



GREEN ADSORBENT SYNTHESIS FROM ORANGE MESOCARP CELLULOSE USING GRAFT COPOLYMERIZATION

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ABSTRACT

The potential of agricultural waste like orange (*Citrus sinensis*) mesocarp is yet to be explored. Thus, in this study the extraction of green adsorbent that will be renewable, low cost and environmentally friendly from orange mesocarp was examined. The extraction was done using alkali pretreatment method followed by bleaching process to obtain cellulose and dissolve the hemicellulose, lignin and other extractives. Then, graft copolymerisation of acrylamide onto the cellulose obtained was done using free radical initiation system. Grafting parameters were studied by varying the effects of initiator concentrations, monomer to cellulose ratio, temperature and time. Distilled water was used to extract the formed polyacrylamide (PAam) for 48 hours. And the characterization of the extracted and grafted cellulose samples was carried out by Fourier Transform Infrared Spectroscopy (FTIR). Orange mesocarp gave a cellulose average yield of 29.1%. The optimum grafting conditions were found to be 30°C at a time interval of 2 hours, ratio of monomer to cellulose being 3:1 and initiator concentration of 0.020M. The percentages of polymerization, graft and graft efficiency were 113.40, 86.83 and 45.90 respectively. Also, the absorbance peaks of the samples confirmed that grafting was effectively carried out on the cellulose backbone.

Keywords: Green adsorbent, orange mesocarp, cellulose, grafting, copolymerization.

INTRODUCTION

Across the globe, agricultural and agro-allied activities generate enormous amount of agricultural by-products and wastes containing cellulose fibers that constitute environmental nuisance (Ogali and

Owhonda, 2011; Sath *et al.*, 2018). Orange mesocarp, maize stem and cobs, banana and plantain pseudostem, coconut shell, groundnut husk, wheat, sugar cane bagasses, soybean, rice hull, and oath are common examples. Some of these could yield

cellulose content as high as 62% and could be alternative sources of cellulose (Onigbinde, 2014). An important agricultural waste of note is orange peel and mesocarp.

Orange production global estimation is at 60 million tons per annum, while orange peel wastes annual production is 32 million tons (Michael-Igolima *et al.*, 2023). From previous studies, the water uptake of orange peel is lower than 1 mg/g while its adsorption capacity ranges from 3 mg/g to 5 mg/g (Michael-Igolima *et al.*, 2023). Due to the low water uptake of orange peel and its abundance, orange mesocarp, a component of orange peel is considered a potential biosorption material worthy of study. There are several adsorbents that have been used in decontaminating wastewaters. They include synthetic, natural inorganic and organic adsorbents. Synthetic adsorbents are expensive and non-biodegradable. They have been known to be toxic, capable of having harmful impact on the environment and

human life (Yue *et al.*, 2017). This necessitate the use of green adsorbents like orange mesocarp which is rich in cellulose.

Cellulose is a naturally occurring, biodegradable and renewable linear biopolymer. It is a promising raw material owing to its pliable chemical nature, low cost, easy availability and abundance. Cellulose, a polysaccharide containing anhydroglucose units linked at C-1 and C-4 by β -glycosidic bonds do not melts nor dissolves easily in common solvents as a result of its inter and intra-molecular hydrogen bonds (Adinugraha *et al.*, 2005). For cellulose to be useful in various industrial applications, its chemical and physical properties must be modified. Chemical modifications of cellulose can be done by preparing ether or ester derivatives, cross-linked derivatives or graft copolymers of cellulose (Gürdag and Sarmad, 2013).

Graft copolymerization is a veritable tool for the modifications of surfaces of polymers and the transformation of

polymers' physical or chemical properties. Various researchers have explored the amazing possibility of cellulose modification through graft copolymerization (Nada *et al.*, 2007; Ren *et al.*, 2014). During the grafting process, the side chains are covalently bonded to the main polymer backbone resulting into a material with many different properties which are superior to individual properties. However, the properties of the graft copolymers are dependent on the type of monomer used, grafting medium, initiation mechanism, grafting condition and efficiency among other factors. Depending on the chemical structure and type of the monomer grafted to cellulose, graft copolymers acquire new properties like hydrophobic and hydrophilic character, water absorption, improved elasticity, heat resistance and ion-exchange capability (Gürdag and Sarmad, 2013).

Previous reports showed that copolymers have several important

applications. They are used for example, for reclaiming ion of precious metals from wastewater, in water treatment, and for personal care products (Khullar *et al.*, 2008; Nada *et al.*, 2007). Cellulose graft copolymers produced from the grafting of vinyl monomers containing functional groups like acrylic acid, acrylonitrile and acrylamide have been used in the adsorption of contaminants from solutions like heavy metal ions and dyes (Abdel-Halim and Al-Hoqbani, 2015; Mahdavi *et al.*, 2011). Hubbe, (2013) in his work also considers the utilization of modified cellulosic material in water clean-up through biosorption of heavy metals, dyes and spilled oils.

The current focus of interest is on the development of effective and eco-friendly copolymer materials as green adsorbent from orange mesocarp and the optimization of their graft copolymerization conditions.

MATERIALS AND METHODS

Orange mesocarp (OM) preparation

Orange (*C. sinensis*) was gotten from farmers at Ogwa market, a community in Esan West Local Government of Edo State. To generate orange mesocarp from the oranges, the epicarp and endocarp were removed. Then mesocarp was first sundried and oven dried at 60° C for 6 hours before grinding. The pulverized mesocarp was sieved using a standard sieve (600 micron).

Extraction of Cellulose

The extraction of cellulose was done using Okhamafe *et al.* (1991) method. After the proper sample preparation, forty grams (40.0g) powder was subjected to delignification with about 600ml of 2% w/v sodium hydroxide solution for 30 minutes and the resulting mixture filtered. The residue was treated with 100 ml of 17.5% w/v sodium hydroxide solution at 80°C for 1 hour. The resulting cellulose was thoroughly washed with distilled water. The extraction was completed by bleaching with about 150ml of 3.5 % w/v sodium hypochlorite solution for

20 minutes at 80° C and subsequent washing with water until the residue was neutral to litmus paper. The extracted cellulose was oven dried at 60°C for 6 hours.

Grafting of Acrylamide on the extracted cellulose

Graft copolymerization of acrylamide on OM was done using the method described by Nada *et al.*, (2007). Five grams (5.00g) cellulose was steeped in aqueous acrylamide for 5 minutes followed by the addition of dissolved ceric ammonium nitrate(CAN) in nitric acid at 20° C for 2 hours. After the grafting process, the sample was filtered and washed with distilled water, then air dried (w_1). The dried sample was extracted with distilled water for 48 hours for the dissolution of the formed homopolymer. After the extraction, the sample was washed with distilled water, air-dried and weighed (w_2). The different grafting variables of the grafted copolymer was studied; ratio of monomer to cellulose (w/w) (1:1 – 3:1), initiator concentration (0.005 – 0.020M) and grafting

time (0.5 – 3 hours).The polymerization, graft and graft efficiency percentages for the grafting reaction was calculated using the equations below:

$$\% \text{ Polymerization (\%P)} = [(w_1 - w)/w] \times 100 \quad (1)$$

$$\% \text{ Graft (\%G)} = [(w_2 - w)/w] \times 100 \quad (2)$$

$$\% \text{ Graft efficiency (\%GE)} = [(w_2 - w)/(w_1 - w)] \times 100 \quad (3)$$

(Onigbinde *et al.*, 2016)

Orange mesocarp characterization

The ash, moisture, cellulose, hemicellulose and lignin contents, of the orange mesocarp were determined by

standard methods reported in the literatures (Abdel-Halim, 2014).

Characterization of unmodified and modified cellulose

The unmodified and modified cellulose were characterized using Fourier Transform Infrared Spectrometer. The spectra was gotten from a pellet made by grinding the sample with KBr and transmission measured at the wave number range of 400 - 4400cm⁻¹.

RESULTS AND DISCUSSION

Compositional analysis of Orange mesocarp (OM)

Table 1: Compositional content of the OM used for this study

Parameters	Percentage (%)
Ash	2.87
Moisture	3.025
Lignin	15

Hemicellulose	26
Cellulose	32.44

The compositional properties of the agricultural wastes (OM), used as source of the cellulosic material for this study is captured in Table 1. The physico-chemical properties determination of any agricultural waste of interest is essential. This is because, it gives an insight into the suitability of the material for green adsorbent production. The results confirmed the presence of sufficient cellulose in the orange mesocarp.

Cellulose percentage yield

In this work, the modified extraction process used gave an average percentage cellulose yield of 29.1 % for OM. The result is similar to the results obtained by previous researchers (Agbini and Etienajirhevwe, 2021; Bakre and Odumala, 2014). Yi *et al*, (2021) got 20.28% average percentage yield of cellulose from orange peel with extraction

process using alkaline and bleaching treatment. Akhabue and Osubor, (2017), using a similar method got 14.21% α -cellulose from orange peel waste. Bakre and Odumala (2014), also got 34.45 and 15.50 % cellulose from bagasse and sugarcane scrapping respectively. Khullar *et al*. (2008) used standard Tappi method (TAPPIT2003OM-88) and got 35% yield from *Dendrocalamus striticus*, a bamboo in India. Also, Ekebafé *et al*. (2010), used the same Tappi method of extraction using acetic acid and nitric acid and had 55.52% yield from rubber seeds shells. Bono *et al*. (2009), used acidified sodium chlorite extraction process and got 13-20% cellulose yield from palm kernel cake. Furthermore, Azubuike *et al*., (2011) employed sodium hypochlorite for bleaching after delignification process and

had 30% of α -cellulose from maize cob. From the above studies, it can be seen that the extraction methods and the source of the materials have noticeable effects on the cellulose produced.

Effect of Different Variables on Grafting Process

Four grafting conditions were varied; monomer to cellulose ratio, initiator

concentration, reaction temperature and time. The results of the optimization of these conditions are presented in Figures 1 to 4. Keeping other conditions constant, the effect of the variation of the monomer to cellulose for OM was studied.

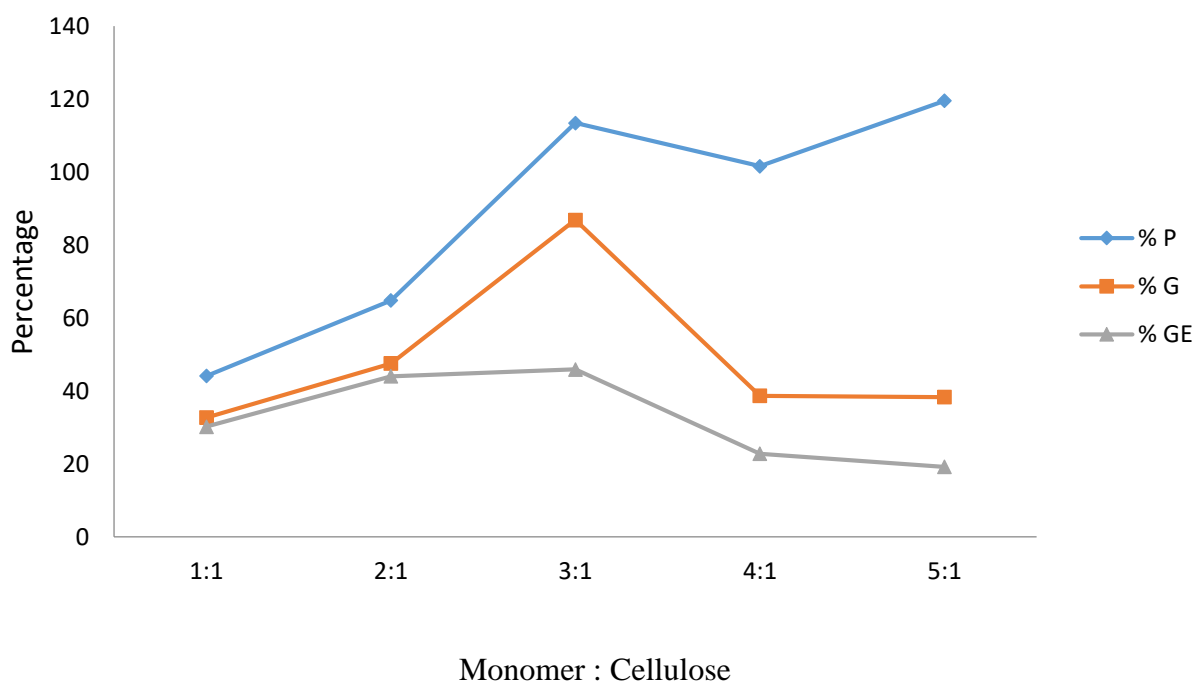


Fig.1: Effect of monomer to cellulose ratio on percentage polymerization (%P), percentage grafting(%G) and percentage graft efficiency (%GE) for OM.

The %P increasing from 44.10 to 113.60, %G from 32.70 to 86.83 and % GE from 30.20 to 45.90. The highest percentage was observed at cellulose ratio 3:1 in all the

three parameters. The initial increase in the grafting parameters was expected because the amount of acrylamide available for copolymerization is higher than the available grafting sites. Around the cellulose, the radicals formed are sessile and to initiate grafting, the monomer molecules must get attached to the radicals around the cellulose. This would help in chain initiation and propagation and invariably leads to increase in graft chains. However, the graft parameters were observed to fall at a higher monomer to cellulose ratio. This normally was expected to be true because there is limited number of active sites for grafting which was competed for by the acrylamide molecules.

At a higher monomer to cellulose ratio, there was an excess of the monomer molecules compare to the available sites for graft formation which could cause the molecules participating in more of the homopolymer formation. Also, it led to increased viscosity of the mixture which caused restricted movement of free radicals onto polymer backbone (Jideonwo and Adimula, 2006). The decrease could also be attributed to the competition between homopolymerization and graft copolymerization, where the former overrides the latter at higher concentration of the acrylamide (Khullar *et al.*, 2008). Figure 2 showed the effect of the concentration of the initiator (CAN) on grafting of AAm onto OM cellulose.

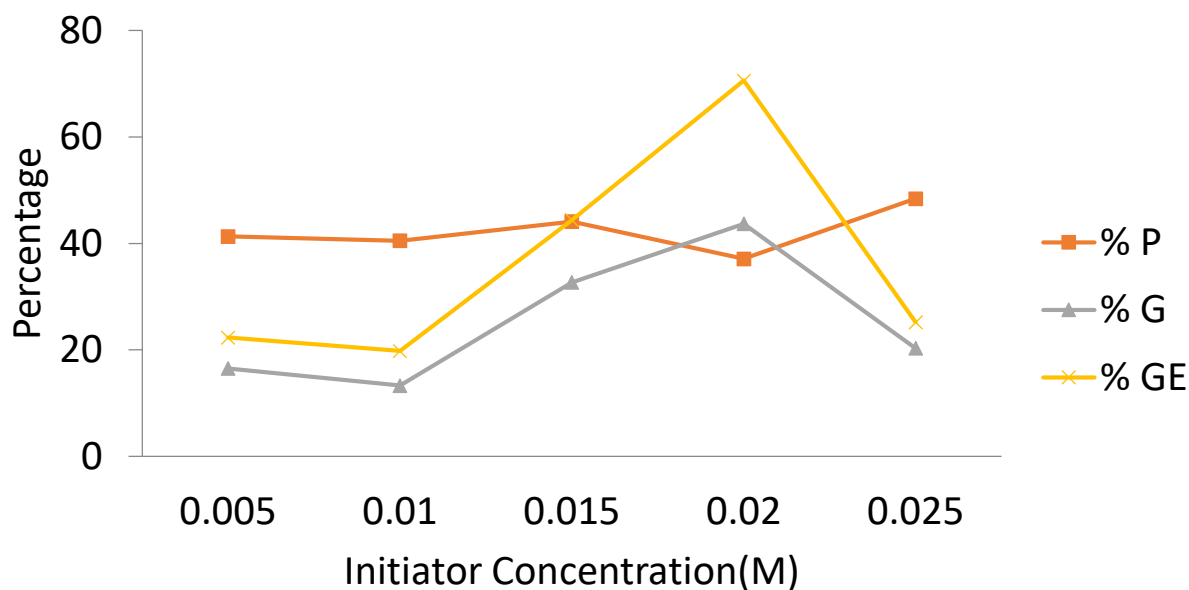


Fig.2: Effect of initiator concentration on percentage polymerization (%P), percentage grafting(%G) & percentage graft efficiency (%GE) for OM.

It was observed that the graft and graft efficiency increases as CAN concentration increases up to 0.015 M and thereafter decreases. The increase is due to the formation of a great number of grafting sites on the cellulose backbone. This in the presence of the monomers, induces grafting. When the initiator concentration increased more than this, it caused a reduction in the graft and graft efficiency. This may be as a result the fact that with high concentration of

the initiator, several homopolymers were formed. This is obvious since ceric ion is a very good oxidizing agent with very high reduction potential which could interact with the AAm to form the homopolymer rather than the graft copolymer at higher concentrations. Ekebafé *et al* (2010); Khullar *et al* (2008) and Nada *et al.* (2007) report similar results.

The effect of the variations in reaction temperature was also studied using

the optimized conditions for the other parameters. It was observed that there was a

dependence of the graft parameters on temperature (Figure 3).

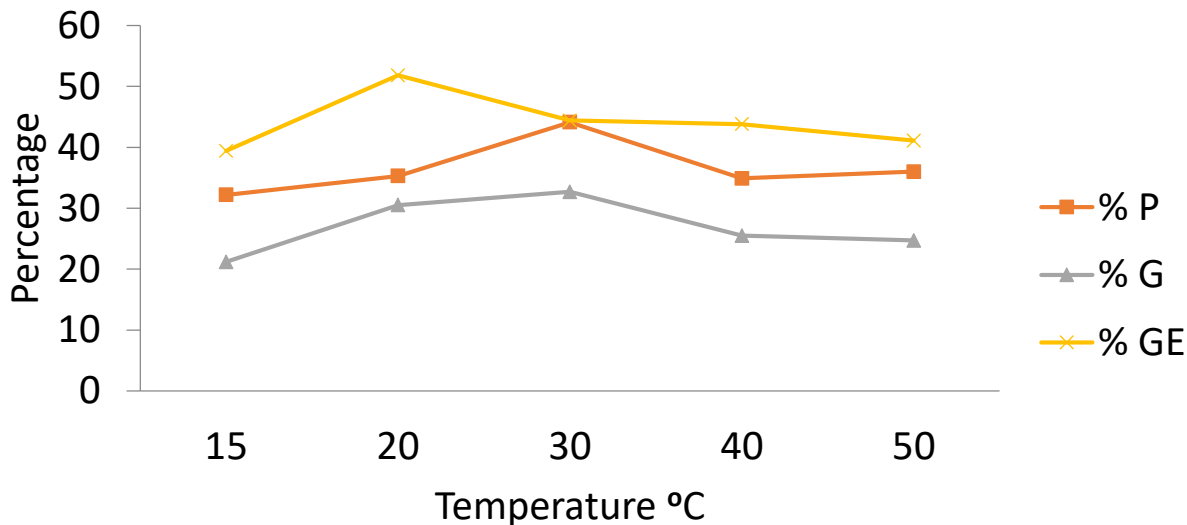


Fig.3 : Effect of temperature on percentage polymerization (%P), percentage grafting (%G) and percentage graft efficiency (%GE) for OM.

It is known that temperature accelerates the rate of molecules collision leading to a faster reaction in every chemical process. This is also relevant in grafting. As the temperature increased from 15 to 30°C for OM, the rate of the penetration of the monomer through the cellulose backbone was high and an increase in the chain length could be observed due to increase in initiation and propagation rate. This therefore led to increase in the graft parameters (Nada *et al.*,

2007). According to Mahdavi *et al.* (2011), this could also be attributed to a faster decomposition of the redox system which leads to radical formation for initiation and propagation reaction to take place and a higher mobility of the monomer from the aqueous phase to the cellulose backbone leading to a pronounced increment in the graft parameters.

The last grafting condition considered was the reaction duration. Graft copolymerization of acrylamide monomer

onto orange mesocarp cellulose was carried out from 0.5 to 4hours (Figures 4).

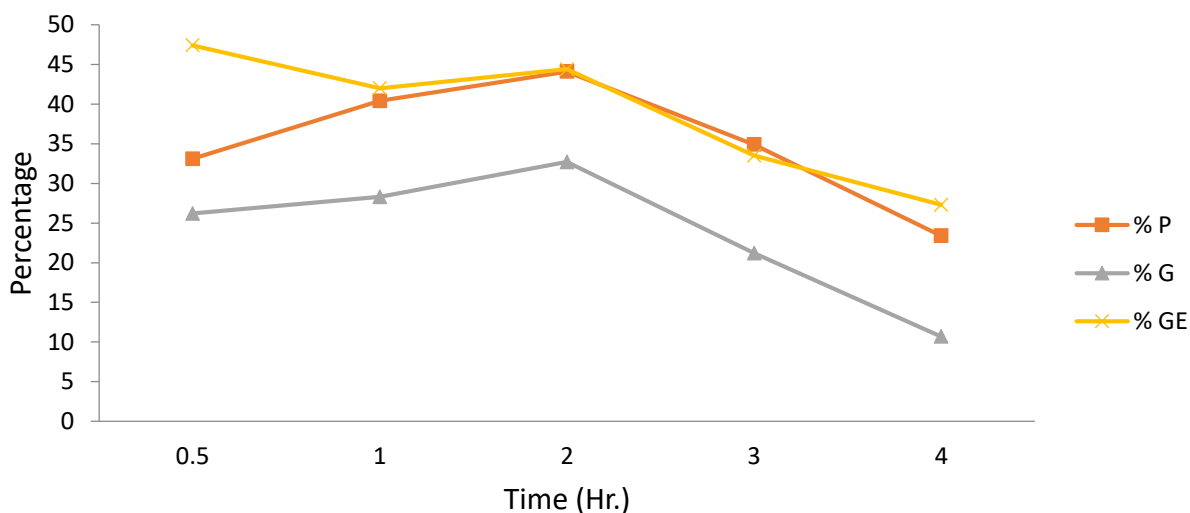


Fig.4: Effect of reaction time on percentage polymerization (%P), Percentage grafting (%G) & percentage graft efficiency (%GE) for OM.

In a chemical reaction, the effect of time on reaction rate is a very important factor. From the figure 4, it can be deduced that the %P, %G and %GE increased with increase in reaction time up to 2 hours and then there was a fall in the trend. The time used for the reaction allowed the ceric solution to diffuse into the OM backbone prior to grafting reaction thereby allowing

initiation of free radicals on the cellulose by oxidation with the Ce^{IV} ions. Adama *et al.*, (2014) had reported that increase in reaction time beyond 120 minutes led to decreased graft and graft efficiency in a typical graft copolymerization reaction. This was attributed to the decay of free radical activity of Ce^{IV} oxidized cellulose arising 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 the initiator and monomer as well as shortage of grafting sites. Similar findings had also been reported by Khullar, *et al.* (2008).

FTIR spectroscopy

FTIR spectra of the extracted and grafted cellulose of orange mesocarp are shown in figures 5 and 6. The spectra (Cm^{-1}) of the cellulose for the extracted samples

were those obtained by the modified extraction process. The absorption band found at 3422.26 for the OM cellulose indicated the stretching vibrations of the OH-group. The band at 1049.40 showed the presence of an ether group and while the peak observed at 2920.77 is an indication of C-H stretching vibrations. Furthermore, the 1430.78 and 1322.70 corresponds to $-\text{CH}_2$ scissoring and OH- bending vibrations for the material OM.

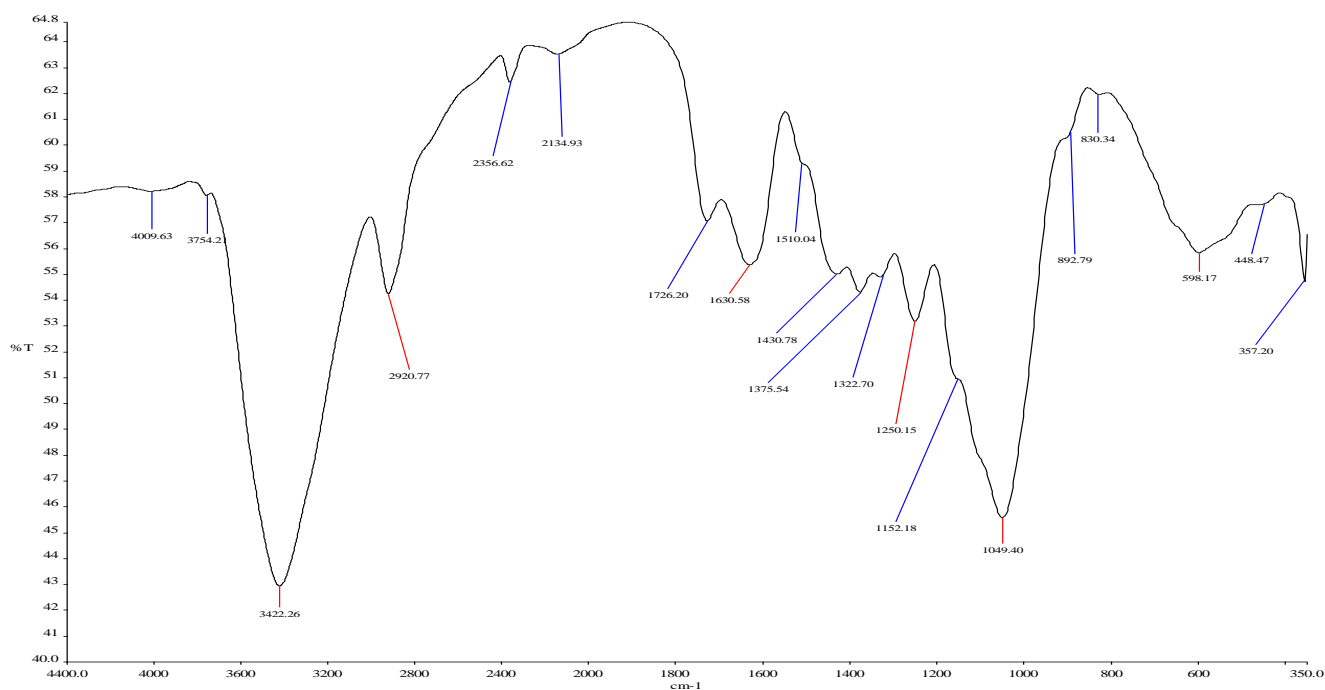


Figure 5: FTIR spectrum for extracted OM cellulose.

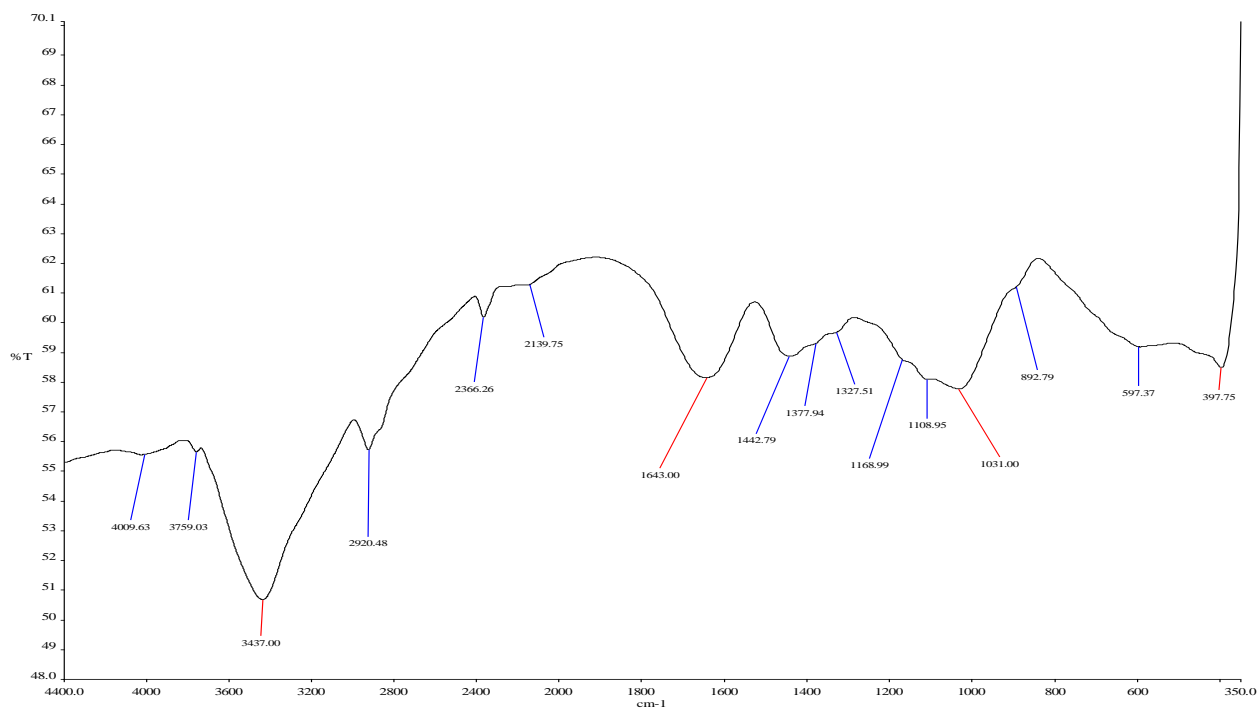


Figure 6: FTIR spectrum for grafted OM.

The absorption bands (Cm^{-1}) observed at 1643 for grafted OM cellulose indicated the stretching of the carbonyl ($\text{C}=\text{O}$) of the amide group in acrylamide while the band at 892.79 indicated the $-\text{C}-\text{H}$ -bending vibrations of the polyacrylamide molecules. These values established that the grafting were comparable to values in

previous research studies (Hamma`Adama *et al.*, 2014; Mahdavi *et al.*, 2011).

CONCLUSION

Green adsorbent could be generated from orange mesocarp, an agricultural waste material abundantly released and littering our environment; by extracting and modifying their cellulosic materials. The results of this research have established the possibility of

grafting acrylamide monomers on the extracted OM cellulose with good grafting parameters to produce very good bioadsorbent comparable to commonly used but expensive powdered activated carbon in the treatment of industrial effluents and wastewaters.

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