Use of Nutrient Anchored Polystyrene Substrate Soil Less Material for Growth of Crops

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ABSTRACT

Loss of available land for plant growth has made other options that allow an efficient use of water and fertilizers which increase crop quality and productivity. Some systems such as hydroponics need a constant air and fluid circulation as well as nutrient refill that put strain on the cost of production. Without such a system, many growers dump the nutrient solutions at short intervals which affect the environment negatively. Due to such shortcoming, there is a need therefore to come up with a method that will address such challenges. This study reports on the growth of some selected plants on nutrient anchored modified polystyrene material. The material was characterized using FTIR, NMR, FAAS and XPS. Nutrient release parameters were investigated by differential pulse anodic stripping voltammetry at a glassy carbon electrode. Available spaces between the solid particles provided a sufficient supply of air to the plant roots. Mineral release increased with decrease in pH up to a value of 4.0 at which 90% of the nutrient was available for plant uptake. The anchoring of minerals was by complexation whose stability constant was found to be 1.99×10^{14}. This implies that the non biodegradable material has a potential application as a fertilizer and media for plants growth.

Keywords : Crop Nutrients, Fertilizer, Polystyrene, Modified And Non-Biodegradable Wastes

I. INTRODUCTION

Scarcity of land has made available land for plant growth a real challenge in many parts of the world. This has resulted to insufficient surface enough for food production, as most of the land is turned into a concrete jungle. However, growth and propagation of plants for food crop or ornamental flowers in homes can be made possible through other process such liquid nutrient culture solutions. This has led to the use of nutrient dissolved water solutions as a medium for plant growth usually referred to as hydroponic crop production. This method mostly done in green houses, allows a more efficient use of water and fertilizers, plus a better control of climate and pest factors. The main challenge in hydroponics is the need for a system which can be manipulated on managing the flow of nutrient solution. It is also limited to a selection of plants such as climbers which do not require any firm support. The cost of a system to manage and re-circulate as well as refill the nutrient solution puts a strain on the cost of production which makes many growers dump nutrient solutions and refill them at short intervals [10]. Growth of various food crops (in season and out of season) has further been exacerbated by erratic

climatic conditions that have negatively affected their production.

Due to such limitations, this has compelled other options to be considered. By provision of an artificially prepared favorable climate, plant nutrients and an adequate water supply, there is a possibility of growing plants without soil. Such a method can be adopted by ordinary people in high rise buildings and amateur gardeners to meet their supply of vegetables, ornamental plants or floral needs. The only requirements in this case are a supply of appropriate nutrients, knowledge of factors such as plant growth, habits of plant growth, climatic needs or adaptations of pollination requirements and sanitation measures to prevent disease and insect infestation. The supply of nutrients alone is not enough for the well-being of plants alone, but an adequate aeration of the roots is needed reported by Guevarra and co-workers (1980) [10]. Who achieved a successful growth of some selected plants by maintaining the water dispersed nutrient media in circulation. Other studies exploited the Wick, Water Culture, Ebb and Flow, also known as Flood, Drain and Drip methods [14]. In all such cases, an external source of energy was needed to facilitate the flow of the fluid habouring the nutrients that are required.

To overcome the challenge, this study proposed to synthesis an inert support material which has a high surface area and mechanical stability on which the requisite plants nutrients will be anchored. The nutrients were made available for plant uptake by regulating the pH of the soilless media which resulted in the protonation of the substrate material.

$$\text{MSubstrate} + H^{+} \rightarrow \text{HSubstrate} + M^{+} \qquad (1)$$

The substrate was hydrated by mixing it with suitable hydrogels. The synthesized solid particles were mixed with volume changing hydrogel that also enabled adequate air to reside within the pockets. The solid soilless media also provided an appropriate support base for plants such as corn, lettuce and Irish potatoes

used in this study. Thus, in our study we report on the preparation of chemically modified polystyrene material and its subsequent application for the supply of plants nutrients. The anchoring was by complexation with a high stability and as such nutrients cannot be leached off the media as is the case in normal soils. This offered a solution for the utilization of a non biodegradable material initially used as packing material and latter bound to the waste. The resulting soilless media is a low density material suitable for use even in space experiments. This is then an environmental friendly and sustainable method for mitigating effects of littering the environment by this low density material affecting the scenic beauty.

II. MATERIALS AND METHODS

2.1 Chemicals and Reagents

All the solutions were prepared in distilled water and the reagents were of analytical grade. The standard reference solutions for calibrations, metal ion salts, hydrochloric acid, sodium nitrate, tin granules, filter paper and ethylenediamine were of analytical grade were supplied by Kobian Kenya limited which is an outlet of Sigma-Aldrich of U.K. The nutrient solutions anchored on the substrate were prepared using the method of [10]. Iron (II) ions standard solutions and other metal solutions were prepared by dissolving suitable masses to make stock solutions of 1000 μg ml $^{-1}$ from which subsequent dilutions were made. All solutions for differential pulse anodic stripping voltammetry (DPAS) were dispersed in a 5 M potassium nitrate buffer solution was used to maintain a constant ionic strength.

2.2 Instrumentation

The functional groups on the polystyrene material before and after modification were characterized using Fourier transform infrared (FT-IR) spectroscopy (Perkin Elmer 100 made in Waltham, MA, USA). The resulting material was also characterized using a solid-state NMR- Bruker 600 13C NMR spectrometer

(Hanau, Germany) operating at a frequency of 10 MH which had a cross-polarization/magic angle spinning (CP/MAS). The cross-polarization (CP) was adjusted with glycine at 10 kHz, and the spinning rate was set at 10,000 Hz. The contact time for CP was set at 1 ms and the delay time for acquisition was 5 s. The presence of metal anchored on the modified polystyrene material was confirmed using X-ray photoelectron spectroscopy (technical parameters of the TXRF spectrometer S2 PICOFOX, Bruker). The metal ion concentration in the solution released from the polystyrene material at different pH values was done using a voltametric analyzer (Episilon model E2 USA UK) on a glassy carbon electrode. The three electrode system measurements were made against a silver/silver chloride electrode with platinum wire as the counter electrode. Prior to use, the glassy carbon electrode was cleaned by successive polishing on aqueous slurries of 1 μm, 0.3 μm and 0.05 μm alumina abrasive powders, followed by thorough rinsing with de-ionised water. The substrate was placed in the voltammetric cup and then purged with nitrogen for one minute and the instrumental settings optimized [23].

2.3 Sample preparation and anchoring nutrients culture

2.3.1 Nitration of polystyrene

A known weight of polystyrene (5.0 g) was placed into a 250-ml round-bottomed flask. To this, concentrated nitric acid (80.0 ml) was added to the mixture with vigorous stirring under a dry nitrogen atmosphere. This was followed by the slow addition of sulphuric acid (20.0 ml) while maintaining the temperature at 0.0˚ C. After addition of all these reagents, the mixture was subsequently left stirring at 50.0˚ C water bath for up to 24 hours. The reaction mixture was poured slowly into an aqueous sodium hydroxide (60.0 ml) to bring the pH to neutral. The resulting precipitate was then filtered and washed with water until a neutral pH was achieved. The product was dissolved in N, N'-dimethylformamide,

re-precipitated in water and left stirring for 24 hours at 40.0˚ C. The polymer was recovered by filtration, washed with water then methanol and dried to constant weight at 50.0° C under vacuum [14; 11]. Sufficient amount material was prepared and then used in the reduction experiment.

2.3.2 Reduction of the nitrated polystyrene

The reduction process was carried out in a round bottomed flask (400 ml) which was fitted with a reflux air-condenser. This was done by placing the nitrated polystyrene (20.0 g) and granulated tin (45.0 g) in the round bottomed flask and to this mixture, 105.0 ml of the hydrochloric acid, in portions of 20.0 ml, was added, while cooling under the tap to prevent boiling [28]. The resulting mixture was refluxed for 24 hours [18; 15]. The solid product was azotized for the purpose of confirming the reduction process. This was done treating the resultant with 75 ml of 1 M sodium nitrite followed by 100 ml of 1 M hydrochloric acid in an ice bath. The mixture was stirred and violet product resulted which was a confirmation of azotization and hence substitution of the ring [21]. The product in ice-cold water was then coupled with ethylenediamine to produce and the resultant was recovered by filtration, washed with water then methanol and dried to constant weight, then used for attachment of nutrients.

2.3.3 Attachment of the basic nutrients for crop growth

The nutrients of interest were attached on the substrate by treating the modified polystyrene material in section 2.3.2 with solution of ammonium nitrate, calcium nitrate, calcium chloride, potassium nitrate, potassium phosphate, phosphoric acid, magnesium sulfate, boric acid, copper sulfate, zinc sulfate, iron nitrate, manganous sulfate, sodium molybdate, soluble trace element mixture (S.T.E.M.) all of known concentrations. The mixtures were allowed to interact and react for three days. Excess nutrient solution was filtered and the solid dried at 50.0 °C under vacuum [11]. The resulting product was

used for protonation experiments in the study of the release of minerals.

2.3.4 Release of minerals from the substrate material

Dissolved iron (II) ions were used in this analysis as a case study. This was achieved by taking the substrate initially and dried it at $65\,C$ then cooled in a desiccator. From that, a sample, 0.100 g was accurately weighed into a conical flask and 0.1 M hydrochloric acid (25 ml) added. The mixture was boiled for ten minutes. It was then left to cool and filtered through a Whatman No. 41 ashless filter paper into a 100 volumetric flask. The resulting solution was made to the mark with de-ionized water. The sample was then analysed for the metal ions. This was done by dispersing it in a support electrolyte, 10 ml, already in the polarographic cell, followed by purging the mixture with nitrogen, and an initial voltamograms of sample acquired. This was followed by spiking with volumes of 0.01 M ferrous ions (5 μl) in the same cell (standard addition method) without changing the machine settings and the resulting voltamograms acquired. The peak currents obtained from the voltamograms were treated with the Nernstian equation to calculate the concentration of the iron ions in the substrate [1; 15].

2.3.5 Determination of labile metal content by DPASV

Samples ranging from 0.01 to 0.1 g of the substrate-iron complex were dispersed in a support electrolyte, 25 ml, already in the polarographic cell, followed by purging the mixture with nitrogen, and an initial voltamogram of sample acquired. Cyclic voltamograms (CV) were then obtained at a scan rate of 50 mV s^{-1} under the diffusion-limited conditions starting from a range of –0.8 V to 0 V. Starting with the blank followed by volumes of 0.001 M nitric acid (5 μl) which were spiked in the same cell (standard addition method) without changing the machine settings and the resulting voltamograms acquired [23].

2.3.6 Potentiometric determination of stability constants

A pH titration study was carried out on 0.1g of substrate–Fe metal ligand complex to measure stability constant and to investigate the effect of ternary complexes on the solubilization of Fe (II) system. According to Onindo (2003), mono glycinato complex held copper in solution in physiologically important pH range. His procedure was adopted to study the ligand system on iron complex [20].

III. RESULTS AND DISCUSSION

3.1 Synthesis of substrate material

Polystyrene material contains no functional groups capable for metal ions attachment. To enable this material to be a source of the essential metallic nutrients for plants, suitable ligands were anchored within its structure so as to form complexes with metal ions of interest. This modification process involved nitration of the aromatic rings within it followed by reduction to form an amino compound which was then complexed with a metal ion.

3.2 Characterization and optimization studies

1) 3.2.1 FTIR Characterization

The modified and unmodified materials were characterized using FTIR on ATR mode. The results obtained were as presented in Figures 1-4. The spectrum presented in Figure 1 is of polystyrene material.
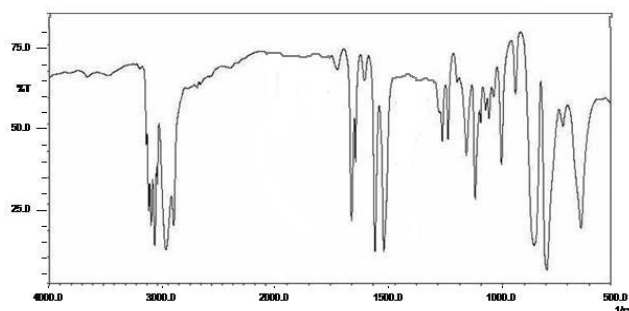

Figure 1. FTIR spectrum of polystyrene

Multiple bands at 3030-3080 cm^{-1} are assigned to -C-H stretching in the mono substituted benzene [31; 15].

The band at 2935.5 cm^{-1} was assigned to C-H stretches while the bands at 1400 cm^{-1}, 1500 cm^{-1}, 1585 cm^{-1} and 1600 cm^{-1}are attributed to C=C stretch in the ring [31; 15]. The bands at 1020- 1200 cm^{-1} are due to C-H def. in plane and the bands at 690- 800 cm^{-1} are due to C-H def. out of plane [26; 15]. It is evidence in figure 1 that polystyrene material contains no functional groups capable for metal ions attachment. The polystyrene material was nitrated and the resulting spectrum presented in Figure 2 show the results after the nitration of the polystyrene material.
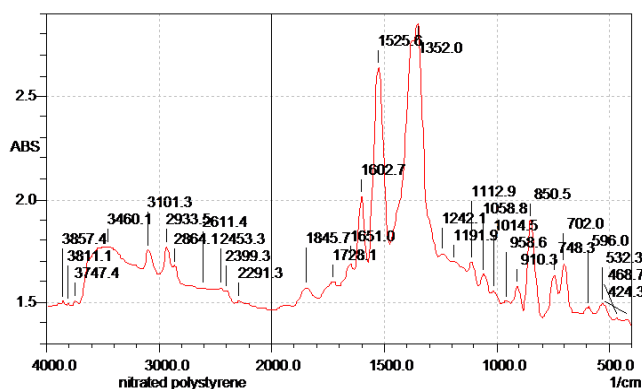
Figure 2. FTIR spectrum of nitrated polystyrene

The results show the presence of a peak observed at 1525.61 cm^{-1} which could be due to a nitro group within the ring structure which is characteristic of a nitrogen substituted ring, a peak observed at 1602.7 cm^{-1} could be due to NO$_2$ attached to the ring. Signals at 1242.6 cm^{-1} and 1651.0 cm^{-1} could be due to N=O stretch [31; 15]. The group could be as a result of nitration of polystyrene which is an electrophilic aromatic substitution reaction [17; 15]. The nitration process is through the formation of a nitronium ion (NO$_2^+$) which is an electrophile that reacts with the polystyrene to insert the group within the ring structure. The nitronium ion is formed through the protonation of nitric acid by sulfuric acid, which results in the loss of a water molecule hence a nitronium ion [17; 15].

The nitrated product was then reduced using granulated tin and concentrated hydrochloric acid, the resulting spectrum is as presented in Figure 3.
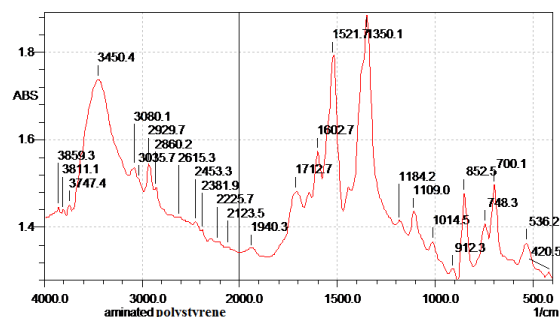

Figure 3. FTIR spectrum of reduced nitrated polystyrene

After the reduction of the nitro compound, the peaks observed at 1525.71 cm^{-1}, 1651.0 cm^{-1} and 1242.0 cm^{-1} disappeared due to the formation of an amino group. A strong band at 3450.4 cm^{-1} is attributed to either -OH or -NH groups [26; 15]. But the band appears broad and as two peaks. This is an indicator that it is most likely due to -NH groups [26; 15]. The band at 2929.7 cm^{-1} was assigned to C-H stretches while the band at 1602.7 cm^{-1} was assigned to stretching -OH or N=C [26; 15]. New peaks such as 1712.7 cm^{-1} and 2453.2 cm^{-1} could be due to NH$_2^+$ group [31; 1)]. The peaks observed at 1521.7 cm^{-1}and 1350.1 cm^{-1} were assigned to N-H bend while the peak at 3450.4 cm^{-1} is due to N-H stretch [26; 15]. The peak observed at 3080.1 cm^{-1} could be due to NH$_3^+$ group [31; 26; 18; 15].

After the formation of the amino group, the material was treated with dilute metal solution of 1M for complex formation between the metal ions and the amino modified solid substrate material. The resulting material was characterised and the resulting spectrum is as presented in Figure 4.
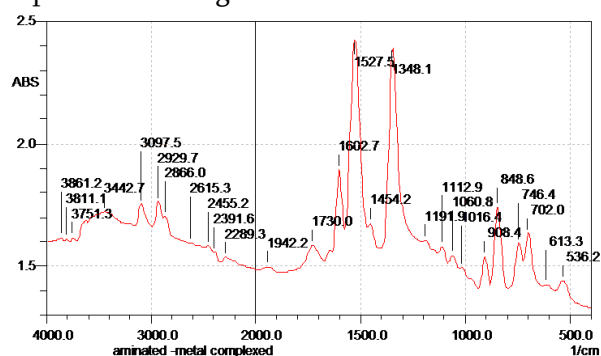

Figure 4. FTIR spectrum of aminated-metal complexed polystyrene

After anchoring the metals the strong band at 3450.4 cm⁻¹, 2455.2 cm⁻¹, 1521.5cm⁻¹, 1697.2 cm⁻¹ and 3080 cm⁻¹ disappeared and new bands observed at 1112.9 cm⁻¹,1191 cm⁻¹,1348.1 cm⁻¹ and 1527.5 cm⁻¹. This may be due to the anchoring of the metal within the structure [31; 15]. New bands in the 536.2 and 613.3 cm⁻¹ region, may probably be due to the formation of metal-nitrogen bonds [19; 27; 15]. The shift in C=N predict the concept of coordination of ligands through the nitrogen atoms [19; 6].

The solid substrate chelating agent forms two bonds with the metal ions resulting to bi-dentate complexes. The azomethine nitrogen donor heterocyclic ligands are known due to their wide range of applications and they can accommodate different metal centers involving various coordination modes thereby allowing successful synthesis of homo and hetero metallic complexes with varied stereochemistry [6]. The formation of more than one bond between the metal and the organic molecule usually results in high stability of the complex [6; 7]. This is done by the redistribution of a charge in the chelate chain (the π-electron delocalization in a -CN=Metal chain) [16]. The charge transfer results from electrons interaction between the metal and the ligands involving the metal to ligands or ligands to metal electron transfer [27]. The stability of the complex depends on the number of atoms that form a bond with the metal ion, the number of rings that are formed, the nature and concentrations of the metal ions and pH.

3.2.2 NMR Characterization

The parent polystyrene material was characterized using ¹³C NMR and the result obtained were as presented in Figure 5
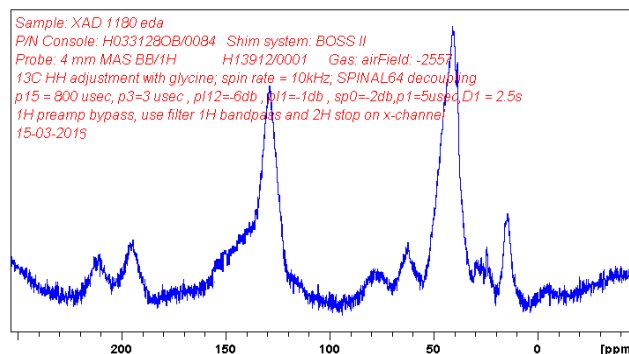

Figure 5. NMR spectra of the parent material

Carbon atoms in the benzene ring usually absorb radio signals at 128.5 ppm [12]. This is in agreement with the results obtained in ths study. The material was then nitrated, reduced and the resultant azotized and then treated with ethylenediamine. That product was analysed and the results obtained were as presented in Figure 6
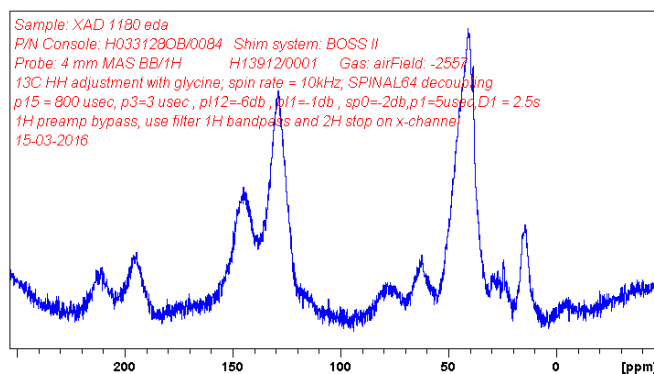

Figure 6. NMR spectrum of the modified material

It was observed that an increment in shifts of absorption by carbon atoms of the aromatic ring from 125 to130 ppm downfield. This was due to the influence of the substitued group [12]. Thus the nitrogen group contributes to the shift of the peak with respect to the position of the carbon bearing it. A new peak at 145 δ (ppm) was observed and was assigned to the carbon atoms from the coupled ethylenediamine [25]. This is in agreement with similar observations made by other researchers as they studied the deprotonation of catechins who observed peaks in phenolic ring at 145.5 δ [8]. Our findings confirmed that the ring was successfully substituted. A similar deduction has been made in a study carried out by Xie and Seto (2007) [32] who diazotized an

aromatic amine with sodium nitrate as they carried a research on protein tyrosine phosphate inhibitors, and observed a peak at 146 δ which was due to the diazonium ion.

Methylene groups between phenols in the polymer were assigned the peaks at the region between 40-41 δ [7]. This peaks in that region are at times referred to as the para methylene bridge, while the small peak at the region between 10-20 δ are suggested to be due to CH_3 group [8].

The modified material was then treated with some selected metal ions. The resulting complex material was then analyzed using Electron Spectroscopy for Chemical Analysis (ESCA) also called X-ray photoelectron spectroscopy analysis

3.2.3 X-ray photoelectron spectroscopy analysis

A modified solid substrate material was treated with three different metals (iron, nickel and zinc) to confirm complexation. The surfaces of metal anchored substrate material was analysed by irradiating with a beam of X-rays. The results obtained were as presented in Figure 7.
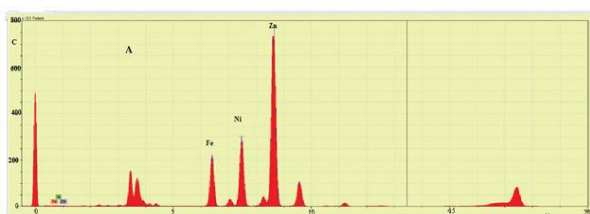

Figure 7. Photoelectron energy spectra for iron, nickel and zinc anchored in substrate material

The results confirm that metal ions were indeed complexed on the functional groups anchored on the polystyrene material [30]. This implies that if the material was used a nutrient reservoir, it could easily be replenished upon exhaustion. The release of the metals was then monitored by varying the pH of the media dispersing the nutrient anchored substrate material.

3.3 Optimization studies

3.3.1 Protonation by acid washing and calibration of the voltammeter

The instrument was calibrated by acquiring cyclic voltamograms using varying samples of substrate material. Iron (II) ions (used as a case study) attached to different masses of the polystyrene material were stripped using different volumes of 0.01 M hydrochloric acid. A series of voltamograms were obtained and the results obtained are presented in Figure 8.
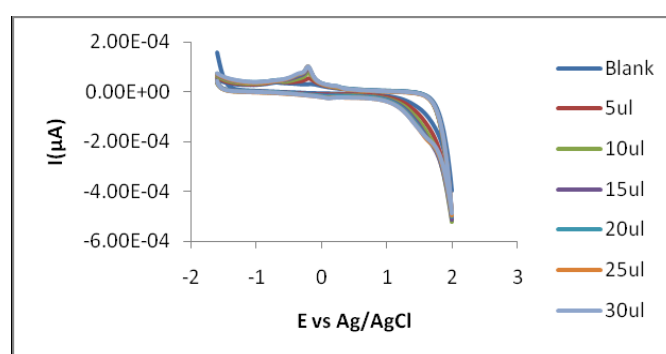

Figure 8. Cyclic Voltamogram (CV) for 0.10g substrate, 30 μl of 0.01 M hydrochloric acid Instrument settings –1.6 V to 2.0 V, scan rate 50 mV s-1, DPASV (CV Mode)

Cyclic Voltammetry is a tool used for qualitative and quantative information about electrochemical processes and to validate the equipment. The difference between cathodic and anodic peak potentials should be 0.591-0.684 for one electron transfer [23]. In this study it was observed that reduction potential for the forward and reverse scans were 0.04 V and 0.7 V respectively. These reduction potentials gave a difference of 0.66 V, which is acceptable, and thus validated the instrument for analysis as with reference to manufacturers' specifications [23].

A table of current versus concentration was extracted from the data in Figure 8 and are as presenred in Table 1.

Table 1 Determination of the concentrations of the iron ions in the standard

Volume of the acid (µl)	[Fe(II)](M)	ip (µA)
5	1.50×10^{-6}	0.298
10	3.60×10^{-6}	0.947
15	6.40×10^{-6}	1.83
20	9.45×10^{-6}	2.72
25	12.3×10^{-6}	3.89

A plot of volume of the acid versus [Fe²⁺ ions], gives Figure 9, Linear regression gives the equation for the calibration curve as: volume of the acid(µl) = 0.549 × 10^{-6}[Fe(II)] -1.585. From the sample's peak current, one can get the concentration of Fe(II) ions in the sample and fitting the respective concentration of Fe(II) ions into the regression equation gives the volume of the acid required to strip off a given number of iron (11) ions from the sample as per plant requirements..
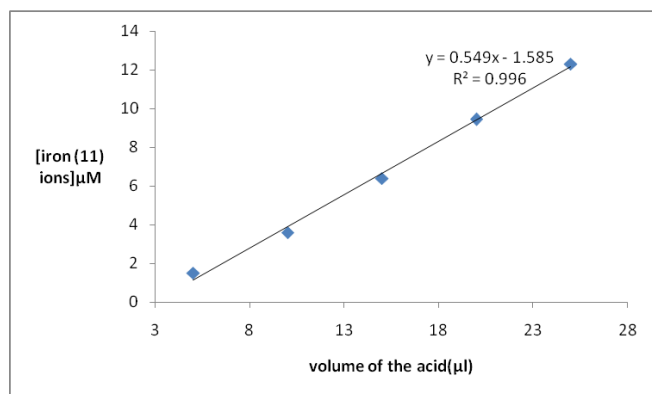

Figure 9. current as a function of the of the iron ions in the standards

This graph was used to obtain the volume of the acid and the concentration of iron ions in the substrate using the respective peak current potential. From Figure 9 it was observed that the concentration of metal ions increased with increase in the volume of 0.01 M hydrochloric acid. This information tells that the minerals will not easily leach from the solid substrate but can only be released intentionally. This can be done by buffering the media at an appropriate pH.

3.3.2 Effect of mass variation on concentration of iron ions in the solution

The variation of the mass of substrate (0.01 -0.40 g) was studied using a constant volume of acid. Samples were analyzed and respective Voltamograms acquired were as shown in Figure 10.
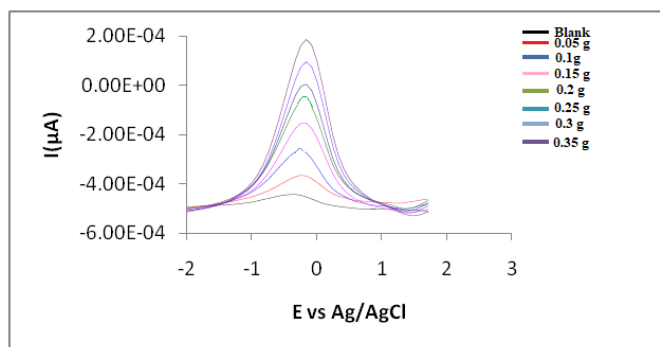

Figure 10. Voltamograms on Mass Variation with 25 ml of 0.01M hydrochloric acid solution Instrument settings --0.8V, scan rate 50 mV s-1, DPASV (CV Mode

The Voltamograms in Figure 10 show an increase in current as the mass of nutrient anchored substrate was increased. This implies that the more the substrate, the more the ions anchored. From the results of machine response against concentration, a calibration curve for the concentration of ion was done as shown in Figure 11.
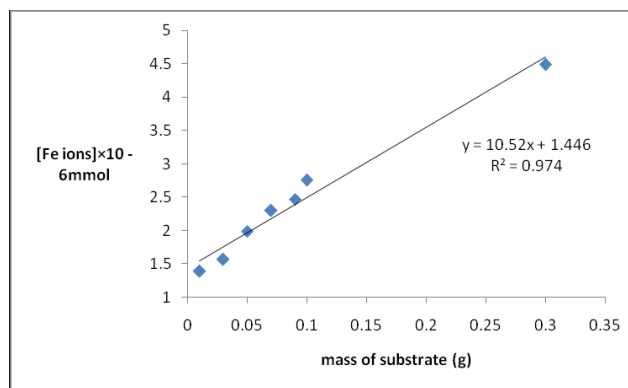

Figure 11. Effect of mass variation on concentration of iron ions in the solution

The results show that the metal ion concentration increased with increase in the mass of the substrate. This means that the mass of the substrate had a direct relationship with the quantity of iron (II) ions released. Complexation of the metal ions is based on its number of valence d electrons, as metal ion may prefer certain binding geometries over others. This preference is based on Ligand Field Stabilization Energy (LFSE). The common biologically relevant

oxidation states of iron are Fe^{2+} and Fe^{3+}, which prefer octahedral and distorted octahedral geometries. The more the substrate the more the binding sites and high denticity, hence more metal ions attaches to the substrate.

3.3.3 Effect of pH variation on concentration of iron ions in the solution

The peak currents from the voltamograms in pH titration studies and the Nernstian equation were used to calculate the concentration of the metal ions in the substrate and the results tabulated and presented graphically in Figure 12
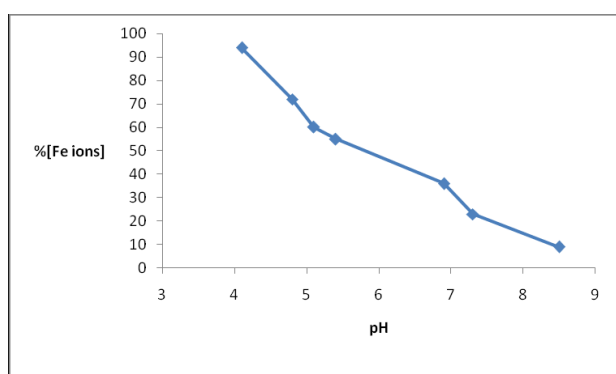
Figure 12. Effect of pH on [Fe $^{2+}$ ions]

It was observed that the concentration of metal ions increased with decrease in pH. The more acidic the environment, the more metal ions are released. At pH 4.0, it was realized that 90% of the complexed metal ions were stripped of the substrate due to protonation of the matrix. This is due to the decrease in the competition for the binding sites on the substrate anchored material enhancing the release of the metal ions [11].

A plot of peak current versus [Fe^{2+} ions] in the sample, gives a straight line and the results obtained were presented in Figure 13.
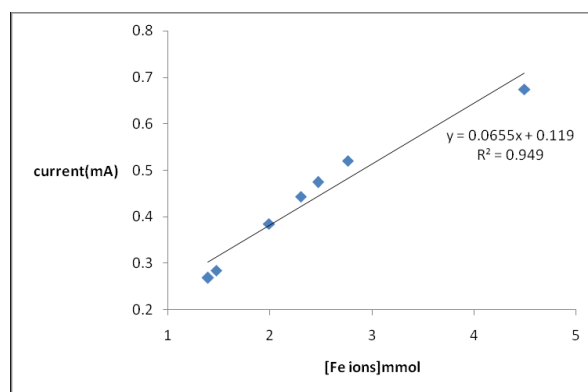
Figure 13. current as a function of the of the iron ions concentration

The plot shows a straight line graph with a slope of 0.655 and a correlation coefficient of 0.949. The linear regression curve was used in determination of the stoichiometric coefficient, *p,* and the *y*-intercept gives the value for the formation constant β_p [1; 21].

The plot of i_p as a function of the metal ions concentration is shown in Figure 13

Linear regression gives the equation for the straight line as

$$i_p = 0.0655\,[\text{Fe (11)}] + 0.419 \qquad (2)$$

From the slope and the y- intercept and solving the equations 2 and 3

$$0.0655 = \frac{o.5916P}{2} \qquad (3)$$

$$0.419 = \frac{o.5916}{2}\log\beta_P \qquad (4)$$

This gives the stoichiometric ratios of the species in the complex ML_{x2} as ML_2 ($p = 2.22$), with a formation constant of $\beta_2 = 1.99 \times 10^{14}$ [1; 27].

The value observed from the formation constants, indicate that, the metal ions are safely held by the substrate and can only be released by varying the pH [1; 27]. This implies that the release of minerals can be achieved by a controlled regulation of pH of the media.

The study has confirmed that when the metal ions concentration is relatively low, most of metal ions are bound to form complexes with the amine groups in

the substrate moiety [29]. This is because of the availability of active sites on the substrate for mineral attachment. Due to this strong binding power of the substrate to capture metal ions, metal ions release and thus availability of labile metal ions for plant uptake dramatically decreases. The complexation phenomenon inhibit the interaction of the substrate with water molecules through H-bonding. Therefore, the more the number of functional groups complexed with nutrients, less water will be taken up by the substrate [29]. The choice of iron (III) was made due to it is unique to biological transition metal ions in that it has a high charge-to-radius ratio and as a hard acid forms high-affinity complexes with ligands [12]. Protonation of metal complexed substrate material was done to investigate the release of metal ions with reference to pH. The results obtained were prented in Figure 14
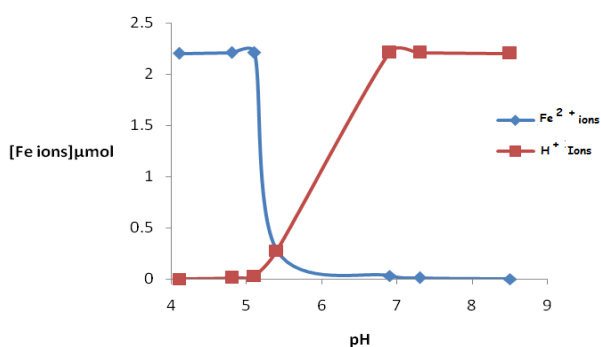

Figure 14. A comparison of hydrogen ion uptake and iron ion release as a function of equilibrium concentration of iron in the solution

The results show the hydrogen ion uptake and iron released as a function of equilibrium concentration of iron ion in the solution. At low concentrations, the molar quantity of hydrogen ion uptake is more than two times that of iron ion release. This is because in addition to exchange between iron and hydrogen ions, some hydrogen ions in the substrate dissociate and enter the solution phase [33; 29]. However, at relatively high iron concentrations in the solution, the iron ions will complex with the amide groups, resulting in a hydrogen ion uptake to iron release ratio of slightly lower than 2 [16].

Based on the above analysis, it can be seen that, at sorption equilibrium, all iron ions and hydrogen ions will reach equilibrium between the solution phase and the substrate phase. The sorption uptake of hydrogen ions influences the equilibrium of iron ions and water between the solution phase and substrate phase significantly [29].

3.4 Application of the material on plant growth

3.4.1 Relationship between the growth rate and nutrients concentration

In order to investigate the relationship between the growth rate and both the nutrients and water in the substrate, a plant raising schedule was designed for spinach (*Spinacia oleracea L.*) and Irish potato (*Solanum tuberosum L.*) [2]. The measurements of leaf breadth/length and also to the wet and dry weight of the leaves for spinach (*Spinacia oleracea L.*) and harvested Irish potato (*Solanum tuberosum L.*) was subjected to a tool downloaded, from the Annals of Botany*'s* (http://aob.oupjournals.org/cgi/content/full/90/4/485/DC1), the data was subjected to analysis of variance using the standard fitting procedures in order to assess the homogeneity and standard error of the estimated parameters.

3.4.2 Relationship between growth rate and total nutrients concentration

The variations of the mass of the substrate in relationship to growth rate as function of time was investigated and the results presented in Figure 15:
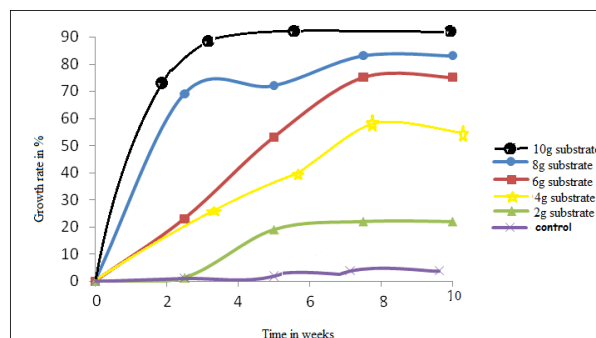

Figure 15. % Relative growth rate against time

The nutrients release rates from the substrate with respect to the growth rate shows similar profile for different masses. In particular, the nutrients release rate at 10 g substrate, exhibit the growth rate, which may be related to the nutrients reserve, which are available for plant uptake. The control curve showed minimal growth which is attributed to lack of nutrients in the sand, the little growth could be due to the nutrients reserved in the plant before transplanting [22]. The 2 and 4 g substrate show a decrease in the amount of nutrients release as indicated by the lower growth rate, a decreasing amount of the substrate content, resulted in decreasing nutrients release and therefore lower growth rate [24]

For the substrate, a high equilibrium nutrient content indicates that the diffusion of nutrients in this highly concentrated environment could be described by the free volume theory (Chapin, 1988). While the release of the nutrients from a low concentrated level was marginal and did not follow the free volume theory [3; 24].

3.4.3 Relationship between leaves population and total nutrients concentration

The leaf number per plant in relationship to growth rate as function of time was investigated and the results presented in Figure 16:
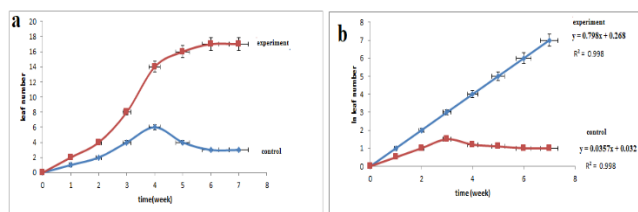

Figure 16. A plot of leaves population against time

A high leaves population of the plant presented with abundant resources (experiment) increased exponentially (Figure 16 a). Population doubling time is a function of an inherent capacity for plant enlargement which is expressed according to environmental conditions [5]. In Figure 16 a, a doubling time for these two experiments are 1 and 2 week(s) for experiment and the control respectively, where the experiment shows a fast-relative growth rate [5].

In this study, for the experiment with a doubling time of y week, starts on week 0 with a population of 2 leaves and increases to 30 leaves by week 7, from the experiment curve y=2. The control, with a doubling time of 2 weeks takes twice as long to reach that same number of leaves. When data for leaf numbers are natural logarithm transformed, exponential curves (a) become straight lines (b), where slope equals relative growth rate (r) [4]. The exponential curves (Figure 16 a) can be described mathematically as in Equation 29 Section 3.8.4. The experiment is doubling every week whereas the control doubles every 2 weeks, thus r is 0.798 week^{-1} and 0.358 week $^{-1}$, respectively. As indicated by the two straight lines with contrasting slopes in (Figure 16 b).

IV.CONCLUSION

The study successfully modified the polystyrene material by introducing an amino functional group through substitution in the aromatic rings and this was confirmed by FTIR analysis. These anchored groups were used as chelating agents for metal attachment through complex formation. The presence of metals in the substrate material was confirmed by XPS analysis. The substrate anchored nutrients culture was characterized using FTIR, NMR and XPS for functional groups, flame atomic absorption spectrophotometry (FAAS) for total ions while the labile fraction was determined by differential pulse anodic stripping voltammetry (DPASV) at a glassy carbon electrode and pH titrimetry. From the substrate anchored nutrients culture, it was observed that the concentration of metal ions increased with decrease in pH up to pH 4.0 where a plateau on concentration was realized with 90% of the complexed metal having being deprotonated. The

sample (0.10 g) had a total metal content of 3.50 µmol of iron (11) ions, with formation constant (2.22) and stability constant of 1.99×10^{14}. This proves that with pH variation nutrients can be released as per the plants requirements. The exploitation of a thermally stable and non biodegradable material to be a source on plant nutrients for the growth of plants is like preparing a fertilizer from environmentally unfriendly source. Minerals of choice can be anchored on the solid substrate and the release of the same be regulated by buffering at an appropriate pH. This therefore confirms that modification of the polystyrene material has a potential application for and cleaning the environment and subsequent use the growth of plants as a source of nutrients.

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VI.   REFERENCES

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