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SYNTHESIS AND CHARACTERIZATION OF GRAPHENE OXIDE MODIFIED CROSS-LINKED STARCH

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ABSTRACT

This study is aimed at evaluating the synthesis and characterization of cross-linked starch modified by graphene oxide. Starch was extracted from maize grains and cross-linked with sodium trimetaphosphate (STMP). Graphene oxide was synthesized from the oxidation of graphite powder using the modified Hummers method. Both the Extracted starch (ES), cross-linked starch (CLS), Graphene oxide (GO), and the synthesized CLS-GO composite were characterized using Fourier Transform Infrared (FT-IR) Spectroscopy, X-Ray Diffraction (XRD) Analysis, Differential Scanning Calorimetry (DSC), and Scanning Electron Microscopy (SEM). The XRD of the composite reveals the nature of the polymer while the DSC results indicate a glass transition temperature of 29.9 ^{0}C, the crystallization temperature of 123.43 °C, and melting temperature of 151.60 °C. Also, the surface morphology of CLS-GO determined using SEM reveals a rough and porous material.

Keywords: Starch, Cross-linked Starch, Graphene oxide,

INTRODUCTION

Currently, biopolymers are industrially attractive adsorbents because of their ability to bind with metal ions and are environmentally safe (Gumel *et al.,* 2015). One of such biopolymers is starch. Starch is a natural semi-crystalline biopolymer of D-glucose and is composed of linear amylose and amylopectin moieties responsible for its crystalline and amorphous properties (Atichokudomchai *et al*., 2000: Miculescu *et al*., 2017). Starch is constituted by hydroxyl groups with valency and electronic characteristics that can initiate the adsorption of aqueous heavy metal ions (AHMIs). However, this can be enhanced using various modification sequences. As a natural polymer, starch has attracted considerable research attention due to its wide availability*,* low cost, renewability, sustainable biomaterials, self-healing composites e.t.c (Bradshaw *et al*., 2010: Kim *et al.,*2017). Starch has limited application due to low shear resistance, pore-volume, insolubility in water at room temperature, easy retrogradation, instability of its pastes and gels, small surface area, and high susceptibility to thermal decomposition which lower its practical applications (Sancey *et al.,* 2011). The modification of starches has become a popular approach to achieve desirable physicochemical characteristics and to enlarge their application scope. The functionality of starch can be modified in several ways such as chemical modification, genetic modification, and physical modification. The most important in use is a chemical modification (Coativy *et al*., 2015). This entails turning the chemical composition and functionality of the starch to obtain new products with desired properties via reactions with some chemical reagents. The presence of a large number of hydroxyl groups on starch provides more reactive sites for the starch. Typically, hydroxyl groups on starch molecules are attacked, resulting in replacements and inter or intra-molecular bonds (Ashogbon, 2014: Cui *et al*., 2011). There are various methods of chemical modification of starch, but some important methods are etherification, esterification, grafting, cross-linking, dual modification, etc (Wang *et al*., 2015). A common procedure is the cross-linking and substitution of the hydroxyl groups via esterification and/or etherification reactions to produce starch derivative adsorbents (SDAs) with improved structural and functional properties for adsorption. In order to cross-link polymers containing hydroxyl groups on the backbones, such as starches, the cross-linkers must have the capability to react with at least two hydroxyl groups in a single polymer molecule or in adjacent molecules (Kling, 2001:Vandenbossche *et al*., 2015). Cross-linking in starch can be initiated via physical and chemical means; however, chemical cross-linking is cheaper and simpler. Chemical cross-links stabilize the structure and mechanical activities of starch molecules which occurs when bi-functional or multi-functional reagents capable of forming ether or ester linkages with hydroxyl groups interact with starch macromolecules to form intra and intermolecular bonding that creates three-dimensional network structures in the starch polymer matrix (Alcazar *et al.*, 2015: Hirsch *et al.*, 2002).

Graphene oxide is a two-dimensional carbon atom sheet in a honeycomb structure exfoliated from graphite. It has a hexagonal structure with two sub-lattices atom bonded together with σ bonds. The π orbital in each carbon atom is partially filled below and above the plane (Zhu *et al.*, 2010). Graphene oxide was synthesized from graphite as a result of the oxidation of graphene and the plane of it is attached with oxygen functional groups which make it become hydrophilic and easily to be dispersed in a polar solvent (Edward *et al.*, 2013). Graphene oxide is a kind of novel adsorbent and can be prepared from low-cost graphite. Graphene has large quantities of oxygen functional groups (hydroxyl, carboxyl epoxy groups) on the graphitic backbone of graphene oxide which possesses high water solubility and a large specific surface area (Zhao *et al.*, 2011). In the past, Graphene oxide and its derivatives have been studied for their adsorption properties for organic and inorganic contaminants in aqueous solutions and it's an efficient adsorbent for the safety of the environment especially concerning wastewater treatment (Gonavelli *et al.,* 2013).

In this work, composites of cross-linked starch modified by graphene oxide (CLS-GO) were prepared as an adsorbent.

MATERIAL AND METHODS

Extraction of Starch

A wet method described by Olayinka *et al.* (2013) was used for the extraction of starch.

Table 1: The Reagents Used

Reagents	% Purity	Grade	Manufacturer
Sulfuric acid	98.0	Analar	Sigma Aldrich
Hydrochloric acid	37.0	Analar	Sigma Aldrich
Acetic acid	99.9	Analar	Sigma Aldrich
Methanol	98.9	HPLC	Sigma Aldrich GmBH
Ethanol	99.9	HPLC	Sigma Aldrich GmBH
Hydrogen peroxide	30.0	Analar	Sigma Aldrich
Sodium hydroxide	99.0	Analar	Sigma Aldrich
Sodium chloride	98.0	Analar	Sigma Aldrich
Sodium carbonate	99.9	Analar	Sigma Aldrich
Sodium nitrite	98.0	Analar	Sigma Aldrich
Potassium persulfate	99.0	Analar	Sigma Aldrich
Potassium permanganate	98.0	Analar	Sigma Aldrich
Phosphorus pentoxide	98.0	Analar	Sigma Aldrich
Graphite flake	98.0	Analar	Sigma Aldrich

Table 2: The Equipments used

Equipments	Model	Manufacturer
UV/VIS Spectrometer Winlab Data	35 LAMBDA	Perkin Elmer
Atomic absorption spectrometer (AAS)	AA220	Zahner Scientific
Fourier transforms infrared spectrometer (FTRI)	S30	Perkin Elmer
Scanning electron microscope (SEM)	S50	FEI Compony
Differential scanning calorimeter (DSC)	DSC8000	Mettle Toledo
X-ray diffraction (XRD)	G600	MiniFlas
Ultrasonicator	S5510	Bransom
Incubator shaker	S40	Perkin Elmer

Preparation of Cross-Linked Starch

Gao *et al.*, (2014) method were adopted for cross-linking of the extracted starch. Starch powder (25 g) was added to 50 ml distilled water. Then 0.5 g Na_2CO_3 and 1.25 g NaCl were added. Sodium trimetaphosphate (5 g) was dissolved in the mixture. Then, the mixture was stirred using a magnetic stirrer for 90 min at 50 °C in a thermostated water bath. HCl (1 M) was used to adjust the pH to 6.5. A solid portion formed was precipitated and the supernatant layer was discarded, washed with deionized water, and allowed to dry overnight.

Synthesis of Graphene Oxide (GO)

GO was synthesized from natural graphite powder using a modified Hummers method. Graphite flakes (5 g) were added into a 250 ml round-bottomed flask, and then 60 ml of 98 % H_2SO_4 was transferred into the flask. P_2O_5 (5 g) and $K_2S_2O_8$ (5 g) were then added into the above flask. The flask was refluxed for 6 hrs by raising the temperature gradually to 80 ˚C. The preoxidized graphite was diluted using deionized water and left overnight. It was then filtered and washed with deionized water to remove the residual acid. The sample was finally dried at room temperature. Exactly, 5 g of preoxidized graphite, $NaNO_3$ (4 g), and 150 ml of 98 % H_2SO_4were blended into a beaker flask and placed in an ice-water bath on top of a hot plate for an hour using a bar magnetic stirrer. $KMnO_4$ (20 g) was added slowly into the flask with stirring and cooling for 3 hrs. The s ample mixture was kept at 35 ˚C for 48 hrs. Subsequently, 150 ml of deionized water was added under vigorous stirring and 30 ml of 30 % H_2O_2 solution was slowly added to the mixture. The color of the mixture changed from black to yellow. The synthetic product was washed by rinsing and centrifugation at 4000 rpm for 5 min with 5 % HCl and deionized water respectively. The products were dried overnight (Ali *et al*., 2016).

Preparation of Cross-linked Starch modified by Graphene oxide (CLS-GO)

The CLS-GO composite was prepared by the following process. GO (1 g) prepared was dispersed into 20 ml of 1 % acetic acid solution and ultrasonicated for 30 min at room temperature to form a homogeneous suspension. Starch powder (0.5 g) was dissolved into the solution under stirring and ultrasonicated for 60 min. The solution was allowed to diffuse thoroughly for 12 hrs. Aqueous sodium hydroxide solution (30 ml of 5 %) was added, at about 40 drops per minute. The beads solidified after 24 hrs and were washed several times with deionized water to remove any residual alkali and some traces of acid. Methanol (30 ml) and sodium trimetaphosphate (5 ml of 50 %) were added into the mixture and stirred for 5 hrs at room temperature. The beads were separated and washed several times with ethanol and deionized water, respectively and were dried overnight (Yang *et al*., 2014).

Fourier Transform Infrared (FT-IR) Spectroscopy Analysis

Analysis of Starch, Cross-linked starch, Graphene oxide, and CLS-GO was characterized by a Fourier transform infrared (FT-IR) spectrophotometer, Perkin Elmer, to verify its composition and chemical structure based on the functional groups. The samples were analyzed at 8.0 cm^{-1} resolution and the spectra were recorded at 25 ˚C in the range of 4000 - 650 cm^{-1} (Dong *et al*., 2015).

X-Ray Diffraction (XRD) Analysis

The XRD diffractograms of the cross-linked starch modified by graphene oxide was obtained using an X-ray diffractometer. The sample was scanned in the angular range of 10 – 90 ˚C (2 Ø) with a scanning rate of 5 min and a sampling interval of 0.1°. The analysis was then performed at a voltage of 40 kV and current of 15 mA radiation. The diffracted radiation was detected using a proportional detector.

Differential Scanning Calorimetry (DSC) Analysis

Differential Scanning calorimetry (DSC) measures heat flow associated with the thermal transition of material such as glass transition, melting point, and crystallization temperature. Samples were placed into an aluminum pan (40 µl) and the sample pan bottom area was covered and then weighed on the scale balance. The lid was placed on the pan with indention facing down and the lidded pan on the sealer holder was pushed clockwise until it makes one complete turn,. The sample pan one and on the reference pan two were punctured for identification. The furnace chambers were open and the sample pan on the sample tray labeled (S) and reference pan on the reference tray labeled (R) were placed in the furnace chamber and closed. The power, DSC module, and the software of the computer system were all turned on an experiment to mark the start of the experiment. At the completion stage of the experiment, the thermograph was saved, cooling of the furnace and finally deactivation of the DSC module.

Scanning Electron Microscopy (SEM) Analysis

The surface morphology of the composite was examined on scanning electron microscopy. The samples were analyzed using the microscope operated at an accelerated voltage with a focused beam of electron microscopy. The morphologies of the composite were produced by scanning the surface of samples with a focused beam of electron microscopy. The Scanning SEM image of loaded cross-linked starch modified by graphene oxide at selected magnifications was observed and the micrograph displays the surface morphology of the adsorbent (Benu *et al*., 2014).

RESULTS AND DISCUSSION

FT-IR ANALYSIS: The FT-IR spectra of the starch and the cross-linked starch are presented below:

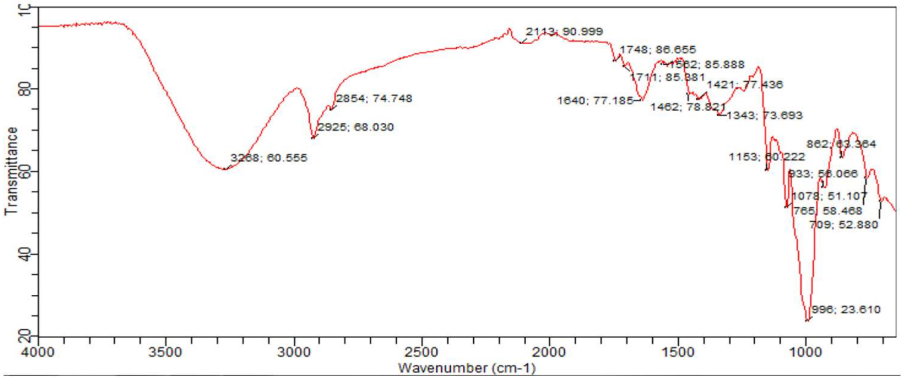

Figure 1: FT-IR Spectra of starch

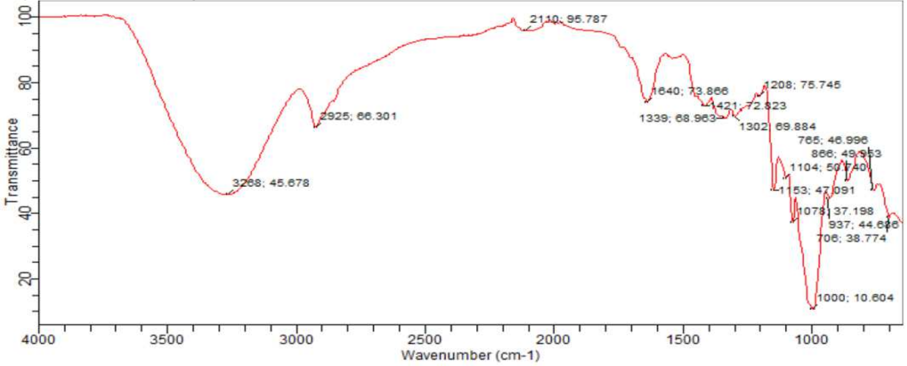

Figure 2: FT-IR spectra of cross-linked starch

Table 3: The FT-IR Absorption Bands of Extracted starch (ES), Sodium Trimetaphosphate (STMP), Cross-linked Starch (CLS), Graphene Oxide (GO), and CLS-GO composite.

Functional Groups	ES	STMP	CLS	GO	CLS-GO
O-H	3268	-	3268	3569 - 3164	3298 - 3164
C-H	2925	-	2825	2925- 2854	29818 - 2851
C=O	-	-	-	1722	1737 - 1719
C=C	-	-	-	1622	1581 - 1510
OH	1343	-	1339	1369	1365
C-O-C	996	-	937	1231	-
P=O	-	1290	1208	-	-
PO_2	-	1160	1153	-	-
P-O	-	870	866	-	691

Table 3 shows the FT-IR Absorption Bands of extracted starch. The band observed at 3268 cm^1 indicates the stretching vibration of the O-H bond, while the band at 2925 cm^{-1} corresponds to C-H stretching vibration (Wittaya *et al.*, 2014). The band at 1640 cm^{-1} is the C-O-O stretching vibration in a carbohydrate group. The absorption band at 1348 cm^{-1} indicates -CH_2OH related mode and the band at 1078 cm^{-1} is the C-O-H bending (Sechia *et al.*, 2017). The band at 966 cm^{-1} is the skeletal mode vibrations of α-1, 4 glycosidic linkages of C-O-C (Mirinda *et al.*, 2017).

In Table 3: the FT-IR absorption bands of starch cross-linked with Sodium trimetaphosphate (STMP), Small intensity variations were observed in some bands about the absorption, as well as a new low-intensity band in the 1339 cm^{-1} region that can be associated with water present in the material. However, specific bands of bound phosphate groups were not observable, probably due to the reduced number of phosphate introduced. The band at 3268 cm^{-1}could be due to O-H stretching of unbound water, probably adsorbed on the surface of the sample. The band v at 1290 $cm^{-1}$was assigned to symmetrical stretching P=O, while a band at 1160 $cm^{-1}$was related to asymmetrical stretching of the PO_2 group and a band at 870 cm^{-1} may be related to the P-O bond. Such alterations in the absorption in the infrared region evidenced occur in the phosphorylation process (Li *et al.*, 2009).

Also, the FT-IR absorption bands of graphene oxide (GO) at 3569 $cm^{-1}$and 1369 cm^{-1} was related to the O-H stretching vibrations, the bands at 1722 and 1622 cm^{-1}could be due to the stretching vibration of carboxylic acid and carbonyl at the edge of graphene (Caotivy *et al.*, 2015). The bands at 2854 and 2925 cm^{-1} are assigned to C-H symmetric and asymmetric stretching vibrations, the bands at 1231 and 1150 cm^{-1} are assigned to C-O-C and C-OH stretching vibrations. These polar groups make it easy to form hydrogen bonds with water (Dariush K, 2016: long *et al.*, 2012).

For the FT-IR absorption bands of CLS-GO, the broad absorption bands at 3298 cm^{-1} and 3264 cm^{-1}were are attributed to O-H symmetrical stretch from CLS and graphene oxide. The bands at 2918 cm^{-1} and 2851 cm^{-1} represented the C-H symmetric and asymmetric stretching vibration (Liu *et al.*, 2013). The absorption bands at 1737-1719 cm^{-1} indicated the C=O asymmetric stretching from GO and the bands at 1581-1510 cm^{-1}areC=C of the aromatic rings. While the band at 1365 cm^{-1} represents the C-OH bending in the miscibility of CLS-GO (Manoratne *et al.*, 2017).

X-ray Diffraction Pattern of Graphene oxide Modified Cross-linked Starch (CLS-GO)

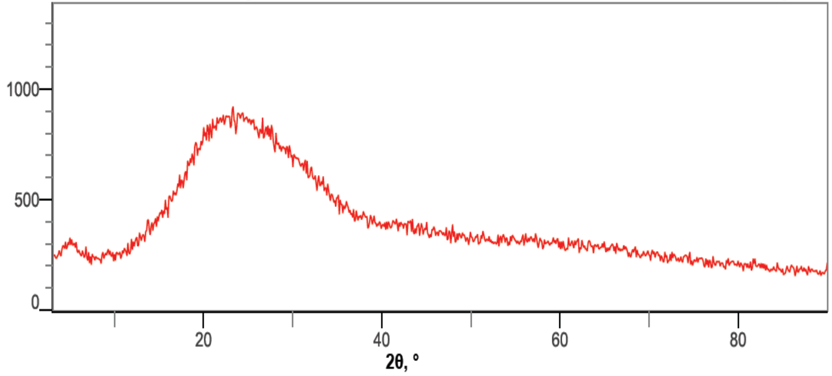

Figure 3: The XRD pattern of CLS-GO Composite adsorbent

In Figure 3, the XRD analyses were used to characterize the crystalline nature and phase purity of the material. The XRD pattern obtained in cross-linked starch modified by graphene oxide has a strong and broad diffraction pattern which indicates that it is amorphous. This could be due to the reaction with STMP, forming new groups along the chain with random spatial distribution in the spectra resulting in alkalization of the previous reaction with the phosphates and also the presence of partial gelling. A similar result was also reported by Wittaya *et al.* (2014).

Differential Scanning Calorimetry of Graphene Oxide modified Cross-Linked Starch (CLS-GO).

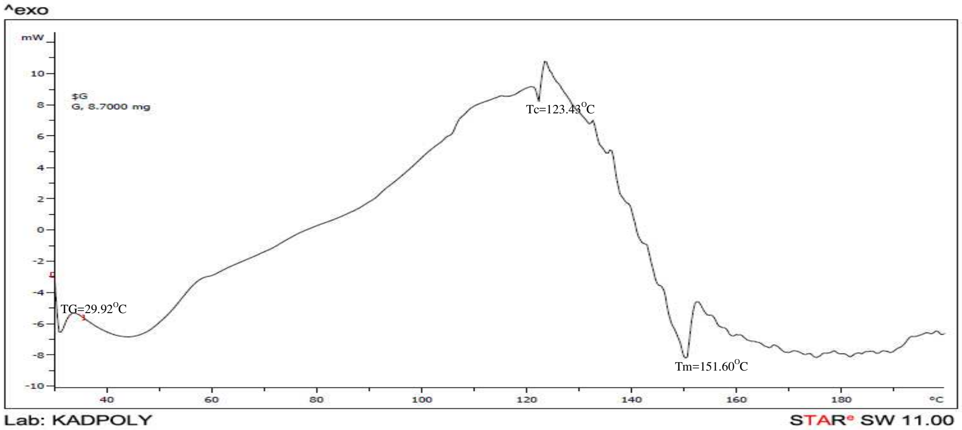

Figure 4: Differential Scanning Calorimetry Curve of CLS-GO

In Figure 4, the DSC analysis shows the thermograph stable curve of cross-linked starch modified by graphene oxide, from the graph curves shows that the mixture of cross-linked starch modified by graphene oxide is miscible. The peaks from the DSC analysis showed that, the glass transition temperature (Tg) of 29.92 ˚C, crystallization temperature (Tc) of 123.43 ˚C, and the melting point temperature (Tm) of 151.60 ˚C. This means that the composite adsorbent is thermally stable. Therefore, a higher temperature is needed to melt the composite adsorbent (Haruna *et al.*, 2021).

SEM Images of (CLS-GO) Composite Adsorbent

Figure 5: SEM image of composite adsorbent

From figure 5, the SEM micrographs of cross-linked starch modified by graphene oxide (CLS-GO) adsorbent show that GO was partially transparent with some crumples of starch and has lateral dimensions of several micrometers with small holes caused by overexposure to sonication which is also found to be the rough and porous surface of the adsorbent (Wang *et al.*, 2013).

CONCLUSION

The introduction of graphene oxide (GO) on the cross-linked starch surface can significantly, increase the adsorption capacity of metal ions. The hydroxyl groups and acetyl oxygen functional group in starch and the hydroxyl and carboxyl groups on the GO surface can make GO-CLS an excellent adsorbent. Results of FT-IR, SEM, XRD, and DSC analyses show the successful synthesis of graphene oxide modified cross-linked starch (GO-CLS) as adsorbent.

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