the micropore surface area decreased when the bulky molecules of the HDTMA are adhered on the external surface and pore openings of the zeolites.

Table 2: BET results of Specific surface area, Pore volume and Pore size

	Specific Surface Area (m^2/g)	**Pore Volume (cm^3/g)**	**Pore Size (nm)**
Zeolite A	296.178	0.137	0.4523
Modified Zeolite A	65.257	0.017	0.3488
Phosphate loaded Zeolite A	46.724	0.014	0.3469
Nitrate loaded Zeolite A	62.272	0.018	0.3423

Adsorption optimization using Response Surface Methodology (RSM)

The process of occluding oxyanions (phosphates and nitrates) in zeolite pores require reverting the negative surface charge of the zeolite A to positive by ion exchange mechanism to cause an intense attraction between the surfactant (HDTMA) and the zeolite A adsorbent. This adsorptive process requires optimization in the development of a zeolite based slow release fertilizer. Table 1 showed zeolite A with maximum adsorption capacity of 7.55mg/g at an initial HDTMA concentration of 162.6 mmol/kg, adsorption temperature of 25 ºC and contact time of 16 h. The statistical significance as inferred from the p- values of the model terms further provides information concerning the relationship between the adsorption capacity of zeolite A and the adsorption process variables as shown in Table 3.

Table 3: Analysis of variance (ANOVA) for HDTMA adsorption on Zeolite A

Source	Sum of Squares	Degrees of freedom	Mean square	F value	P- value	
Model	89.97	9	10.00	22.85	<0.0001	significant
A-conc.	20.32	1	20.32	46.46	< 0.0001	
B-Temp.	32.63	1	32.63	74.61	< 0.0001	
C- Contact time	0.70	1	0.70	1.60	0.2347	
AB	1.80	1	1.80	4.13	0.0696	
AC	0.91	1	0.91	2.08	0.1795	
BC	1.80	1	1.80	4.13	0.0696	
A^2	12.47	1	12.47	28.50	0.0003	
B^2	17.94	1	17.94	41.01	< 0.0001	
C^2	1.69	1	1.69	3.87	0.0775	
Residual	4.37	10	0.44			
Lack of Fit	3.93	5	0.798.83	0.0160		

The model F-value of 22.85 implies the model is significant. There is only a 0.01 % chance that a "Model F-Value" this large could occur due to noise. The values of "Prob > F" less than 0.0500 indicate that the model term significantly influence the adsorption capacity of zeolite A. Table 3 shows A, B, A^2, B^2 as significant model terms. The p-values greater than 0.0500 indicate the model terms do not significantly influence the adsorption capacity**.** The "Lack of Fit, F-value" of 8.83 implies the Lack of Fit is significant which indicates that the model does not fit all the experimental data. There is only a 1.60 % chance that a "Lack of Fit F-value" this large could occur due to noise. The guiding rule is that lack of fit should be low for a model to fit. The coefficients in Equation 1 were evaluated and the p-values showed that linear coefficients A and B were more significant than their quadratic terms and interractive terms. The regression model representing the adsorption process of HDTMA on zeolite A was found to fit into the second order polynomial equation as shown in Equation 1.

$$q = 1.01 + 1.22A - 1.55B - 0.23C - 0.48AB + 0.34AC + 0.48BC + 0.93A^2 + 1.12B^2 - 0.34C^2 \quad (1)$$

where q is the adsorption capacity.

Given that A = HDTMA concentration, B = Adsorption temperature and C = Contact time. Equation 1 is valid within the range of HDTMA concentration of 25.87 to 299.33 mmol/kg, Adsorption temperature of 25 – 65 ºC and contact time of 2.55 to 29.45 h

The adequate precision measures the signal to noise ratio. Patil and Deng (2009a and b) reported a statistical analysis that showed a ratio greater than 4 was desirable. The ratio of 15.194 obtained with the model indicated an adequate signal. The model can therefore be used to navigate the design space. The coefficient of determination (R^2) with value 0.9536 obtained for the model indicated that only 95.36 % of the experimental data are well represented within the range of the study. The optimized conditions obtained from the Design Expert software were suitable for the various types of adsorption process carried out. The value of coefficient of variation (CV) of 30.37 indicated a better precision and reliability of the experimental runs (Karmakar and Ray, 2011).

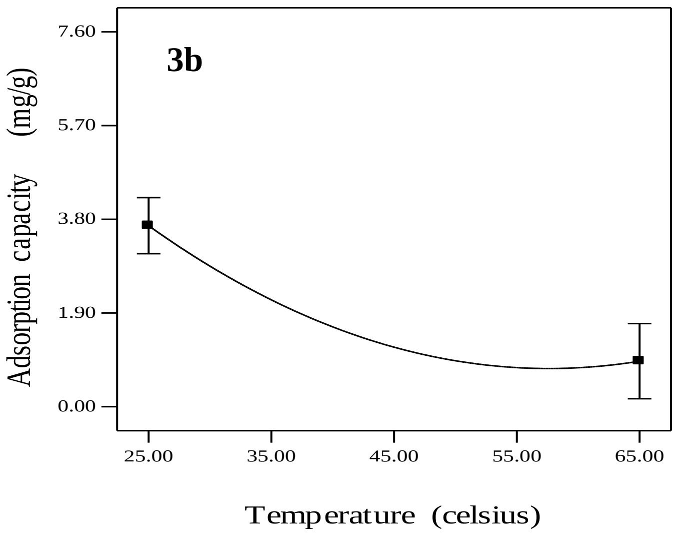
Table 4: Statistical model parameters for the adsorption of HDTMA on Zeolite A

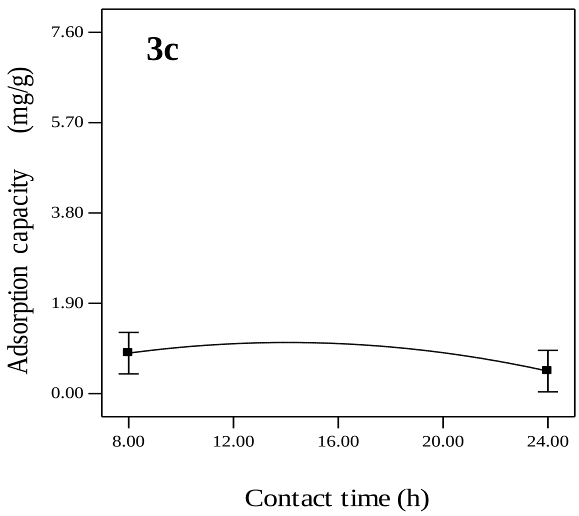
Standard deviation	**Mean**	**C.V. %**	**PRESS**	**Pred R-Squared**	**Adj R-Squared**	**R-Squared**	**Adeq Precision**
0.66	2.18	30.37	31.59	0.6652	0.9119	0.9536	5.194

The "Predicted R-Squared of 0.6652 is not as close to the Adjusted R-Squared of 0.9119 as one might normally expect. This may indicate a large block effect with the model.The smaller the value of the predicted error sum of squares (PRESS) with value of 31.59, the better the model's precision in predicting responses in a new experiment (Musyoka *et al*., 2012).

The main effects of HDTMA concentration, temperature and contact time on adsorption capacity of Zeolite A

The observation shown in Figure 3a revealed that as the concentrations of HDTMA increased from 81.3 - 243.90 mmol/kg, the adsorption capacity of zeolite A also increased from 0.72 – 3.16 mg/g indicating a positive effect on adsorption capacity. This trend is similar to Demircvi and Saygili (2014) who reported that HDTMA sorption percentages on vermiculite, perlite, and zeolite clays increased with increasing initial concentration of HDTMA. It was also observed in Figure 3b that as temperature increased from 25 to 65 ^{o} C, the adsorption capacity of zeolite A decreased from 3.68 to 0.58 mg/g. Thus increase in temperature had a negative effect on adsorption capacity of zeolite A. This trend is similar to that of Jin *et al*. (2008) who reported that though the optimum temperature was found to be 25 ^{o}C, there was variation of adsorbed methylene blue with increasing temperature for SDS – modified zeolite. Figure 3c showed the plot of adsorption capacity and contact time. It was observed that there was a slight increase in adsorption from 8 to 13.78 h and thereafter a noticeable decrease in adsorption capacity as contact time increased from 16 to 24 h. The reduced adsorption capacity at higher HDTMA concentration may have been as a result of excess, loosely bound HDTMA from admicelles on the organo-zeolite into the aqueous solution (Haggerty and Bowman, 1994).





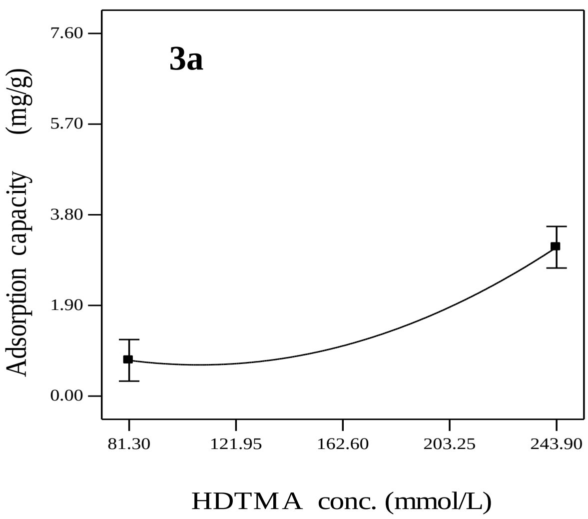


Figure 3(a, b and c): Main effects of HDTMA concentration, Temperature and Contact time on adsorption capacity of zeolite A

Effect of interactive variables on adsorption capacity of zeolite A

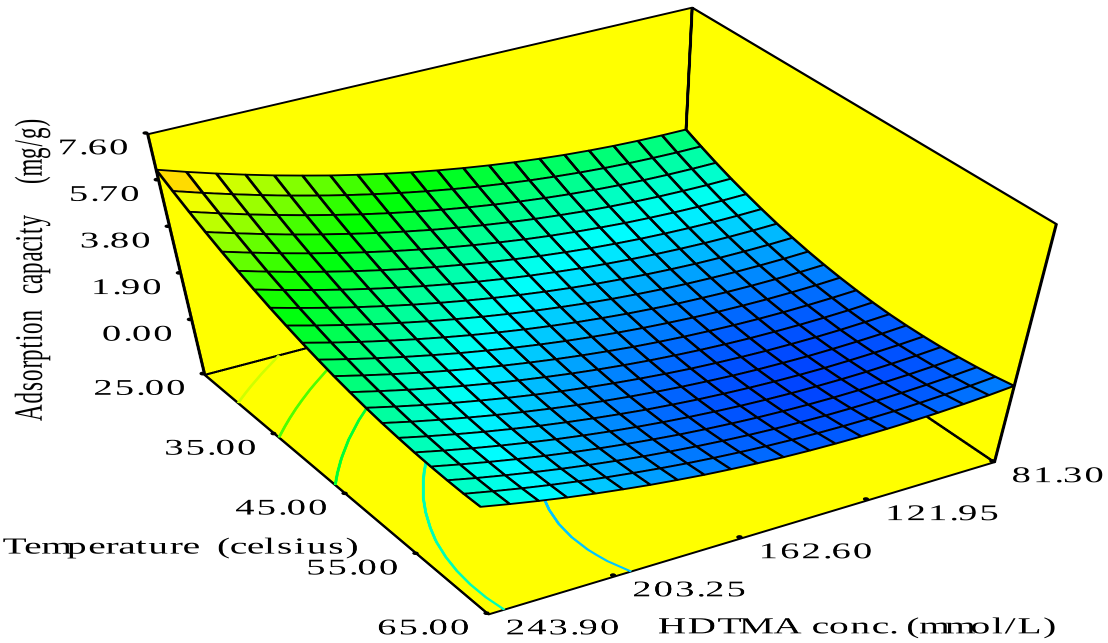


Figure 4a: 3D response surface plot of the interactive effect of temperature and HDTMA concentration on the adsorption capacity of zeolite A

Figure 4a shows the relationship between adsorption capacity, temperature and concentration of HDTMA on zeolite A. The 3D plot showed that as temperature increased from 25 to 65 ^{o} C and concentration of HDTMA increased from 81.30 to 243.90 mmol/L, there was a general increase in the adsorption capacity of zeolite A. The maximum adsorption capacity was 6.27 mg/g when the HDTMA concentration was 243.80 mmol/L and temperature was 25.21 ^{o} C.

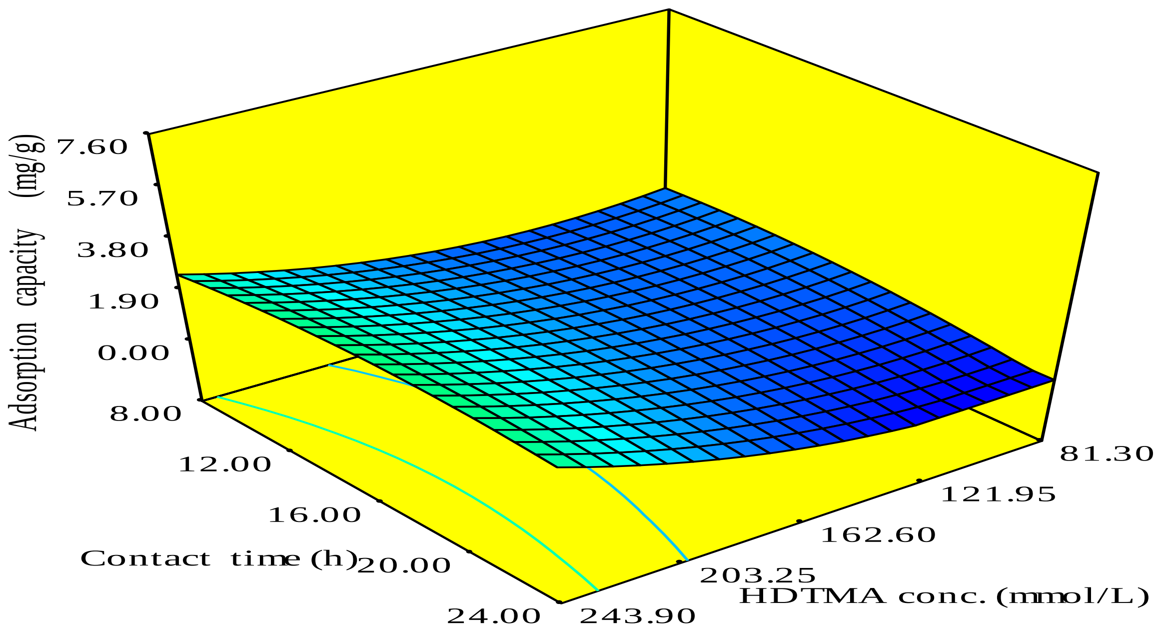


Figure 4b: 3D response surface plot of contact time and concentration of HDTMA on the adsorption capacity of zeolite A

Figure 4b showed the interactive effects of contact time and HDTMA concentration on adsorption capacity of zeolite A. The response surface plot shows that as contact time increased from 8 to 24 h, the adsorption capacity of zeolite A decreased simultaneously as the HDTMA concentration increased from 81.30 – 243.90

mmol/L. The maximum effect of these two variables resulted to an adsorption capacity of 2.59 mg/g when HDTMA concentration was 243.75mmol/l and contact time was 8.15 h.

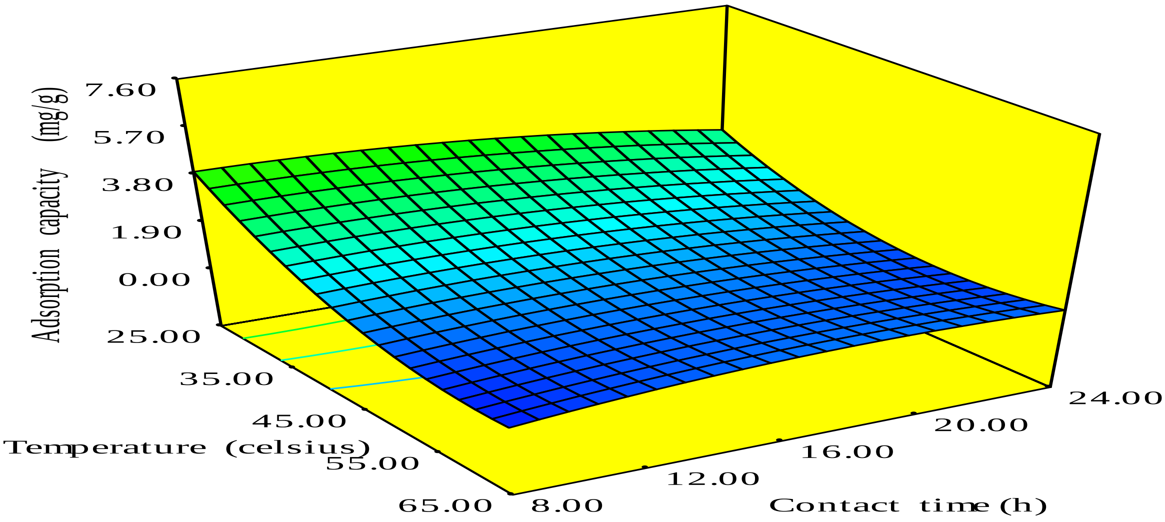


Figure 4c: 3D response surface plot of the interactive effect of contact time and temperature on the adsorption capacity of zeolite A

Figure 4c shows the interactive effects of constant time and temperature on the adsorption capacity of zeolite A. It was observed that as temperature increased from 25 to 65 ^oC, the adsorption capacity reduced as contact time increased from 8 to 24 h. However, it was observed that the maximum interactive effect of the two variables gave an absorption capacity of 4.02 mg/g when contact time was 8.05 h and temperature was 25.09 ^{o}C.

Evaluation of the effects of zeolite A based slow release fertilizer on growth and fruit yield of tomato.

The evaluation of the synthesized NPK-loaded-surfactant-modified zeolite A based fertilizer on two varieties of tomato crop in a completely randomized design to determine their effects on the growth parameters such as the leaf count, plant height, fruit count and fruit yield as presented in Tables 5 to 8.

Effect of varieties, fertilizer sources and rates of fertilizer application on the leaf count of tomatoes for 5 -11 weeks after transplanting (WAT)

In Table 5, it was generally observed that the mean of UC82b variety were higher than the Roma VF variety in the leaf counts from 5 to 10 weeks after transplanting. However, there was no significant difference between the leaf counts of the two varieties. There was generally an increase in the number of leaves from week 5 to 9 with respect to the two fertilizer sources; however, there was generally a drop in the leaf counts from 10 and 11 WAT. This trend might be traceable to the fact that the plant diverts nutrients to the development of the fruits. Interestingly, at the 11 WAT, the zeolite A based fertilizer treated plants were observed to have greener leaves than the plants treated with NPK fertilizer. The mean values of zeolite A based fertilizer treated plants were found to be significantly different from the mean values of the plants treated with NPK fertilizer. It was further observed that the leaves of the plant treated with NPK fertilizer were wilting and dying. The greener leaves on the plants with zeolite A based fertilizer application indicated the presence of more nutrients retained in the soil by the zeolite A carrier in the fertilizer. The zeolite A based fertilizer released their nutrients slowly for a longer period of time than the conventional fertilizers. In the conventional NPK fertilizer, nutrient carriers or fillers have no adherence to the plant nutrients and therefore nutrients leach easily beyond the root zone with percolated water. The consequence is the cutting off of the supply of nutrients to the leaves. The rates of application were not significantly different at 150, 300 and 600 kg/ha at 11 WAT.

Table 5: Effect of varieties, fertilizer sources and rates of application on the leaf count of tomatoes for 5 -11 weeks after transplanting (WAT)

			WAT				
Treatment	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Variety(V)							
UC82b	98.70a	124.92a	131.85a	137.56a	124.54a	80.35a	41.6a
Roma Vf	96.12a	120.94a	128.39a	133.54a	123.16a	79.19a	32.2a
SE±	5.53	5.74	5.55	5.53	5.00	1.84	5.65
Fertilizer Source							
Zeolite A based fertilizer	78.33b	99.56b	107.76b	113.17a	104.38b	81. 35a	54.2a
NPK15:15;15	93.75a	122.22a	128.07a	133.19a	120.47a	82.36a	25.7b
SE±	4.51	3.36	3.25	3.13	2.94	2.37	7.44
Rate (kg/ha)							
0	86.45b	111.54b	118.29b	123.67b	110.67b	78.45abc	31.5a
150	103.04a	129.83ab	137.88a	143.17a	130.14a	83.87ab	46.58a
300	94.63a	119.38ab	127.04a	131.79ab	122.05ab	72.53c	32.21a
600	105.54a	130.96a	137.29a	143.37a	132.43a	84.25a	37.29a
SE±	6.75	7.36	7.04	6.92	6.66	2.52	6.43
Interactions							
V*F	NS	NS	NS	NS	NS	NS	NS
V*L	NS	NS	NS	NS	NS	NS	NS
F*L	NS	NS	NS	NS	NS	NS	NS
V*F*L	NS	NS	NS	NS	NS	NS	NS
CV (%)	22.92	19.03	17.43	16.60	16.86	14.51	15.09

Means with unlike letter(s) in columns or rows are significantly different at $p \leq 0.05$ by Duncan's Multiple Range Test (DMRT), NS stands for not significant

The effect of varieties, fertilizer sources, rates of fertilizer application on the plant height of tomato for 5 -10 weeks after transplanting (WAT)

The analysis of variance for plant height did not significantly differ for the two varieties (Roma VF and UC82b) from 5 – 10 WAT in Table 6 though Roma VF variety had a higher mean of 64.8 than UC82b with 63.3. The effect of the NPK fertilizer source on the plant height of tomato showed it was statistically significant only at 5 and 9 WAT and not statistically significant for 6, 7, 8, and 10 WAT. However, it was observed that at 5 WAT, zeolite A based fertilizer was not statistically different. The maximum plant height with mean of 69.53 was recorded at 7 WAT with NPK 15:15:15 beyond which the plant height decreases. The minimum plant height with mean of 44.13 was recorded at 5 WAT for zeolite A based fertilizer. The effect on plant height with rate of application showed no statistical difference at 5, 6, and 7 WAT while statistical difference was recorded at 8, 9 and 10 WAT. Generally, there was a growing trend in the plant heights from 5 -10 WAT with increase in rates of the different fertilizer application. This is expected because the proportion of fertilizers that was added per level of application was also increasing.

Table 6: Effect of fertilizer sources, rates and varieties on the Plant height of tomato for 5 -10 weeks after transplanting (WAT)

			Week After Transplanting (WAT)			
Treatment	**5**	**6**	**7**	**8**	**9**	**10**
Variety (V)						
Uc82b	45.03a	52.26a	59.15a	62.14a	62.83a	63.33a
Roma VF	45.56a	53.05a	60.64a	63.94a	64.66a	64.85a
SE±	0.83	1.04	0.96	0.83	0.98	0.85
Fertilizer Source						
Zeolite A based	44.13a	52.73a	58.56a	61.55a	67.87a	63.06a

	Week After Transplanting (WAT)					
Treatment	**5**	**6**	**7**	**8**	**9**	**10**
fertilizer						
NPK15:15:15	45.83a	50.67a	69.53a	62.03a	62.67b	62.82a
SE±	0.92	1.21	1.45	1.32	1.36	1.23
Rates (kg/ha)						
0	45.83a	53.13a	58.73a	60.97b	61.33b	61.55b
150	45.73a	53.15a	58.97a	62.34ab	63.00b	63.44ab
300	45.45a	51.84a	59.96a	63.44ab	64.48ab	65.13a
600	45.86a	52.76a	62.04a	65.42a	66.18a	66.57a
SE±	1.36	1.37	1.43	1.14	1.25	1.13
Interaction						
V*F	NS	NS	NS	NS	NS	NS
V*L	NS	NS	NS	NS	NS	NS
F*L	NS	NS	NS	NS	NS	NS
V*F*L	NS	NS	NS	NS	NS	NS
CV (%)	11.05	10.48	8.74	8.11	8.00	7.93

Means with unlike letter(s) in columns or rows are significantly different at p≤0.05 by Duncan's Multiple Range Test (DMRT)

The effect of varieties, fertilizer sources and rates of fertilizer application on tomato fruit count for 5 -10 weeks after transplanting (WAT)

It was observed from Table 7 that tomato variety, UC82b had the highest fruit count at 10 WAT with a mean value of 2.65 while Roma VF variety had a mean value of 2.53 at 10 WAT. There was no significant difference between the means of the two varieties from 5 – 10 WAT. Zeolite A based fertilizer produced the highest fruit count at 7 WAT with a mean of 2.48. The NPK fertilizer had its highest fruit count with a mean value of 2.12 at 9 WAT. The difference in mean values of the zeolite A based fertilizer to the conventional NPK fertilizers is traceable to the steady nature the zeolite A based fertilizer releases its nutrients to the plant. Leaching of plant nutrients beyond the root zone is reduced largely because the plant nutrients are occluded in the pores of the zeolite framework and they are not exposed easily as conventional NPK are mainly supported by fillers for handling purposes. It was also observed that the rate of application of 300 kg/ha which was the recommended rate for applying NPK 15: 15:15 produced the highest fruit count at 9 and 10 WAT (Isah *et al*., 2014).

Table 7 Effect of varieties, fertilizer sources and rates of fertilizer application on tomato fruit count for 5 -10 weeks after transplanting (WAT)

	Weeks after transplanting					
Treatment	**5**	**6**	**7**	**8**	**9**	**10**
Variety(V)						
UC82b	0.00a	1.02a	2.05a	2.57a	2.62a	2.65a
Roma VF	0.00a	0.32b	2.02a	2.54a	2.55a	2.53a
SE±	0.00	0.13	0.25	0.26	0.26	0.22
Fertilizer Source						
Zeolite based fertilizer	0.00a	0.59a	2.48a	2.26a	2.33a	2.36a
NPK15:15:15	0.00a	0.70a	1.83a	2.00a	2.12a	2.11a
SE±	0.00	0.24	0.26	0.22	0.27	0.23
Rates of application (kg/ha)						
0	0.00a	0.47a	1.83a	2.29a	2.22b	2.22b
150	0.00a	0.56a	2.16a	2.57a	2.52ab	2.54ab

	Weeks after transplanting					
Treatment	**5**	**6**	**7**	**8**	**9**	**10**
300	0.00a	0.83a	2.17a	2.86a	3.06a	3.05a
600	0.00a	0.94a	2.24a	2.54a	2.56ab	2.53ab
SE±	0.00	0.34	0.33	0.31	0.30	0.30
Interaction						
V*F	NS	NS	NS	NS	NS	NS
V*L	NS	NS	NS	NS	NS	NS
F*L	NS	NS	NS	NS	NS	NS
V*F*L	NS	NS	NS	NS	NS	NS
CV(%)	0.00	16.43	37.94	23.16	38.77	38.77

Means with unlike letter(s) in columns or rows are significantly different at p≤0.05 by Duncan's Multiple Range Test (DMRT)

The effect of varieties, fertilizer sources and rates of fertilizer application on tomato fruit yield for 5 -10 weeks after transplanting (WAT)

The mean values of the fruit yield of tomato variety shown in Table 8 illustrate that UC82b produced the highest fruit yield with mean value of 92.71 while Roma VF produced the lowest yield with mean value of 87.66. The mean values of the two varieties were not significantly different. It was observed that zeolite A based fertilizer produced the highest fruit yield with a mean value of 84.69. The fruit yield of NPK 15:15: 15 was lowest with a mean value of 69.34. The increase observed in zeolite A based fertilizer is traceable to its slow release property of the adsorption between the plant nutrients and the pores of the zeolite carrier. The rate of application of fertilizer (300 kg/ha) had the highest mean value of 103.57 and it was statistically different from rate of application (600kg/ha).

Table 8: Effect of varieties, fertilizer sources and rates of fertilizer application on tomato fruit yield for 5 -10 weeks after transplanting (WAT)

Treatment	**Fruit yield (g/pla**
Variety (V)	
UC82b	92.71a
Roma VF	87.66a
SE±	7.58
Fertilizer Source	
Zeolite A based fertilizer	84.69a
NPK15:15:15	69.34b
SE±	4.93
Rates of application (kg /ha)	
0	70.36b
150	97.57a
300	103.57a
600	89.25ab
SE±	12.19
Interaction	
V*F	NS
V*R	NS
F*R	NS
V*F*R	NS
CV (%)	25.30

Means with unlike letter(s) in columns or rows are significantly different at p≤0.05 by Duncan's Multiple Range Test (DMRT)

CONCLUSIONS

The study investigated the sorption of quaternary amine compound, HDTMA and oxyanions such as nitrates and phosphates on optimized zeolite A synthesised from an Ahoko kaolin using central composite design. The initial concentration of HDTMA (162.6 mmol/L) equivalent to its external cation exchange capacity (ECEC) was adsorbed to zeolite A surface by coulombic interactions. The study further evaluated the application of synthesized NPK loaded zeolite A based fertilizer and conventional NPK 15:15:15 fertilizer on the growth and fruit yield of tomato crop. Tomato crop treatments with NPK loaded zeolite A based fertilizer showed much greener leaves than the plants treated with NPK fertilizer with less green leaves at 11 weeks. This result indicates better retention of plant nutrients and the slow release property of the carrier, surfactant modified zeolite A. The fruit yield from plants treated with NPK loaded zeolite A based fertilizer also showed higher fruit yields than the plants treated with conventional NPK based fertilizer indicating that plant nutrients which might have leached beyond the root zone in the NPK fertilizer were utilized in the zeolite A based fertilizer to giver higher fruit yields.

ACKNOWLEDGEMENT
The authors appreciate the financial support of TETFUND through grant number TETFUND/FUTMINNA/2016 – 2017/6th/BRT/21.

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