# GRAFTING OF ACRYLAMIDE MONOMER ON SUGARCANE BAGASSE

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## ABSTRACT

*Cellulose modifications through grafting of active monomers have been found to enhance the sorption properties of cellulosic agricultural waste materials in the uptake of materials from solutions and in water treatment. Initial compositional analysis of sugarcane bagasse (SCB), a fibrous matter left after cane sugar extraction from sugarcane, showed a cellulose content of 40.21 %; hemicellulose, 25.8 %; lignin, 22.9 %; ash content, 1.72 % and moisture content of 9.41 %. The cellulose was extracted from the SCB using alkaline extraction with sodium hydroxide followed by bleaching with sodium hypochlorite. It gave a cellulose yield of 53.13 %. Acrylamide monomer was grafted unto the cellulose under optimum conditions of ceric ammonium nitrate (CAN) concentration of 0.015 M, 2 hours reaction time and a monomer to cellulose ratio of 3:1 (w/v). These conditions favoured increase in graft and graft efficiency percent.*

*Keywords: Agricultural wastes, sugarcane bagasse, acrylamide monomer, grafting.*

## INTRODUCTION

Agricultural activities all over the world generate enormous volumes of agricultural wastes that contain cellulose fibre. In Africa semi-processing of various agricultural crops generates close to 300 million tons of agricultural wastes annually [Isreal et al, 2008]. Maize stem and cobs, banana and plantain pseudostem, raffia from Raphia hooker; orange mesocarp, coconut shell, groundnut husk, sugar cane bagasses, soybean, oath, wheat and rice hull are common examples.

Recently, there has been an increased interest in developing techniques for the conversion of these abundant lignocellulosic materials into environmentally friendly chemicals and biomaterials. A great deal of attention has been given to the production of bio-adsorbents from lignocellulosic byproducts such as wood pulp (Sokker, 2005), sugarcane bagasse (Chung et al., 2011; Werkneh et al., 2015; Behnood et al., 2014 ), bamboo lignocellulose (Khullar et al., 2007; Varshney & Naithani, 2011), rubber seed shell (Ekebafe et al., 2011), mulberry branches (Liang et al., 2013c), noxious weeds – Lantana camara (LC) and Parthenium hysterophorus (PH) (Varshney & Naithani, 2011), and other lignocellulose (Bunhu & Tichagwa 2012; Hubbe et al., 2011; 2013; Roy et al., 2012; 2013; Shi et al., 2013). These bio-adsorbents prepared from lignocellulosic by-products have potential application in the removal of heavy metal ions from wastewater, wicking of oil, sugar decolorization and for promoting bio-degradation in saturated environments. The utilization of agricultural wastes as bio-adsorbents currently receiving wide attention is because of their abundant availability and low cost. Furthermore, they have relatively high fixed carbon content and present a porous structure (Ren et al., 2014; Osuide et al., 2006).

Sugarcane bagasse (SCB), a fibrous matter that remains after sugarcane stalks are crushed to extract their juice, is an abundant lignocellulosic agricultural waste. It contains cellulose content as high as 62% based on oven-dry weight and could therefore be an alternative source of cellulose (Wilke, 1994).

Cellulose is a renewable, biodegradable and naturally occurring linear biopolymer. It is a polysaccharide of anhydroglucose units linked at C-1 and C-4 by β-glycosidic bonds which neither melts nor dissolves readily in common solvents due to its inter and intra-molecular hydrogen bonds. For cellulose to be widely applicable in the industry its physical and chemical properties must be modified (Onigbinde, 2014). The chemical modification of cellulose can be achieved by preparing an ester or ether derivative, cross-linked derivative or a graft copolymer (i.e. a branched derivative) of cellulose (Gürdag & Sarmad, 2013).

Grafting is a simple technique used to incorporate desired active functional groups on the backbone of a polymer for different purposes. Grafting copolymerization onto cellulose induces physical changes, since the introduction of side chains leads to different structural characteristics in raw materials. Grafting of cellulose shows new properties such as hydrophobic or hydrophilic character and resistance to chemical and biological agents (Nada, 2007). Common monomers that have successfully been grafted to cellulose are acrylamide and propenoic acid(Nada, 2007; Osuide et al., 2006).

Acrylamide is a white odourless crystalline solid mostly used as a monomer in the synthesis of polyacrylamides which find many uses such as water-soluble thickeners, wastewater treatment, gel electrophoresis, papermaking, ore processing, tertiary oil recovery, and in the manufacture of permanent press fabrics. Some acrylamide is used in the manufacture of dyes and the manufacture of other monomers. However, the largest use of these polymers is in water treatment. There have been many investigations concerning the modification of cellulose with acrylamide. Nada et al, 2007, grafted acrylamide monomer on cellulose for use in water and metal ions sorption. Ren et al, 2014 prepared hydrogels by grafting copolymers of acrylic acid and acrylamide on sugarcane bagasse. Osuide et al, 2006, modified saw dust using 2-propenoic acid for waste water treatment.

The principle of operation of bio-adsorbent in waste water decontamination is adsorption. This is a process in which pollutants are adsorbed on the solid surface. Basically, it is a surface phenomenon and a passive physical-chemical interaction between the charged surface groups of biological material and ions in solution. The process is precisely called biosorption when biological materials are used and it has great advantages over conventional methods. These include low operating costs, high efficiency in detoxifying effluents and minimization of the

volume of chemical or biological sludge to be handled. Also the materials used are environmentally friendly and biodegradable (Ramahali & Mahlangu, 2010; Imran, 2012).
This study aims at grafting acrylamide monomer onto cellulose extracted from sugarcane bagasse, using ceric ammonium nitrate initiator to produce a bio adsorbent from less utilized agricultural waste which is intended for use in the treatment of industrial waste like palm oil mill effluent.

## MATERIALS AND METHOD

### MATERIALS

**Reagent:** All reagents used in this project work are AR grade or equivalent. They include: sodium hydroxide, acrylamide monomer, ceric ammonium nitrate, nitric acid, sulphuric acid, potassium hydroxide, benzene, ethanol, sodium hypochlorite (Hypo), glacial acetic acid and distilled water.

**Sample:** Sugarcane (*Saccharum officinarum*) was obtained from local farmers at Ogwa Main Market, Esan West Local Government Area, Edo State.

### METHODS

#### Sample preparation

The sucrose was extracted by crushing the sugarcane and the bagasse was washed and soaked in water to remove residual sucrose. After soaking, it was sundried and then oven dried at $60^{o}$ C for about 6 hours in order to make the SCB dry enough for grinding. The dried SCB was then manually grinded and sieved.

#### Characterization of sugarcane bagasse

The moisture content, ash content, lignin, hemicellulose and cellulose of the sugarcane bagasse were determined by standard methods reported in the literatures. (Abdel-Halim, 2014)

#### Cellulose Extraction

Cellulose was extracted using Okhamafe et al. (1991) method with a slight modification. 40g powder of sugarcane bagasse was delignified with about 600ml of 2% w/v aqueous sodium hydroxide for 30 minutes and the resulting slurry was filtered. The washed and filtered material was treated with 100 ml of 17.5% w/v sodium hydroxide at 80° C for 1 hour to digest the material. The resulting cellulose was washed thoroughly with distilled water. The extraction process was then completed by bleaching with an aqueous dilution of about 150ml of 3.5 % w/v sodium hypochlorite for 20 min at $80^{o}$ C and subsequent washing with water until filtrate was clear and the residue was neutral to litmus paper. The cellulose material was filtered, the water manually squeezed out to obtain small lumps which were dried at 60° C for 6 hours and labelled as Sugarcane Bagasse Cellulose (SCBC).

### Graft Copolymerization of Acrylamide on SCB

Grafting of acrylamide on SCBC was carried out by the method described by Nada et al. (2007). 5g of cellulose (w) was steeped in acrylamide solution for 5 minutes followed by the addition of dissolved ceric ammonium nitrate in nitric acid at $20^{o}$ C for 2 hours (total liquor ratio was 25:1, i.e. total quantity of grafting liquor was 125ml). After grafting, the sample was filtered, washed with distilled water, and then air dried ($w_1$). This dried sample was extracted with distilled water to dissolve the formed homopolymer. After extraction, the sample was washed with distilled water and then air-dried ($w_2$). The different variables of the grafted copolymerization of acrylamide onto cellulose were studied e.g. initiator concentration (0.005 – 0.020 M), ratio of monomer to cellulose (w/w) (1:1 – 3:1) and grafting time (0.5 – 3 hours).

Polymerization % = $[(w_1 - w)/w] \times 100$

Graft % = $[(w_2 - w)/w] \times 100$

Graft efficiency % = $[(w_2 - w)/\text{weight of monomer}] \times 100$

## RESULTS AND DISCUSSION

### Composition of SCB

**Table 1:** Composition of SCB and the cellulose yield.

| **Component** | Cellulose | Hemicellulose | Lignin | Ash | Moisture | Yield |
|---|---|---|---|---|---|---|
| **Percentage(%)** | 40.17 | 25.8 | 22.9 | 1.72 | 9.41 | 53.13 |

The determination of the physico-chemical properties of any agricultural waste intended to be used for grafting is very important. This is because this preliminary study ultimately determines the suitability of the material for the intended use. Table 1, shows the composition of sugarcane bagasse from which the cellulose was extracted. Also, the percentage yield of cellulose, 53.13% was a good yield which was similar to 55. 52% yield gotten in the work of Ekebafe et al (2010) using Tappi method of extraction of cellulose from rubber seed shell with acetic acid and nitric acid. The optimum yield gotten from this work was due to the experimental conditions and the caution taking so that little or no cellulose was lost in the course of removing the supernatant.

## EFFECT OF DIFFERENT VARIABLES ON GRAFTING PROCESS

### Effect of monomer: cellulose ratio

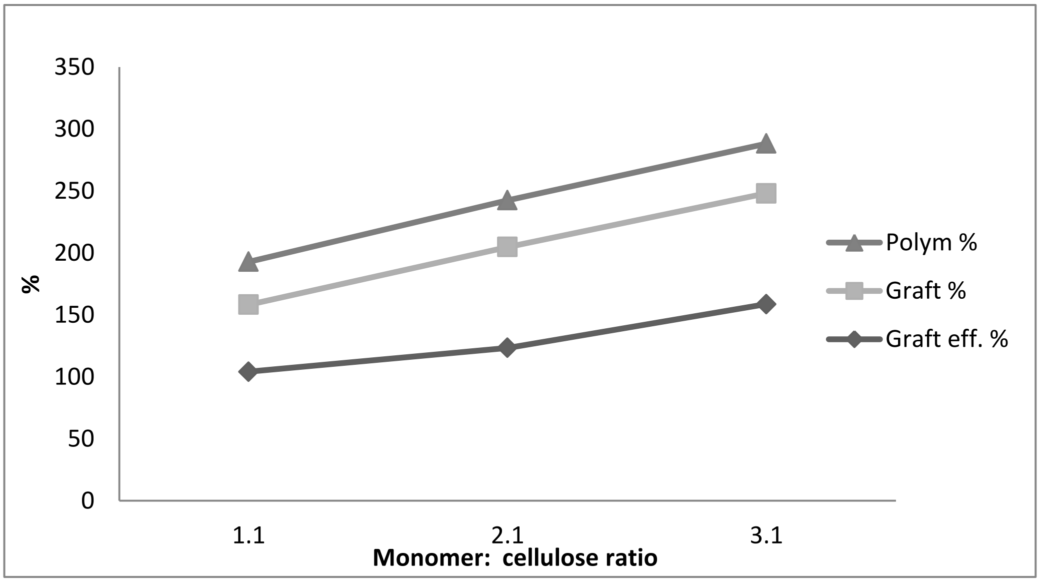


**Fig. 1** Effect of ratio of monomer to cellulose on GE %, G % and Polym %.

(Reaction conditions: Liquor ratio = 125ml, Temp = 27 $^{o}$C, CAN = 0.015 M, Time = 2 hrs)

Fig.1 shows the effect of the ratio of acrylamide to sugarcane bagasse cellulose (SCBC) on the different parameters of grafting. Results show that as the monomer ratio was increased from 1:1 to 3:1, there is a significant increase in polymerization %, graft % and graft efficiency %. Similar trends were observed by other investigators (Nada et al. 2007). With further increase of monomer concentration however, these values decrease. This is mainly due to the formation of homopolymer of acrylamide (AAm) at the higher concentration as well as due to restricted movement of free radicals onto polymer backbone because of increased viscosity. These homopolymers successfully hinders the rate of penetration of monomer molecules to the cellulosic material, resulting in the low percentage of grafting. Furthermore as the monomer concentration increases, the rate of homopolymerization increases thereby decreasing the formation of graft copolymer (Khullar et al., 2008; Nada et al., 2007).

### Effect of Initiator Concentration

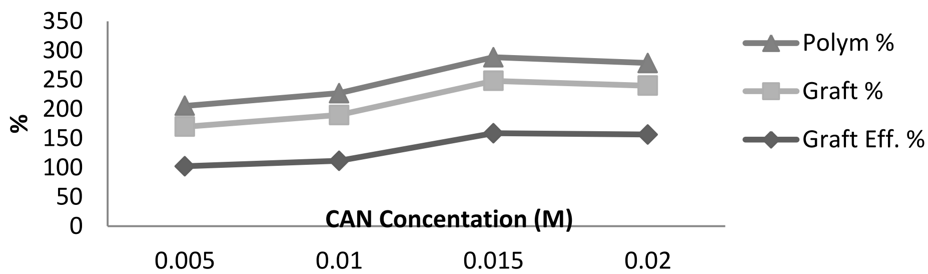


**Fig.2**. Effect of CAN Concentration on GE %, G % and Polym %.

(Reaction conditions: Liquor ratio = 125ml, Temp = 27 $^{o}$C, Mon:Cell ratio = 3:1, Time = 2 hrs)

Fig.2 depicts the effect of the initiator concentration (CAN) on grafting of AAm onto SCBC. It can be observed that the graft and graft efficiency increases as CAN Concentration increases up to 0.015 M. This increase is as a result of the formation of a great number of grafting sites on the cellulose backbone, which in the presence of monomer, induces grafting. Increasing the initiator concentration more than this causes a reduction in graft and graft efficiency. This may be due to the fact that with high concentration of the initiator more and more homopolymers are formed. This is obvious since ceric ion is a very good oxidizing agent with very high oxidation potential and it interacts with AAm forming the homopolymer rather than the graft copolymer at higher concentrations. Similar observations were reported by Ekebafe et al (2010); Khullar et al (2008) and Nada et al. (2007).

**Reaction Time**

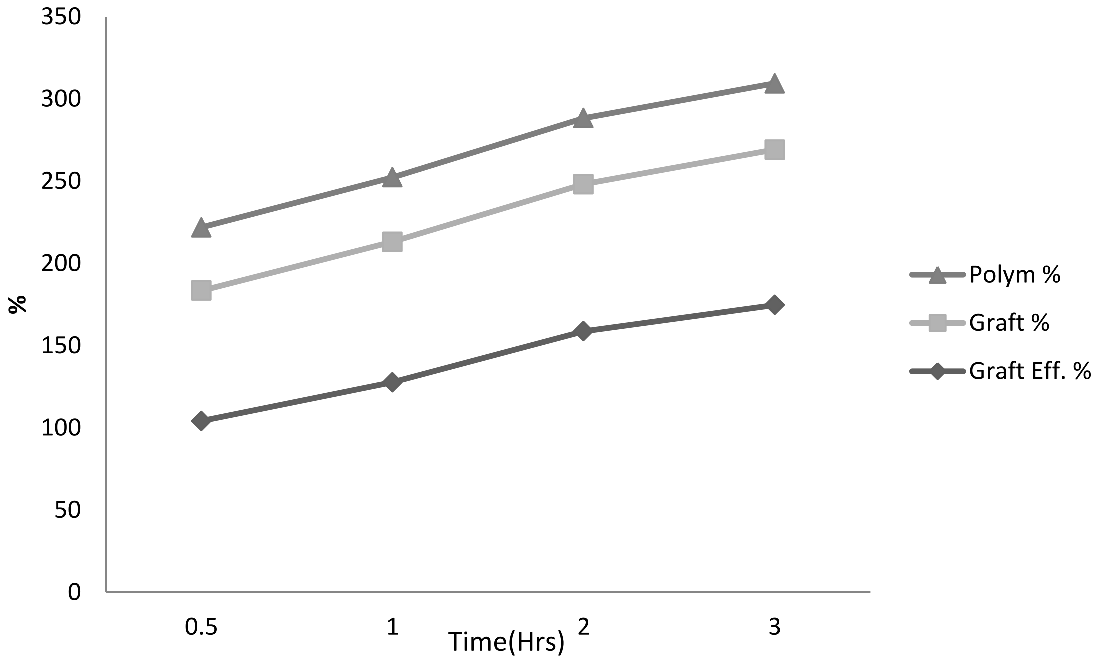


**Fig. 3**. Effect of reaction time on GE %, G % and Polym %.

(Reaction conditions:Liquor ratio = 125ml, Temp = 27 $^{o}$C, Mon:Cell ratio = 3:1,CAN = 0.015M)

The effect of duration of polymerization can be seen in Figure 3. Graft and graft efficiency increases as the time is increased from 30 mins to 3hrs. Reaction time allows ceric solution to diffuse into SCBC backbone prior to grafting reaction thereby allowing initiation of free radicals on cellulose sample by oxidation with $Ce^{IV}$ ions. Adama et al. (2014) reported that increase in reaction time beyond 120 minutes led to decreased graft and graft efficiency which was attributed to the decay of free radical activity of $Ce^{IV}$ oxidized cellulose resulting from the free radical termination by charge transfer. Nada et al., (2007) also reported that increase in reaction time beyond 2 hours caused the reaction rate to level off due to depletion of initiator and monomer as well as shortage of grafting sites.

**CONCLUSION**

Graft copolymerisation of acrylamide monomer unto cellulose extracted from sugarcane bagasse was successfully conducted. SCB gave a high cellulose yield of 53.13% due to proper optimization of extraction procedure. The graft copolymerization using chemical initiator at an heterogenous medium gave optimum result with grafting conditions of CAN concentration 0.015 M, reaction time 2 hours and ratio of monomer to cellulose 3:1 (w/v). There is the need for further studies on the utilization of the bioadsorbent produced for industrial effluent treatment.

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