

Assessment of the Effect of Hydrolysed Starch Graft Copolymers Application on Soil Nutrient (Phosphorus and Nitrogen) Retention

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Abstract: The effects of the application of the graft copolymers (Hydrolyzed starch-g-polyacrylonitrile (HSPAN) and Hydrolyzed starch-g-polyacrylic acid (HSPAA)) on the nitrogen (N) and phosphorus (P) retention capacity of soil was evaluated in this study. Soil nutrient (N and P) retention capacity tests was carried out at three graft copolymers application rates (3.0, 6.0, and 9.0g/kg soil) against a blank soil sample to which graft copolymers was not applied. Diammonium phosphate (DAP) at 0, 100, and 200mg in aqueous solution/kg soil were applied in triplicates. The soil samples were mixed thoroughly and allowed to air-dry. The residual N and P contents of the soil samples were determined and reported as the amounts of nutrients retained as a function of the graft copolymer and DAP application rates. The result of this study has clearly demonstrated the potential of the graft copolymers to alleviate problems related to nutrient loss from the soil media. Leaching of nutrients (N and P) in soil has been found to be reduced to minimal (0.46%N, and 1.13%P) with the application of hydrolyzed graft copolymer and the nutrients are thus available to plant for growth by suction pressure difference.

Keywords: Graft copolymers; starch; soil; nutrient retention; nitrogen; phosphorus

1. Introduction

World population is increasing at a geometrical rate and is estimated to reach six billion by the end of year 2050^[1]. Population growth and its effect on development of high-density urban populations, couple with attendant global industrialization, have placed undue stress on the environment, potentially threatening environmental sustainability, climate change and food security.

This however, has resulted in increasing global warming and the build up of chemical and biological toxics and pollutants in the biosphere, and in the soils and sediments^[2].

The main role of agriculture is in the provision of food supply and security. However, emerging trends indicate an increasing role with respect to soil and nutrient management and conservation.

Hydrolyzed graft copolymers are slightly cross-linked, three dimensional network polymers, which are hygroscopic and sometimes found as colloidal solutions in which water is the dispersion medium. It can absorb large volumes of liquid and retain it^[3], this is realized by increase in volume of the polymer^[4,5]

Soil application of graft copolymer will affect nutrient leaching through several mechanisms: by increasing the retention of water in the rooting zone, by directly binding or sorbing of nutrients or by interacting with other soil constituents, and by facilitating the movement of attached nutrients. These mechanisms may either increase or decrease leaching.

The use of hydrolyzed graft copolymer leads to increased water-holding capacity; and increased availability of water to plants^[6].

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Previous studies indicated that soil water and nutrient retention increases with increasing hydrolyzed graft copolymers (HGCs) concentrations. Hüttermann et al.^[7] reported an exponential increase in water and nutrient retention with increasing HGCs (0.04 to 0.40%) in sandy soil. Akhter et. al.,^[8] reported that the addition of 0.1, 0.2 and 0.3% of HGCs in sandy loam and loam soil increased the moisture and nutrient retention capacity retention at field capacity linearly and thus significantly increased plant water and nutrient availability in both soil types as compared with untreated soils. Arbona et al.^[9], in a substrate composed of sphagnum peat and perlite (80:20), observed that the addition of 0.4% HGCs increased the water and nutrient content by about 128%. In experiments with mixtures of 0.1-0.6% HGCs in sandy soil, Al- Humaid and Moflah^[10] found that the highest concentration of hydrogel prolonged the time it took for water and nutrient to be lost from the soil by about 66% with respect to the control soil.

This study therefore, is an attempt at providing solution to the nutrient leaching and drought stress condition under which plants grow in the food hub of Nigeria (particularly the recent introduction of dry season farming in Nigeria) through the application of hydrolyzed graft copolymers which would act as nutrient leaching inhibitors and water reservoir beneath the soil surface for plant use, possibly retain nutrients and also make data available on the effect of the material on Nigerian soils.

2. Materials and Methods

2.1 Materials

Reagent grade acrylonitrile was supplied by BDH, England and was distilled under reduced pressure and stored in the dark at 5oC before use. Cassava starch was obtained from cassava roots sourced locally from Benin City, Nigeria. Cerium ammonium nitrate and other reagents used were of analytical grade and were supplied by BDH, England.

2.2 Preparation and Characterization of the grafted copolymers

The preparation was done according to the method described by Fanta^[11], reported by Okieimen and co-workers^[12,13] as follows:

Gelatinized starch was prepared by constantly stirring a mixture of 5 g of dried starch with 50ml of distilled water at 75°C for 30 min. The slurry was cooled to 30oC, treated with CAN solution for 10 min and then varying concentrations of acrylonitrile or acrylic acid were added in separate reactions, and the volume of the reaction mixture was made up using distilled water. 5ml of 0.01M of N,N' methylene bisacrylamide (MBA) cross linker was added. The polymerization continued with constant stirring under nitrogen atmosphere. After 180 min., the reaction mixture warmed up to 60°C and neutralized by dropwise addition of 5% NaOH with stirring until it assumed a reddish-brown colour. The slurry was further digested at 60°C in a water bath for about 20 min, until it turned pale yellow. After cooling the slurry to room temperature, it's pH was adjusted to desired value using glacial acetic acid and it was then precipitated in excess of methanol in the case of acrylonitrile, acetone in the case of acrylic acid. The precipitate was washed with ethanol to neutrality and dried under vacuum at 70°C. The dried product was finely powdered and stored.

2.3 Characterization of hydrolyzed starch-g-P(AN) / starch-g-P(AA) copolymers

The dried powder of the grafted copolymer was added to 100ml of N,N dimethyl formamide(DMF) in a glass stoppered conical flask at room temperature while stirring on magnetic stirrer for 30h to remove the free polymer (FP). The weights of polymer after removal were calculated for the amounts of free polyacrylonitrile/polyacrylic acid. The sample was washed with ethanol and dried at 30oC. The percent graft yield (%G) and percent grafting efficiency (%GE) were calculated on an oven dry weight of starch from the increased weight of starch after grafting by using the Equations (2.7) and (2.8)^[14]

$$\% G = \frac{\text{graft copolymer wt.} - \text{initial starch wt}}{\text{initial starch wt}} \times 100 \quad (1)$$

$$\% GE = \frac{\text{Graftcopolymer wt} - \text{initial starch wt}}{\text{Total polymer wt after reaction} - \text{initial starch wt}} \times 100 \quad (2)$$

A dispersion of 2g of starch-g-P (AN)/starch-g-P(AA) in 150ml of 2M hydrochloric acid was heated under reflux for 1.5h. The insoluble polymer was separated by filtration, washed with water, and dried under vacuum at 30oC. “% add-on” in the original copolymer which is the weighted percentage polyacrylonitrile (PAN)/PAA in the grafted copolymer, was determined from the weight difference between the grafted copolymer and the soluble starch which was removed by acid hydrolysis.

$$\% \text{ add-on} = (W1 - W2)/W1 \times 100 \quad [14] \quad (3)$$

W1 = Weight of grafted copolymer

W2= Weight of soluble starch

2.3.1 Thermal Stability

Thermal gravimetric analyzer (TGA) was used to assess the stability to heat of the graft copolymers. Thermogravimetric analyses (TGA) of the starch and graft copolymers were conducted on a TGA with an auto sampling analyzer (Mettler Toledo, Switzerland) at a heating rate of 50oC/min. The thermograms were recorded over a temperature range of 0oC to 800oC in the presence of nitrogen atmosphere at a flow rate of 20ml/min.

2.3.2 Infrared analysis

IR spectrophotometer was used as a tool to follow up changes in graft reaction. Spectra of cassava starch and copolymers after grafting were recorded on a Nicolet impact 410 FTIR spectrophotometer using a KBr pellet.

2.3.3 Copolymers Morphology analysis

Starch and copolymers surface morphology were examined using scanning electron microscope (SEM). Scanning electron microscopic (SEM) studies of starch and the graft copolymers were carried out on a Leo 435 VP electron microscope Thornwood, NY). All the samples were gold plated to become conducting. Scanning was synchronized with microscopic beam for the maintenance of small size over large distance relative to the specimen. All the images were taken at a resolution of 1000X.

2.3.4 Swelling Measurement

Swelling of copolymers were measured by the free swelling method [15] and expressed as a water retention value (WRV) calculated in grams of water per grams of dry polymer. Thus, an accurately weighed quantity of the copolymers under investigation (0.1 g) was immersed in 100ml of distilled water for 30 min and allowed to stand. The swollen copolymers were then separated from unabsorbed water by screening through a weighed No. 41 filter paper in a funnel by normal gravity force. Corrections were made for the water retention of the filter paper. The copolymers were allowed to drain on the paper for 10 min and the paper was then weighed to determine the weight of water which caused swelling of the copolymers. Swelling characteristic was calculated as g/g using the following equation:

$$(g/g) = \frac{(W_2 - W_1)}{W_1}$$

Water retention value

(4)

Where, W2 and W1 are the weights of water swollen copolymers and dry absorbent in grams, respectively.

2.4 Soil Sampling and Characterization

Soil samples from surface to a depth of 30 cm were collected using auger and prepared for further analysis. All the reagents used for analysis were of analytical grade and were used without further purification

The soil samples were analysed as follows: bulk density was measured by core method^[16], Soil pH was measured in 1:1 soil-water ratio^[17]. Soil organic carbon was estimated by combustion at 840°C^[18], while total nitrogen was obtained by microKjeldahl method. Cation exchange capacity was measured using ammonium acetate leaching at

pH 7.0;^[19] . Available phosphorus was determined by Olsen method,^[20].

2.5 Soil nutrient (N and P) retention capacity tests

Soil nutrient (N and P) retention capacity tests was carried out at three graft copolymers application rates (3.0, 6.0, and 9.0g/kg soil) against a blank soil sample to which graft copolymers was not applied.

Diammonium phosphate (DAP) at 0, 100, and 200mg in aqueous solution/kg soil were applied in triplicates. The soil samples were mixed thoroughly and allowed to air-dry.

The test soil samples were packed into columns (1.5cm x 150cm) dry tampered to ensure uniform packing and eluted with deionized water five times the water retention capacity of the soil. The columns were allowed to drain dry and the soil samples removed and air dried. The residual N and P contents of the soil samples were determined and reported as the amounts of nutrients retained as a function of the graft copolymer and DAP application rates^[21]

3. Results and Discussion

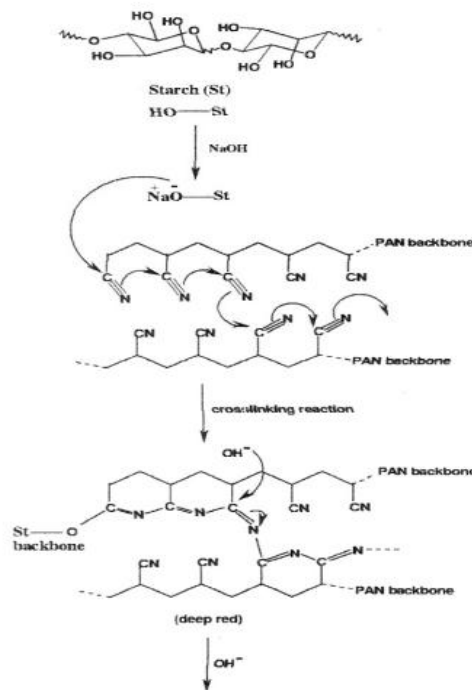
3.1 Characterization of the grafted copolymer

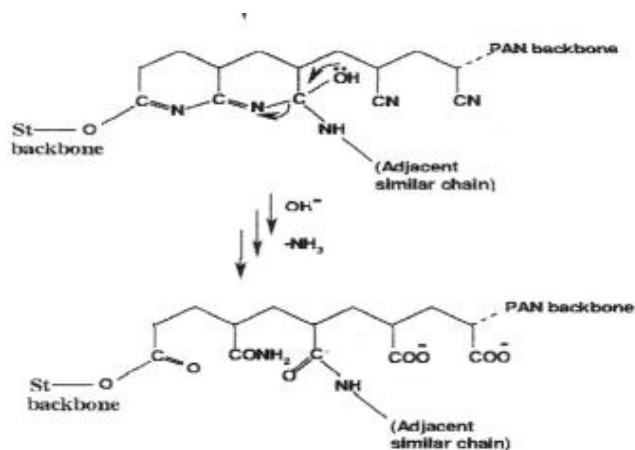
The results of the proximate analysis of the cassava starch, grafting characteristics, spectral and scanning characterization have been previously reported

Parameters	Starch-g-polyacrylonitrile (HSPAN)	Starch-g-polyacrylic acid (HSPAA)
Colour	White	White
Water Retention Value (g/g)	382	480
Water Soluble	No	No
Dimension (μm)	150-350	150-350
Density (g/cm^3)	1.5	1.54
Thermal Stability ($^{\circ}\text{C}$)	250-300	200-250
pH	8.0	8.0
Graft Yield (%)	92.2	86.96
Graft Efficiency (%)	88.55	70.82

Table 1. Characteristics of the starch graft copolymers

Figure 1 shows the mechanism of the grafting reaction between starch and poly(acrylonitrile) as well as the saponification process.





Starch-PAN hydrogel
(Light yellow)

Figure 1; Mechanism for cross-linking during the hydrolysis of the nitrile groups of the Starch-PAN mixture^[22].

The appearance of the characteristics bands of starch and the grafted polymers in the infrared (IR) spectrum is taken as the prime evidence. The graft efficiency (70.82-88.55%) may be due to the greater polarity and solubility of the monomers used in this study.

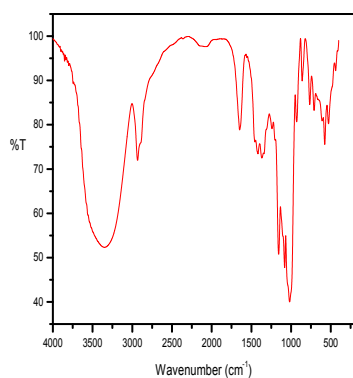


Figure 2; FTIR Spectrum of dried cassava starch.

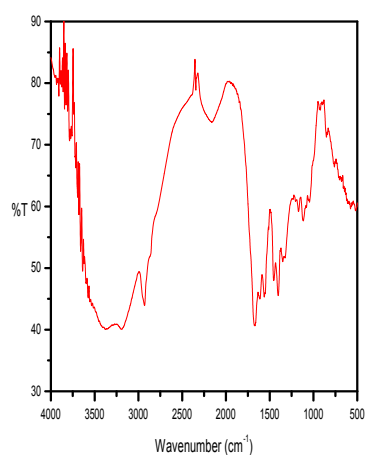


Figure 3; FTIR Spectrum of the starch-g-PAN graft copolymer.

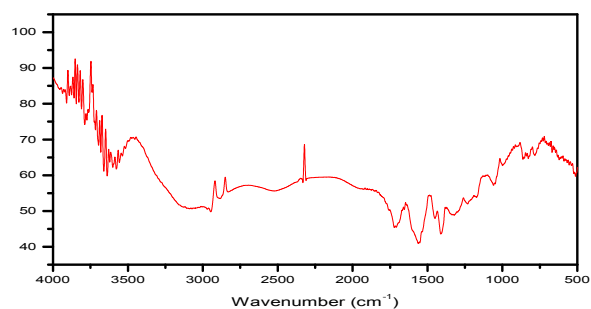


Figure 4; FTIR Spectrum of the starch-g-PAA grafted copolymer.

The IR spectrum of cassava starch in Figure 2, gives absorption bands at 3400 cm^{-1} , an –OH broad and single intermolecular polymeric band the C–H stretching at 2930 cm^{-1} (m), and C-O-C stretching in the 1,000-1100 cm^{-1} band (a triplet peak of starch), characteristic of amylose contained in the starch.

The presence of the nitrile group at 2243 cm^{-1} and the strong asymmetrical stretching at 1570 cm^{-1} and a weak symmetrical stretching at 1430-1390 cm^{-1} coupled with characteristics bands at 3400, 1000-1100 cm^{-1} for amylose contained in the starch indicated the occurrence of grafting in Figure 3. However, the appearance of the nitrile group at 2243 cm^{-1} at grafting and disappearance at alkaline hydrolysis of the starch-PAN copolymer on the other hand resulted in the carboxylate and carboxamide bands. The carboxylate group (-COONa) gave rise to two bands: a strong asymmetrical stretching band at 1570 cm^{-1} and a weak symmetrical stretching band at 1400 cm^{-1} . These peaks are attributed to C=O stretching in the carboxamide functional groups, and symmetric and asymmetric stretching modes of the carboxylate groups, respectively^[23].

The absorption peaks at 2924 cm^{-1} and 1018 cm^{-1} , figure 3, are due to C-H stretching and bending vibrations respectively. The absorption peaks at 1647 cm^{-1} are due to O-H bending vibrations in original sample. The additional peaks were observed in FTIR spectra of grafted sample at 1427 cm^{-1} and 1155 cm^{-1} due to C-H and C-O stretching respectively. It has been observed that the absorption peaks shift towards low intensity. These additional peaks confirmed the grafting of Poly(AA) sample onto cassava starch backbone.

The graft copolymers were characterized by scanning electron microscopy (SEM) and thermogravimetric analyzer (TGA). The granule sizes of the graft copolymers were large, the surfaces were rough, and the shape changed compared with the ungrafted starch. The SEM of starch-g-polyacrylonitrile (HSPAN) and starch-g-polyacrylic acid (HSPAA) showed that the polyacrylonitrile and polyacrylic acid respectively were grafted both on the surface and in the interior of the granules (Plates 1-3).

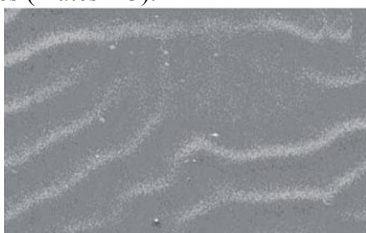


Plate 1: Scanning electron microscope (SEM) picture of the Cassava starch

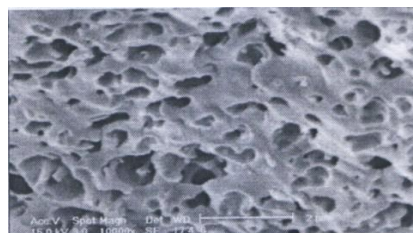


Plate 2: Scanning electron microscope (SEM) picture of the hydrolyzed starch-g-poly(acrylonitrile)



Plate 3: Scanning electron microscope (SEM) picture of the hydrolyzed starch-g-poly(acrylic acid)

The graft copolymers showed thermal stability up to 200oC-300oC. The thermal stability of the starch graft copolymers were higher compared with the ungrafted starch.

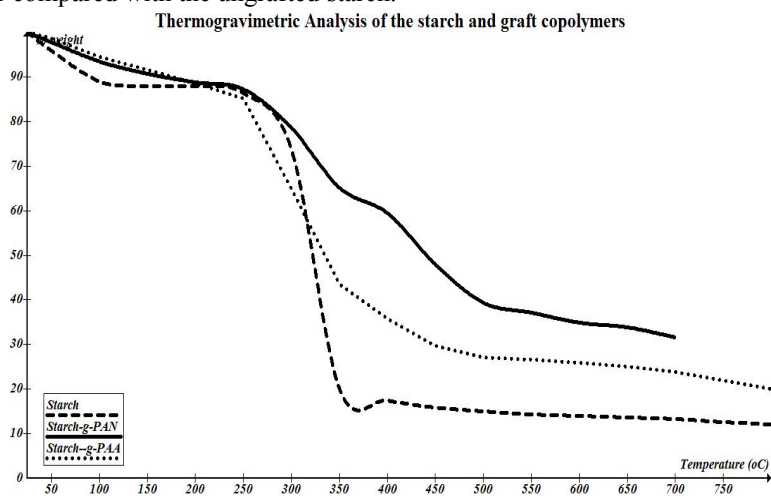


Figure 5; Thermogravimetric analyzer (TGA) results of the starch and the graft copolymers

The TGA of starch-g-poly(acrylonitrile) and starch-g-poly(acrylic acid) copolymers (Figure 4) indicated that grafting lowers the initial decomposition temperature of starch^[24]. An increase in percentage of graft add-on in the copolymers led to an overall improvement in the thermal stability.

3.2 Physico-chemical properties of the Soil

Table 2 shows the some of the physical characteristics and Table 3, the chemical characteristics of the experimental soil

Analytical characteristics	Results
Particle size distribution (%)	Clay 16.38 Silt 14.40 Sand 69.22
pH	8.10±0.01
Bulk Density (g/cm ³)	1.33±0.02

Table 2. Result of physical characterization of the soil sample before planting

Analytical characteristics	Results
Soil organic carbon, g/kg	0.544±0.05
Total Nitrogen, (%)	0.750±0.008
Cation exchange capacity,mg/kg	286.02±0.92
Phosphorus, mg/kg	186.32±0.01
Sodium content, mg/kg	7.18±0.07

Potassium content, mg/kg	2.70±0.05
Magnesium content, mg/kg	67.63±0.25
Calcium content, mg/kg	208.51±0.55
Lead (mg/Kg)	0.05
Cadmium (mg/Kg)	ND
Arsenic(mg/Kg)	ND
Copper (mg/Kg)	0.002
Total acidity	0.2

Table 3. Result of chemical characterization of the soil sample

ND = Not Detected

Preliminary visual inspection showed that the soil was dark grey in colour indicating a low amount of humus. Colour is one of the characteristics of soil, which tells much about the origin of the soil and its composition^[25]. Textural analysis showed the preponderance of sand fraction (69.22%), followed by clay (16.38%), then silt (14.40%), thus classifying the soil as sandy loam soil. Sandy soils are known to have a poor retention capacity for both water and metals because they have more macropores. Soil texture has implications in irrigation of field crops. The slightly alkaline pH 8.10 recorded for the soil is within the range of agricultural soils. The soil pH is an indication of the soil's acidity or alkalinity. The soil pH (8.1) can also be interpreted in terms of the very low level of total acidity (0.2).Which

means low presence of hydrogen ions in the soil.

The soil bulk density (1.33g/cm³) is an indication of the textural nature of the soil. It is useful in estimating the differences in compaction of a given soil. The bulk density as recorded shows a high tendency for free flow/percolation and draining of water through the light soil, in other words, the water retention capacity of the soil is low. This is typical of sandy soil.

The soil had an average cations exchange capacity (CEC) of 286.02mg/kg. The CEC parameter particularly measures the ability of soils to allow for easy exchange of cations between its surface and the solution. The relatively low levels of silt, clay and average level of CEC indicate the high permeability, hence leachability of nutrients and heavy metals in the soil and suggest that it might be amenable to remediation by use of the hydrolyzed graft copolymers (HGCs)^[26,27].

However, the rate of decomposition of organic matter in soil usually depends on the amount of nitrogen present^[28]. The total nitrogen recorded in the soil is given as 0.750%, indicating the low level of humus in the soil assessed by the carbon, nitrogen ratio and the high rate of organic matter decomposition in the soil. Nitrogen is the key nutrient in plant growth and productivity. It promotes vegetative growth, making tissues more tender and succulent and plants healthier.

Phosphorus is second to nitrogen in importance in plant nutrient. The phosphorus recorded of the soil (186.32 mg/kg) gives the level of phosphorus present in the soil. Soil phosphorus unfortunately, is largely of very low solubility and therefore not readily available to plants. Phosphorus plays a role in cell division, stimulates root growth, and hastens plant maturity.

The effects of the application of the graft copolymers (Hydrolyzed starch-g-polyacrylonitrile (HSPAN) and Hydrolyzed starch-g-polyacrylic acid (HSPAA)) on the nitrogen (N) and phosphorus (P) retention capacity of the soil are shown in Figures 6-12.

3.3 Assessment of nutrient retention by the hydrolyzed graft copolymers in unfertilized soil

Figure 6 and 7, showed the amount of N and P retained in the soil after the leaching test was done and the results were significantly high (>90%) and increases with increase in the application rate of the graft copolymers^[29]. Karimi and Naka^[30] observed that by using a Japan made super absorbent copolymer, nutrient (NPK) retention increase according to the application rates.

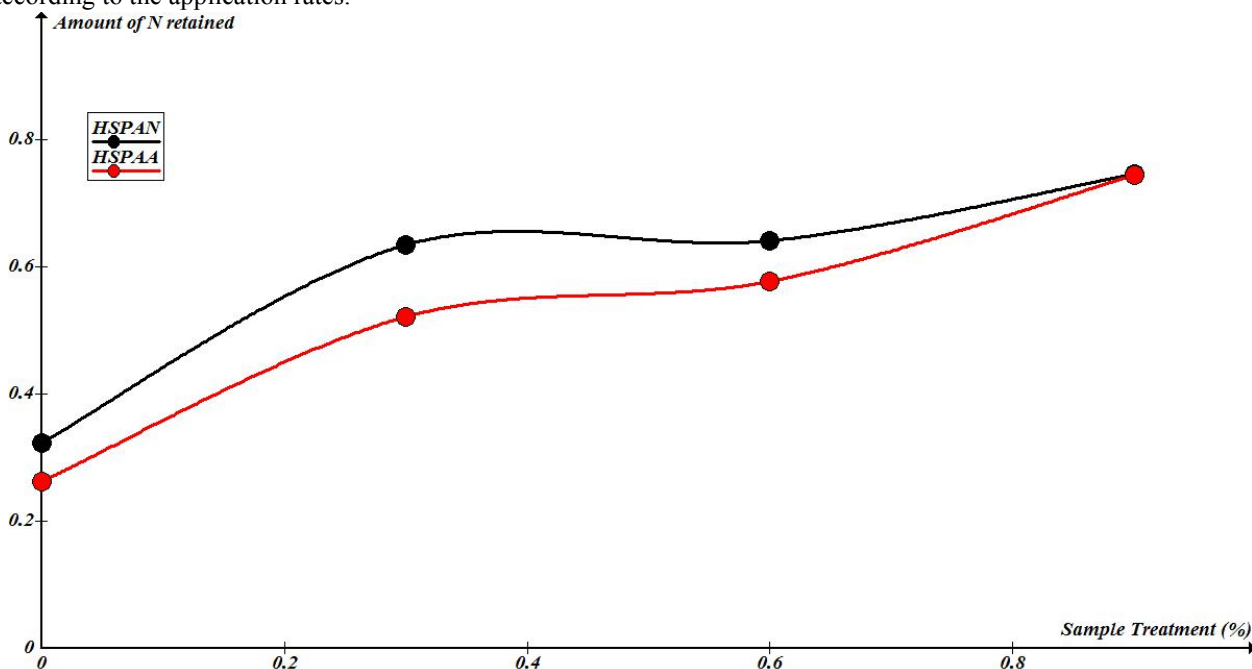


Figure 6; Variation in the amount of N retained by HSPAN and HSPAA in unfertilized soil.

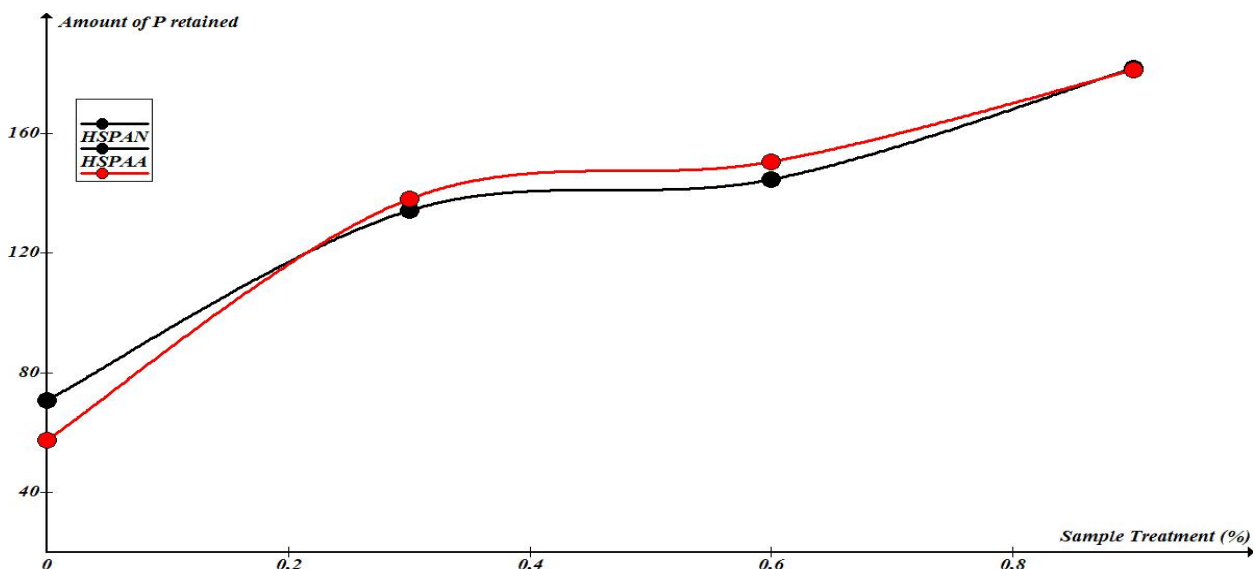


Figure 7; Variation in the amount of P retained by HSPAN and HSPAA in unfertilized soil.

The results indicated that application of graft copolymer to soil is associated with enhanced N and P retention in soil. Increased retention of nutrients in the soil profile should increase the probability that the nutrients will be taken up by plants roots and decrease the risk that they will be leached and transported to surface or groundwater reservoir^[21]. The net impact of these processes should be; increased nutrient use efficiency, which in turn should reduce the need for fertilizer and lime amendments in production agriculture and improve water quality^[31].

3.4 Assessment of nutrient retention by the hydrolyzed graft copolymers in Diammonium phosphate fertilized soil

The effects of graft copolymer application on the retention capacity of N and P in DAP fertilized soil are shown in Figures 8 and 9. The results in Figure 3 to 6, show that the retention capacity of N in the fertilized soil increased as the application rate increases. The retention capacity was higher for HSPAN (99.32%) than for HSPAA (97.46%). The results were of the same trend at both the 100mgDAP/kg and 200mgDAP/kg. The retention capacity of P is higher in the case of HSPAA than for HSPAN.

The enhanced efficiency of the HGCs for nutrient retention may be explained in terms of their excellent ability to absorb large volume of water^[22]. When graft copolymers are loaded with fertilizers placed in contact with water by chemical potential differences (chemical spontaneity), the water molecules tend to diffuse into the polymer matrix through the interaction mainly with the hydroxyl groups, resulting in a chemical competition between the fertilizer chemicals and the water within the matrix.

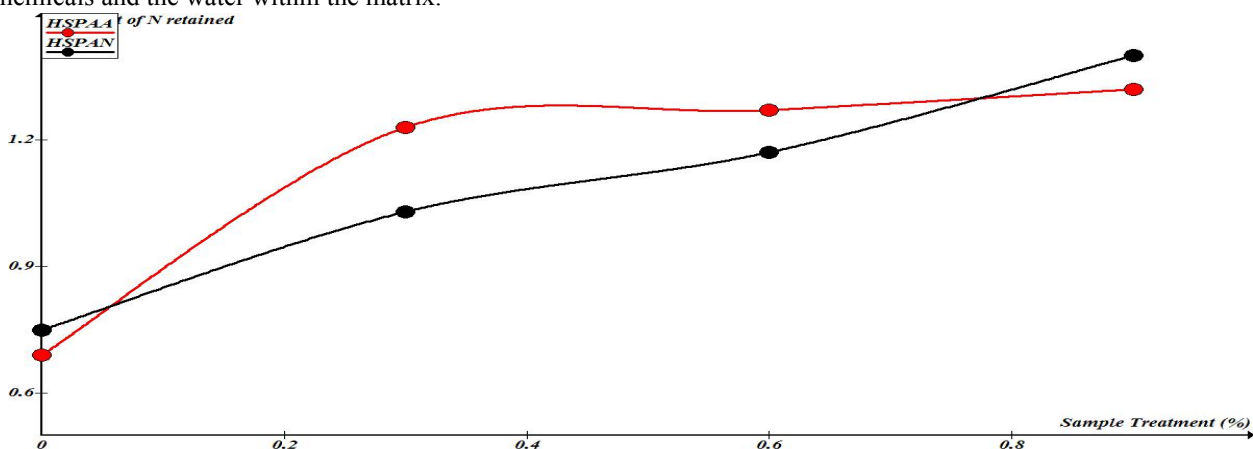


Figure 8; Variation in the amount of N retained by HSPAN and HSPAA in 100mg DAP fertilized soil.

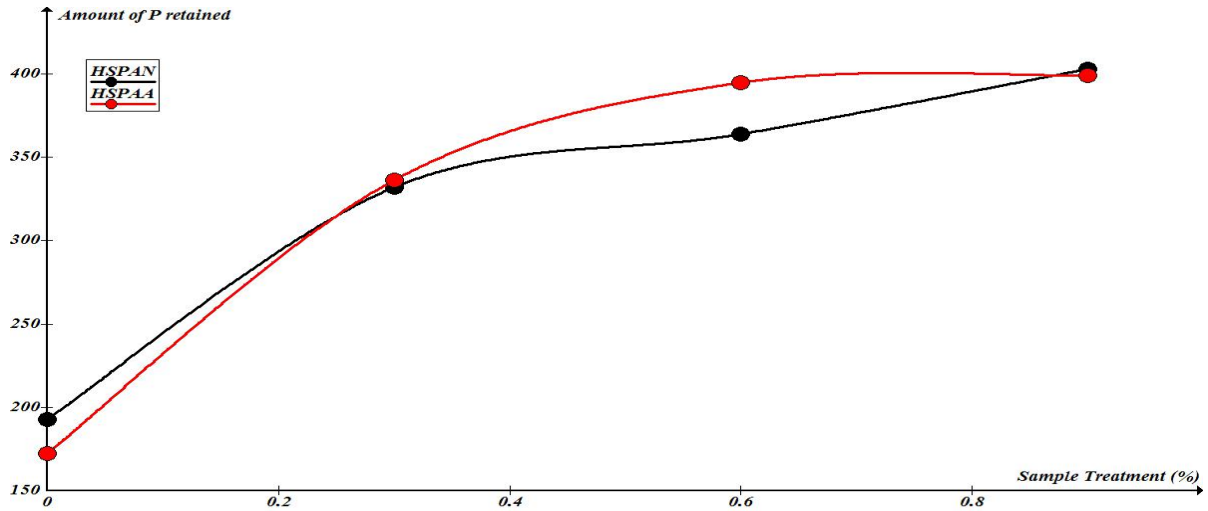


Figure 9; Variation in the amount of P retained by HSPAN and HSPAA in 100mg DAP fertilized soil.

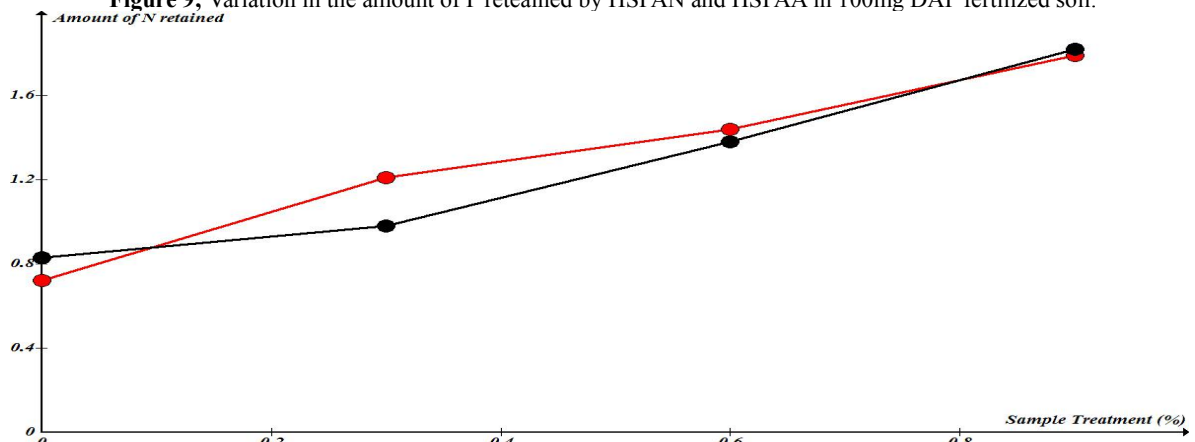


Figure 10; Variation in the amount of N retained by HSPAN and HSPAA in 200mg DAP fertilized soil.

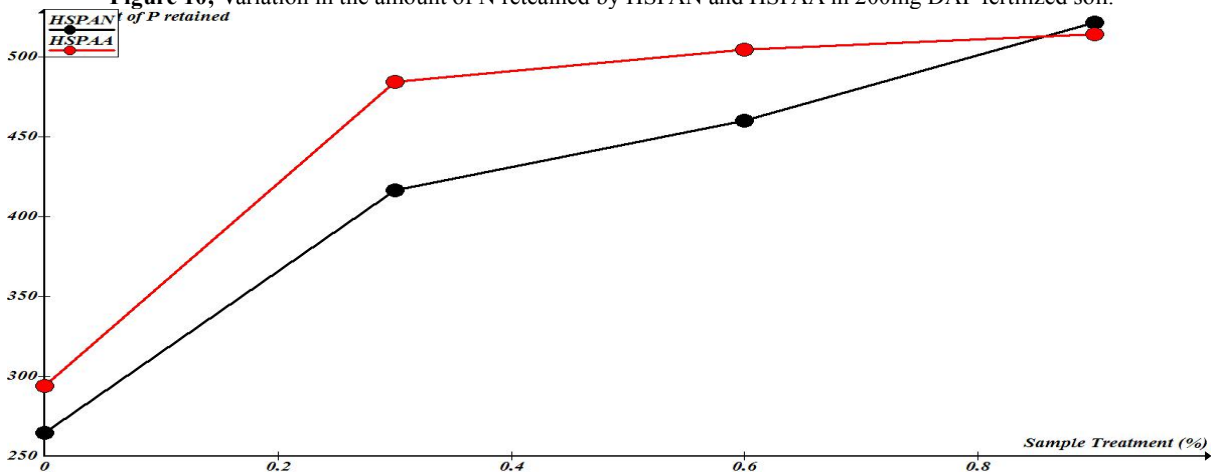


Figure 11; Variation in the amount of P retained by HSPAN and HSPAA in 200mg DAP fertilized soil.

The results in Figure 8-12 show that the retention capacity of N and P in the fertilized soil tended to increase with increase in the level of graft copolymer application and with the fertilizer application rate with the HSPAN higher in N retention than HSPAA.

The positively charged ions are absorbed readily and are retained by negatively charged surface of the graft copolymers. This ionic attraction reduces the leaching of the ammonium ion (NH₄⁺)^[32]. The amine functional group in HSPAN which is an addition to the function of the carboxylate and the hydroxyl ions both present in HSPAN and HSPAA could be attributed to the higher retention of the NH₄⁺ ions accounting for more N being retained by HSPAN than HSPAA.

Tisdale and Nelson,^[32] report is similar to the findings in this study in that the high retention capacity of N and P in graft copolymers treated soil is similar to the reports of large amounts of N, P and K sorbed on polyacrylamide hydrogel from commercial fertilizer solution used in their study. Leaching of nutrients from agricultural soils depletes soil fertility, accelerates soils acidification, increases fertilizer cost for farmers, reduce crop yields and adversely affects the quality of surface and groundwater^[21].

4. Conclusion

The result of this experiment has clearly demonstrated the potential of the graft copolymers to alleviate problems related to nutrient loss from the soil media. The data obtained from the study suggest that graft copolymer retains nutrients (N and P) against leaching losses and the nutrients are thus available to plant for growth by suction pressure difference.

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