Chemical Functionalization and cross-linking of biochar from cow dung for use as supper

ABSTRACT

Water plays a vital role in maintaining the structure and posture of plants, keeps the cells turgid, aids in the transportation of nutrients from the soil, among other functions. It plays an important role in ensuring there's food security in communities, particularly in arid and semi-arid areas, when well managed. This is ensured through irrigation and mulching. Irrigation is a tedious exercise, while mulching is labor-intensive, and natural mulching materials do not retain water for long, hence the need for improvement. In this study, cow dung biochar was functionalized with ethan-1,2-diol, glycerol, and phosphoric acid and then cross-linked with phosphoric acid, citric acid, and urea to develop a super absorbent mulch substrate for agricultural purposes. To begin, cow dung was obtained from a cattle farm in Thika in Kiambu County. It was converted to biochar by burning under a limited supply of air, which was then functionalized and cross-linked to make a mulch for agricultural practices, a technique that has been put to test for the very first time. The modified biochar was tested for conservation of moisture and retention of nutrients based on watering frequency and the improved crop yields. A successful functionalization process was confirmed using Fourier Transform Infra-Red Spectroscopy (FTIR), which showed the additional functional groups in the chemical structure of the modified biochar. The degree of cross-linking was determined by a swelling experiment. The degree of water retention was determined by comparing the mulched and non-mulched maize and Calliandra calothyrsus trees in the field. Field experiments were conducted in Makuyu ward, Maragua constituency, Murang'a County, a semi-arid area where maize was grown using a randomized block design. Growth and yield parameters were monitored periodically. The FTIR peaks were observed for -OH at 3350.73 cm^{-1}, P-OH at 788.87 cm^{-1}, P=O at 1279.5 cm^{-1}, C-H at 2919.68 cm^{-1}, C-N at 1045 cm^{-1}, N-H at 1622.80 cm^{-1} and C=O at 1602.5 cm^{-1}, confirming a successful modification process. Based on the results of this study, it is recommended that the modified mulch be used in arid and semi-arid areas.

1.1 BackgroundInformation

Mulchingistheactofcoveringthetopsoilwithalayerofmaterialssuchasgrassclippings,wood chips, and straw, chopped leaves, twigs, saw dust, and even papers. Their utilization asmulching materials has been used in agriculture (Bach *et al.*, 2016). In nurseries, grass clippingshave been the most widely used mulch because they are readily available, prevents excessiveevaporation and also moderates soil temperatures (Wells *et al*., 2016). Thesemulching materials have been used to improve soil moisture, beautify the land, control weeds and improve the soilfertilitybut do not retainwaterfor longhenceneed foramore reliable mulch.

Biochar is the light weight black residue which remains after biomass has been burnt in theabsence of oxygen.Ithas been found to be more porous (Chrisman, 2015)and can hold morewater for long than natural mulches. It has been made in the past from biomass materials likerice husk, olive shellCrop residues, pig manure, cattle manure and wood (Ma *et al*., 2019).Biocharinthesoilhasmany benefitssomeofwhichincludeincreasingwaterinfiltration,promote better root development, reduce fertilizer run-off especially nitrogen and phosphorous,binds sandy soil together and improves water holding capacity (Lonappan *et al*., 2019).Itadsorbsandimmobilizesheavymetalsandreducestheiruptakebyplantsandsubsequentingestionbyhumans andanimals(Li*et al.*, 2018*)*. It has carbon bonds that readily accept functional groups to form hydrogel (Huff *et al*., 2016).Most of the chemically improved biochar have been used in adsorption of heavy metals but there is limitedinformationonuseof chemically improved biocharinagriculturalpractices.InKenya,intensivelivestock faming system is a major source of environmental pollution especially in urban areas wherepeople live in small plots of land.Even though cow dung has been used for biogas production(Mwangi *et al*., 2019), thebiogas slurryposes aproblem in its disposal.

There are many adverse impacts of climate change especially in agricultural sector which isheavily affected by drastic weather and climate change resulting to food insecurity. There is therefore need to search for anamicable solution to mitigate the impact of climate change on agriculture which is the backbone of oureconomy.Thiscanbe done through development of supper absorbents such as functionalized and cross-linkedcow dung biochar with ability toretainwater,nutrientsandkeepthecropsandtreesgrowingevenwhentheweatherconditionsarenot favorable.

Cow dung is the undigested residue of plant matter which passes through the digestive system ofthe bovine animal species.It is rich in nutrients like nitrogen, phosphorus, potassium and highlevelsofammonia(Randhawa*etal.*,2011).Italsoconsistsoflignin,celluloseand hemicelluloses (Singh *et al*., 2014). It has several benefits some of which include burning asfuel, mosquito repellant, plaster for buildings, bio-pesticides and as a cleansing agent (Mwangi *etal*.,2019). Cow dung manure increase humus and this results to better water seepage and water bindingcapacity together with an improved cation storage capacity (Bio-fertilizers, 2014).It is also used for making biogas which is used for cooking thus loweringdependency on charcoal, firewoodand fossil energy (Guo *et al.*, 2013).Cow dung poses a problem in its disposal since it isproducedin largevolumes especially in town set-up where people live in small plots of land (Dupla*et al.*, 2024).

Biochar is a form of charcoal produced through the thermal chemical conversion of biomass under lowOxygen conditions known as pyrolysis (Guo *et al*., 2013).When air is excluded, oxygenforburningis removed from the biomass leading to its reduction to carbon single bonds of charcoal(Chen*et al.*, 2017). In ordinary burning, biomass would be oxidized intoash,carbon (IV)oxide,vapors and other gases(Ekebafe*et al*., 2013). it has many benefits in the soil like increasing water penetration and water retentioncapacity, it improves the soil configuration thus improving root development which leads tobetteryield(Chrisman,2015).BiocharamendedsoilsimprovesNitrogenuseefficiency,adsorption of ammonium, phosphate and calcium ions (Richardson *et al.*, 2011).It enhancesfertility, nutrient retention, soil biological activity and diversity and reduces fertilizer run-offespeciallynitrogenous and phosphate(Zahra*et al.*,2021).Biochar from animal waste is generally high in nutrient content particularly nitrogen,phosphorous, calcium and magnesiumcompared to plant residue.This has been stated byUtomo and Nugroho (2011) whose research looked at the production of a simple biochar fromcoconut and animal waste and its application in Lombok and the other eastern parts of Indonesia. They also found out that biochar made from animal waste was less alkaline (pH 8.9) comparedto that from coconut shell which had a pH of 9.9 (Utomo *et al*., 2011).The chemical structure of biocharcomponentsproduced bythefast pyrolysisprocess at500-600ºC isshown inFigure2.1

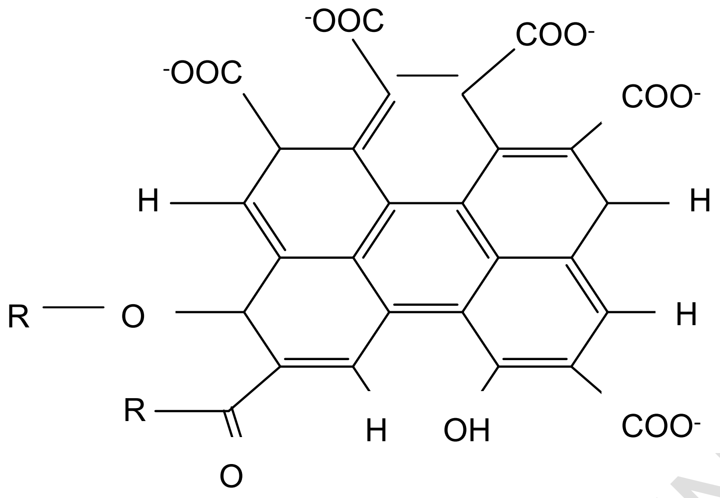

Figure2.1.**Structureof biochar(Chen *etal*.,2017)**

2.1 Chemicalfunctionalizationofbiocharmaterials

Use of organic acids and alkalis solutions have been reported in the pretreatment of biocharmaterials to improve the internal surface area (Usman *et al*., 2015).Chemical modification alters theoutsidechemistryofbiochar,therebyleadingtoimprovedwaterholdingcapacityin comparisonwithun-functionalizedbiochar.Theactivatedandfunctionalizedbiocharhave several applications in diverse field which include soil recreation, carbon dioxide sequestration,and removal of heavy metals and degradation of organic pollutants (Yakout *et al.*,2015). Thecommonly used activating chemicals include H_2SO_4, H_3PO_2, KOH, $ZnCl_2$and K_2CO_2.Chemicalfunctionalizationcanbedone byintroducingspecific chemicalfunctionalgroups like–SO_2H and –COOHintobiochar matrix(Ma*et al.*,2019). In the present study, functionalization of cow dung biochar by incorporating functional groups insidethepolymerchainandthencross-linkingitenhancedwaterholdingcapacity,nutrientadsorptionandincreasedswellingafter water absorption.

Hydrogel are polymers which are loosely cross-linked and exhibits the capacity to swell and holda large amount of water within its structure, but does not dissolve in it (Alkhasha *et al*., 2018).Thecapabilityofhydrogeltotakeupwaterarisesfromthehydrophilicfunctionalgroups attached to the polymeric backbone, while their resistance to dissolve arises from cross-linksbetweenitsnetworkchains(Wu*etal.*,2021).Theycanbeclassifieddependingontheirphysical properties, method of preparation, nature of swelling, ionic charges, rate of their biodegradationandnatureof cross-linking(Larrañeta, 2018).

Hydrogel are extensively implemented as input materials in various biomedical applications duetotheirspongy,stretchy,hydrophilicandquasi-solidnature(Ahmed,2015).Theyarealsoused in bio-separation, tissue engineering, proteomic and chromatography where good water holdingcapacity is of prime importance (Ullah *et al.*, 2015).There are three polymerization techniqueswhich can be applied to formgel, they include homo-polymeric which is derived from the samespecies of monomer(Ahmed *et al.*, 2019), the second one is co-polymeric hydrogel whichcomprise of two or more different monomer species.Multi-polymer interpenetrating polymerichydrogel is the third one which is as a result of two free cross-linking synthetic or naturalpolymercomponents (Chrisman, 2015).

Superabsorbent hydrogel act as humus which join loose soil hence form loam soil which helpbetter root penetration (Ahmed *et al*., 2019), it increases the plant accessible water in the soil,encourage faster growth of plant even under best water conditions and lengthen the survival ofplantsunder watershortage(Ekebafe*et al*., 2013).

3.0 MATERIALSANDMETHODS

3.1 Samplingofcowdungandpre-treatment

Cow dung was collected by random sampling from Thika in Kiambu county from Freshian breed of cattle, sundried for 6-7days until there was no change in weight. Stones and other foreign materials wereremoved and then the cow dung was burnt at a temperature of 300 ºC in the absence of air tomakebiochar

3.2 Preparationprocedure ofBiochar

200 g of cow dung was placed in a tight rid tin where it was burnt for 30 minutes at atemperatureof300 ºC.Itwasallowedtostayinthatstatefor10minutesafterwhichitwascooled at room temperatureforonehour(Pattanik*et al.*, 2019)

3.3 Experimentation Procedurefor functionalizationofbiocharwithphosphoric acid

The reaction of biochar with phosphoric acid was performed by adding 100 cm^3 H_3PO_4 (85%) to 50 g of biochar sample at 40 ℃ as described by Gyarmati *et al* (2015). The system temperature was raised to 100 ℃ and maintained for 40 minutes while stirring at 10 minutes intervals. The reaction mixture was then cooled in an ice-bath at a temperature of 15 ℃. The mixture was decanted from the resulting suspension and washed four times with water. 10 g of urea was added to phosphorated biochar and the temperature raised to 150 ℃ for cross-linking to take place in the biochar chains. The cross-linked biochar hydrogel was then analyzed using Fourier transform Infrared spectroscopy (FTIR).

3.3.2 Functionalizationof biocharwithEthan-1,2-diol

Thefunctionalizationprocedureof biocharwithethan-1,2-diolwas performedasper(Yakout *etal.,*(2015)methodwithslightimprovement where 10 g of biochar was mixed with 100 ml of ethan-1, 2-diol in the presence of sulphuric acid and a temperature of 120º to increase surface area and porosity of biochar. The resulting ester was then cross-linked with phosphoric acid where heating under reduced pressure in the presence of an inorganic base at a temperature of 150°C was done. The crude phosphate ester was purified by first washing with a chelating agent followed by water after which they were dried.

3.3.3 Functionalizationprocedureofbiocharwithglycerol

Inthepresenceofsulphuricacid, 10gof biochar wasreactedwith glycerolat120 ºC for 2 hours to form an ester. The cross-linking method was adopted from Gyarmati, (2015). The ester was heated at 165 ºC for 10 minutes, 100 g of the ester was placed in a beaker with 0.1M NaOH solution with pH of 12.00 necessary for cross-linking for stability to be attained due to the alkali environment. The liquid was stirred with a stirrer at a speed of 250 rpm for one and a half hours and the liquid discarded. The residue was washed four times using 400 ml of water for I hour and then dried on a porcelain tray in the open for 4 hours.

The treated sample was added in to 600 ml of 0.6 M citric acid solution which was then stirred (400 rpm) for 40 minutes. The acid treated hydrogel was washed with water to remove any excess of citric acid until the effluent turned non-turbid with lead (II) nitrate in buffer solution at pH 4.6. Drying was then done in an inert environment.

3.3.4 Procedure for functionalization of biochar with phosphoric acid and cross-link it with urea and citric acid

The hydrogel in procedure 3.2.3 was cross-linked again with citric acid where 200 g of cross-linked biochar with urea was placed in 4 l of 0.1 M NaOH with a pH of 12.00 necessary for cross-linking so as to attain an alkali environment. The mixture was stirred at a speed (250 rpm) for 1 hour and the liquid discarded. The residue was washed 4 times with 400 ml of water for one hour and then dried on a porcelain tray in the open for 4 hours.

The treated biochar sample was added to 120 ml of 0.6 M citric acid solution which was then stirred (400 rpm) for one hour. The acid treated hydrogel was washed with water to remove any excess citric acid until the effluence turned non-turbid with lead (II) nitrate in buffer solution at pH 4.6, it was then dried in an inert environment.

RESULTS AND DISCUSSION

4.1 Functionalization of biochar and cross-linking

4.1.1 Functionalization of biochar with phosphoric acid followed by cross-linking with urea

Phosphoric acid was linked to biochar chain under the form of phosphoric acid group by ester linkage through reactions from biochar hydroxyl to form phosphorylated biochar. The phosphorylated biochar was then cross-linked by the use of urea; the temperature was raised to 150 ℃ because the melting point of urea is 144 ℃ (Martinez-Villadiego *et al*., 2024).

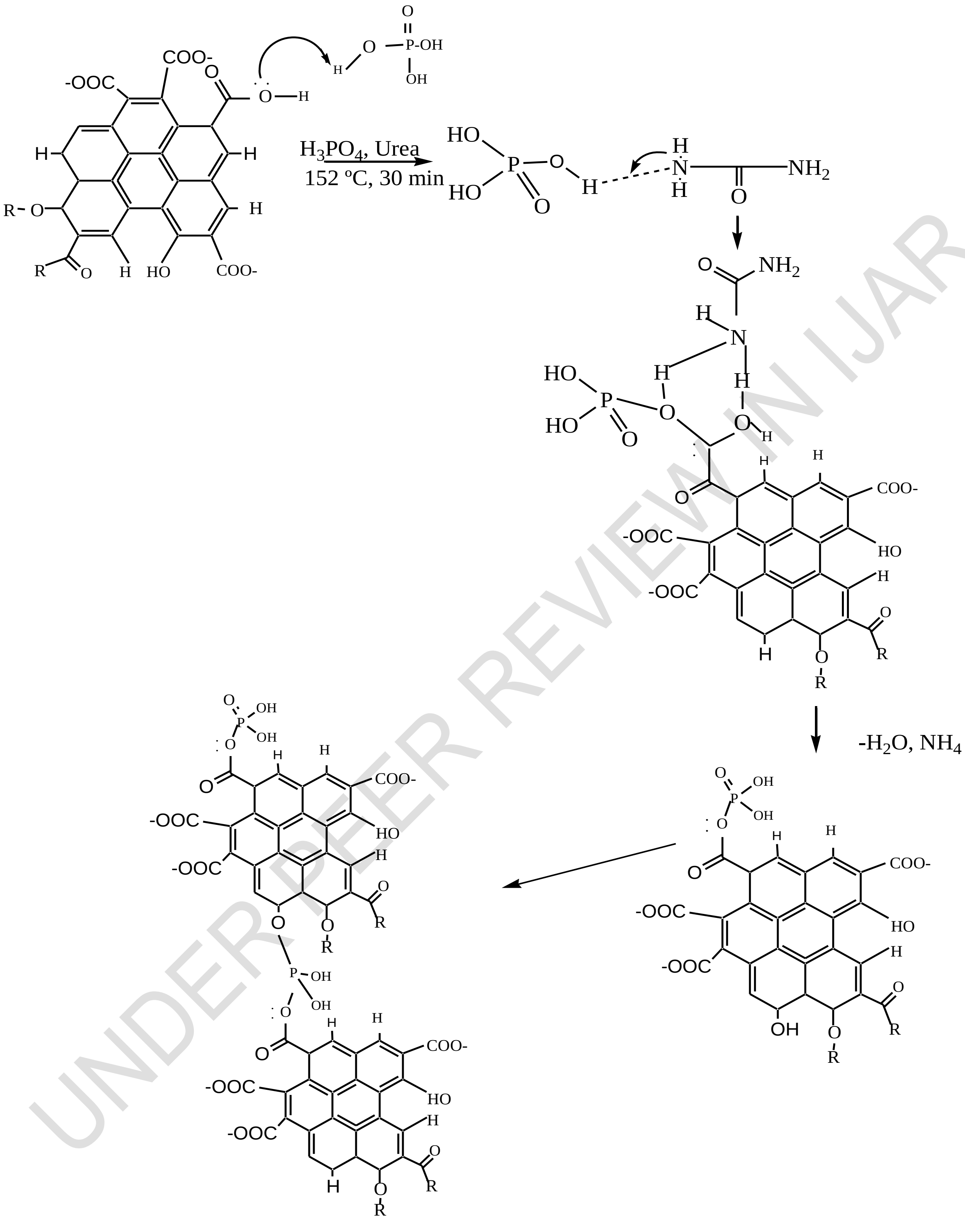

Figure 1. Reaction Scheme for the functionalization and cross-linking of biochar with phosphoric acid followed by urea

4.1.2 Functionalization of biochar with Ethan-1,2-diol followed by cross-linking with phosphoric acid

It involved an esterification reaction of ethan-1,2-diol with biochar in the presence of sulphuric acid which was then cross-linked with phosphoric acid to give a phosphoric Ester hydrogel

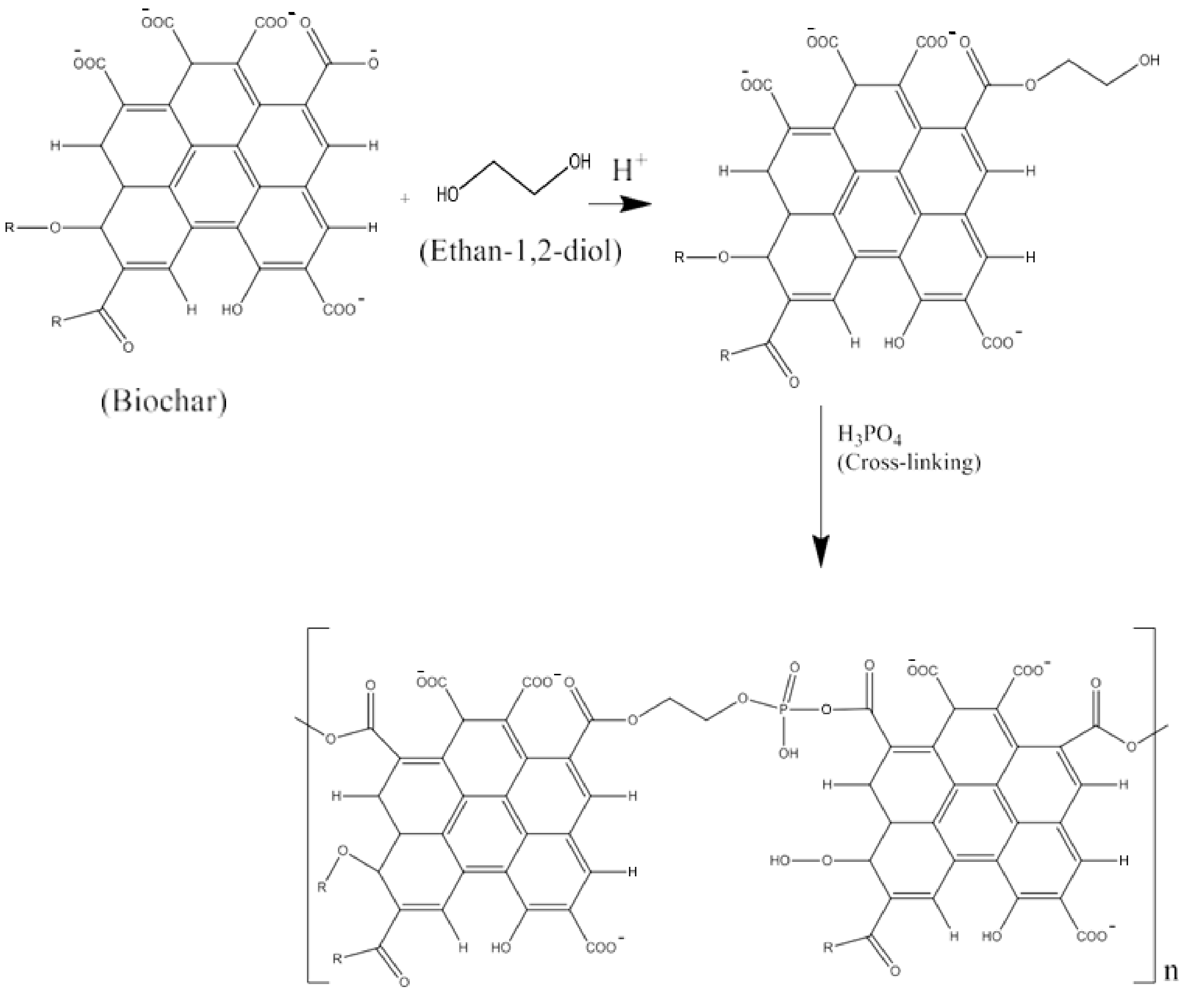

Figure 2. Reaction Scheme for the functionalization of biochar with Ethan-1,2-diol and cross-linked with phosphoric acid

4.1.3 Functionalization of biochar with glycerol and cross-linking with citric acid

It involved reacting 10g of biochar with glycerol at 120 ºC for two hours in the presence of sulphuric acid to form an ester. The cross-linking method was adopted from Gyamati, 2015 where the ester was heated at 90º C for 20 minutes after which 100g of the ester was placed in a beaker with 0.1M NaOH solution at a pH of 12.00 necessary for cross-linking to attain stability due to the alkali environment. The liquid was discarded and a carboxylation reaction followed as shown by the reaction scheme Figure 3.

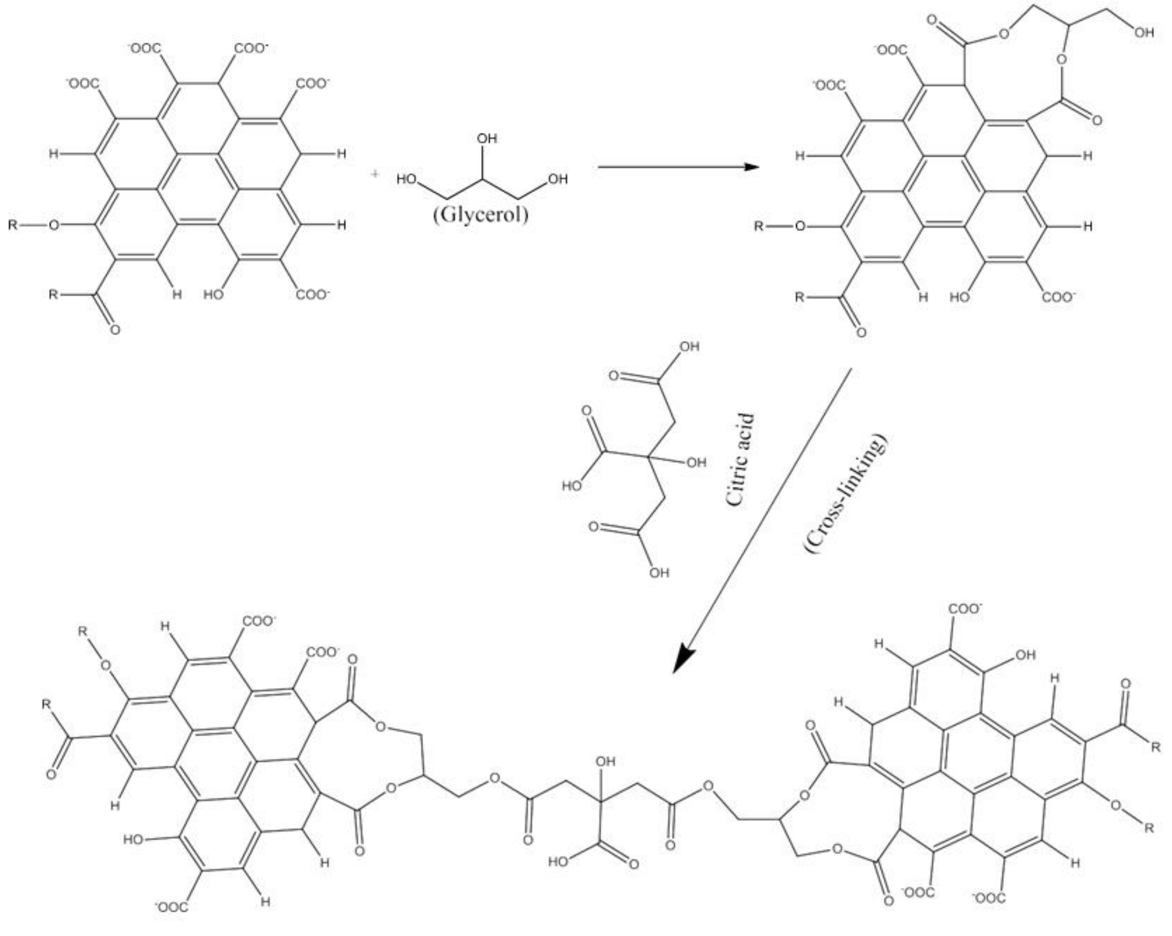

Figure 3. Reaction scheme of functionalization of biochar with glycerol then cross-linked with citric acid

4.1.4 Functionalization of biochar with ethan-1,2-diol

Biochar was reacted with ethan-1,2-diol by ester linkage and then cross-linked twice by the use of phosphoric acid to get a phosphoric Esther followed by a second cross-link with urea to give urea phosphate. The mulch did not hold a lot of water as one would expect as compared to the mulches with single cross-link since its swelling was 7.76 times its weight as compared to phosphate functionalized with urea cross-link which had a swelling capacity of 12.09 times its weight. This result was in line with a study which was done by An *et al*., (2021) on the relationship between cross-linking and swelling capacity. He found out that if too much cross-linking agent is used, then the high cross-linking degree causes a low swelling degree of hydrogel hence little water is held. However, if the amount of cross-linking agent is too small, then the physical interaction between polymer bonds breaks easily causing the hydrogel to become water soluble.

4.2 FTIR Spectra characterization of modified and unmodified biochar

Functionalized and non-functionalized mulch were characterized using FTIR. The spectra of biochar, phosphate functionalized and urea cross-linked biochar are given in Figure 4.1

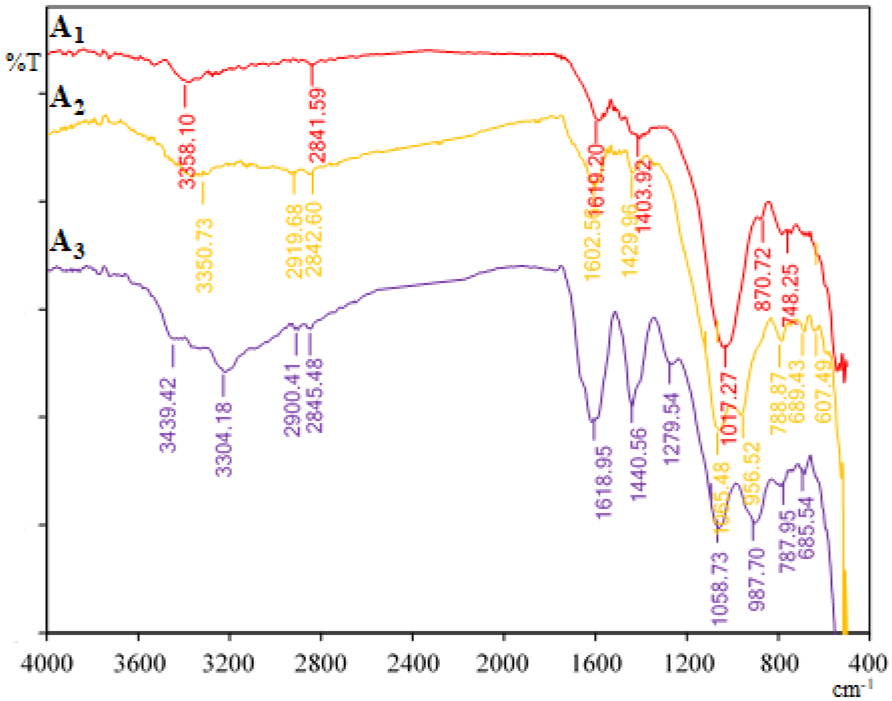

Figure 4.1: **The FTIR spectra of non-functionalized biochar ($A_{1)}$, phosphate functionalized Biochar ($A_{2)}$ and urea cross-linked mulch ($A_{3)}$**

All the spectra bands about 3350.73-3439.42 cm^{-1} are attributed to either -NH or -OH groups (Petit *et al*., 2018). The bands at 2919.68cm^{-1} and 2900.41cm^{-1} were attributed to C-H stretches while 1618.95 cm^{-1}, 1610.20 cm^{-1} and 1602.5cm^{-1} were attributed to stretching C=O, N-H or -OH (Nandiyanto *et al.*, 2019). The peaks at 788.87 and 956.52 cm^{-1} correspond to P-OH stretching vibration mode of phosphoric group (Zhang *et al.*, 2021) which was used to functionalize biochar. A band at 1279.5 cm^{-1} corresponds to the P=O stretching mode (Kubicki *et al*., 2012) and a peak at 1058.73 cm^{-1} was attributed to C-N stretching which indicate a successful cross-linking with urea.

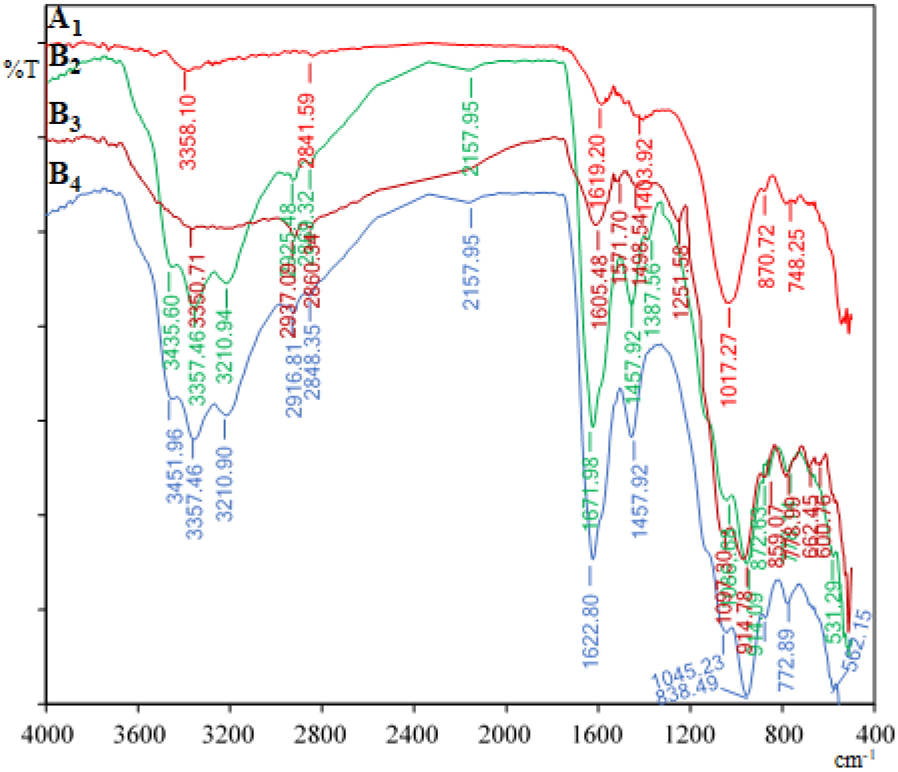

Figure 4.2 FTIR spectra of non-functionalized biochar (A_1), Ethan-1,2-diol functionalized (B_2), Phosphate cross-linked (B_3) and second cross-linking with Urea (B_4)

There are broad and strong bands at about 3451.96 cm^{-1}, 3435.60cm^{-1} and 3358.10 cm^{-1} which were attributed to -OH or -NH groups (Enders *et al.*, 2021) from biochar. A peak at 1387.56 cm^{-1} corresponds to C-H stretching from Ethan-1,2-diol while a band at approximately 1251.58 cm^{-1} correspond to the P=O stretching mode (Kubicki *et al.*, 2012) and a peak at 859.07 cm^{-1} is attributable to P-OH stretching vibration mode (Frost *et al.*, 2013).

A band at approximately 3357.46 cm^{-1} corresponding to N-H stretching vibration mode (Branca *et al.*, 2016), a peak at 1622.80 cm^{-1} can be attributed to N-H bending vibration of amines according to Asyana, (2016) and a band at approximately 1045.23 cm^{-1} correspond to C-N stretching vibration mode (Krichen *et al.*, 2019)

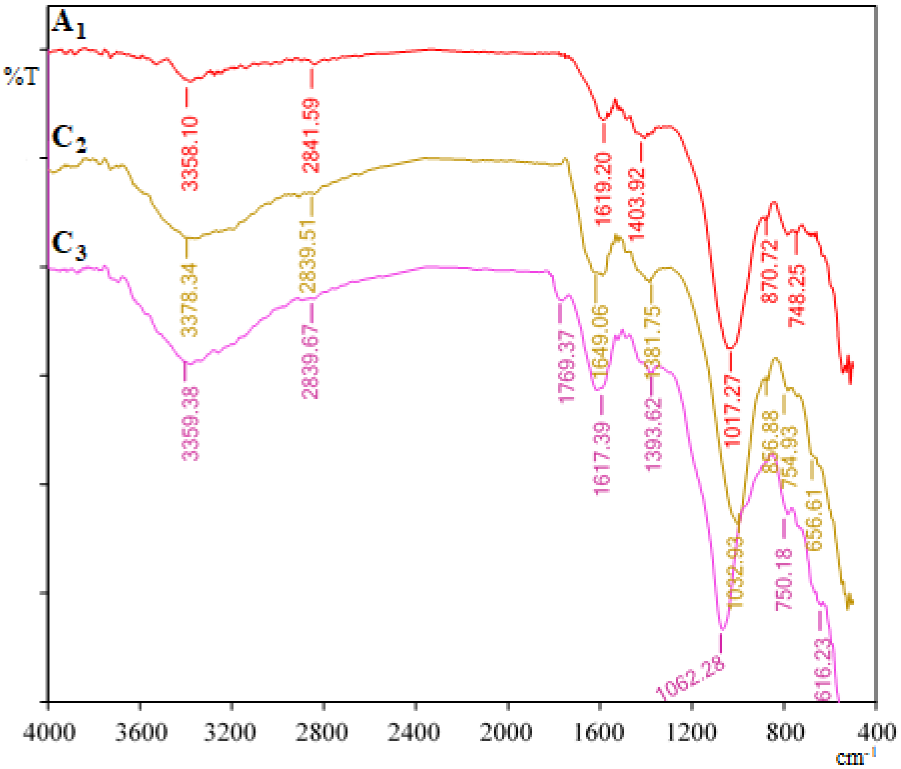

Figure 4.3: FTIR spectra of non-functionalized biochar (A$_1$), glycerol functionalized (C$_2$) and citric acid cross-linked (C$_3$).

The observed peaks at 3359.38, 3378.34 and 3558.10 cm^{-1} in all the three spectra's is due to -OH Stretching vibrations (Fontues *et al.*, 2021), the peak around 1617.39 cm^{-1} stretching was attributed to a carbonyl (Cai *et al.*, 2019) which indicates that the C=O from citric acid cross-link was successively anchored.

Conclusions

The functionalization with Ethan-1,2-diol, glycerol, phosphate and cross-linking with urea, phosphate and citric acid were confirmed with the FTIR spectrum which showed peaks for -OH at 3350.73 cm^{-1}, P-OH at 788.87 cm^{-1}, P=O at 1279.5 cm^{-1}, C-N at 1045.23 cm^{-1}, N-H at 1622.80 cm^{-1}, C-H at 2919.68 cm^{-1} and C=O at 1602.5 cm^{-1}. This confirmed that the diol, phosphate and amino used for functionalization and cross-linking had been successively anchored.

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