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Extraction and modification of cellulose from peanut shells and cornstalks and for use as adsorbents for removal of lead

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ABSTRACT

The requirement for novel adsorbents from inexpensive sources, directs this research towards innovation of new adsorbent materials through extracting and modifying cellulose fibres from peanut shells and corn stalk. The processes involved delignification, alkaline hydrolysis, acetylation of pure cellulose and the adsorption of Lead Pb^{2+}. The adsorbents obtained are pure celluloses of peanut shells (PSC), Corn stalk (CSC) and Acetyled Celluloses of Peanut Shells (PSCA) and Corn Stalk (CSCA). The Structural and functional properties were analyzed by Fourier transform infrared spectroscopy (FTIR) and Atomic Absorption Spectrometer (AAS). The four adsorbents all exhibited high removal percentage of Lead from the solutions. However, acetyled Cellulose of peanut shells exhibited the highest adsorption capacity of 397.5 mg/g with final Lead (Pb) concentration of 0.125 mg/L, the removal of Lead from solution amounted to 99.3% as compared to the other adsorbents. This research proved the efficiency of agro-waste cellulose acetate for use as novel adsorbents through the Lead Adsorption. An extensive exploration in researches involving biodegradable waste materials is required to utilize this source and control environmental pollution.

1. Introduction

It has become a challenging quest to replace toxic and non-renewable petrochemical products in the world with hopes of reducing contamination of the Ecosystems. These Ecological concerns have resulted in a renewed interest in natural, renewable resources- based and compostable materials. For these reasons, material components such as natural fibers, biodegradable polymers can be considered ‘environmentally safe’ alternatives for the development of new biodegradable adsorbents, which can be used as media for pollution control [1]. It is of utmost relevance that environmental pollution in affected parts of Nigeria and other developing states should be tackled with in order to ensure healthy progression of these nations. The purification of water and other systems against heavy metals has long been under study using low-cost absorbents from plant wastes. Bioremediation and other conventional methods of purification have been implored but have not yet proven satisfactory due to some technical and economical constraints.

Cellulose is one of the most widespread biopolymer found globally, existing in a variety of living species such as plant, bacteria and some amoebas [2]. Cellulose is the primary component of the cell walls of higher plants. It comprises at least one third of the vegetable matter of the world [3].

Natural fibers mainly consist of cellulose, lignin, and hemicellulose but also include low quantities of pectin, pigments and extracts. The natural fibers themselves act as composite materials, assembling in a mainly lignin matrix [4]. These cellulosic materials are well known for their abundance, economic and environmental advantages.

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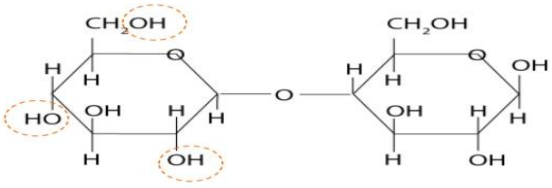

Structure 1. Structure of Cellulose

The availability of OH groups facilitates the degree of Hydrogen-bonding in cellulose. The degree of substitution is the term used to express the average number of hydroxyl group replaced [5]. The Drawbacks of cellulose are the high number of hydroxyl groups, which lead to strong hydrogen interactions between two fibers and to the gel-like structure once produced. The second drawback is the high hydrophilicity of the material, which limits its uses in several applications such as in paper coating (increase of dewatering effect) or composites (tendency to form agglomerates in petrochemical polymers [6]. However, surface modification with addition of substances such as silica SiO_2 have been discovered to reduce hydrophilicity of cellulose composites [7].

This investigation purports to discover the high adsorption capacity of extracted cellulose before after its modification to cellulose acetates. Peanut shells and corn stalks are abundant and inexpensive agricultural waste products that have relatively high cellulose content of 65.5 - 79.3% [8]. Nigeria is the third largest peanut producer in world, having a record of producing 2,755,649 metric tons annually, according to WorldAtlas (2016). Nutritional analysts found Peanut shells to be composed of 65.7% cellulose, 21.2% carbohydrates, 7.3% protein, 4.5% minerals and 1.2% lipids [9] Chemical content of corn stalk contains cellulose (35-50%), lignin (5-34%) and petosan around 20-41% [10]. The utilization of peanut shells and corn Stalks is of substantial benefit and at low costs due to its abundance in the country. Their richness in cellulose provides its aptness to serve as raw material for cellulose modification[11].

In recent years, surface modifications of cellulose have been a subject of increasing interest because of their significantly enhanced mechanical properties and thermal stability compared to conventional polymer composites and adsorbents. Abundance, high

Tensile strength and stiffness, low weight and biodegradability are some special useful features of cellulose fiber materials [12]. Isolation, characterization, and search for applications of novel form of cellulose, is generating much activity currently. Isolated cellulosic materials are able to combine important cellulose properties such as hydrophilicity, broad chemical-modification capacity, and the formation of versatile semi-crystalline fiber morphologies to form better adsorbents [13]. The adsorption and recovery capabilities of cellulose acetate are being investigated for separation of precious metals such as gold and platinum from leaching processes [14].

2.Experimental

2.1 Sampling

The waste samples of peanut shells and corn stalks were obtained from a local farmhouse in Maiduguri. Samples were thoroughly milled, washed and dried to reduce waxes and debris [15].

2.2 Procedures

2.2.1 Delignification and Bleaching

A solution of 3.5% w/v $NaClO_2$ and 6 ml glacial acetic acid was prepared in two 1000 ml beakers. Solution is mostly active at given pH and temperature therefore a thermometer and universal litmus was used to ensure the standard pH of 3-4 and heated to 75^0C. Grounded dry samples of 50 g cornstalk and peanut shells was weighed and added to heated solution. Allowed to stir gently for 1hr 30mins. The sample colour became yellow. The residue was washed thoroughly with cold water and filtered [16].

2.2.2 Alkaline Hydrolysis

This process required a solution of 18% NaOH in 800 ml of water at ambient temperature in order to dissolve the remaining hemicellulose present in delignified sample. The delignified residue was added to the solution and allowed to soak for 24 hrs [7,11]. The mixture was further neutralized with 14 ml glacial acetic acid. It was then washed and filtered repeatedly until pH became neutral[13]. The resulting product was alpha (pure) cellulose.

2.2.3 Acetylation

This process required strict measures of using a gas mask and the reaction was carried out in a fume cupboard. 100 ml glacial acetic acid was added to 20 g of each cellulose sample. 50 ml acetic anhydride and 5 ml H_2SO_4 as catalyst, was added to the mixture and stirred with a glass rod. The Reaction was at ambient temperature under a fume cupboard. Time was set for 24 hrs. 200 ml of water was added and Cellulose acetate precipitated[17]. Filtration was carried out using vacuum filter apparatus. Cellulose acetate was washed and dried at room temperature [18].

2.2.4 Adsorption of Lead Pb^{2+}

1 g of Adsorbents, Peanut shell and corn stalk cellulose and cellulose acetate were placed in four 50 ml-beaker. 20 ml standard solution of $Pb(NO_3)_2$ having Pb at 1000 mg/L of, was poured into each beaker using a measuring cylinder. The mixture was allowed to react for 15 mins and subsequently filtered out using whatman filter paper. The filtered was subjected to AAS analysis, while the residue was dried out [10,19].

2.3 Determination of percentage yields from experimental procedures

The yields of alpha cellulose from both peanut shell corn stalks were determined using equation (1.0). This formula was use to calculate the percentage yields of the extraction process of cellulose from both peanut shells and corn stalk [20,21].

$$\alpha\ cellulose = \frac{final\ weight}{inital\ weight} \times 100\text{---------}(1)$$

2.4 Atomic Adsorption Spectroscopy

The adsorption capacity Qe is calculated using the formula:

$$Qe = \frac{(C_i - C_f)V}{W}\text{---------------------------------}(2)\ [11,22]$$

The percentage removal of Pb ion from solution was calculated using the following formula:

$$\%\ Removal = \frac{C_i - C_f}{C_i} \times 100\text{---------------}(3)\ [11,23]$$

Where *Qe* is adsorption capacity, C_i is initial concentration, C_f is final concentration, V is solution volume and W is mass of adsorbent.

3. Result and discussion

3.1 Percentage Yield

The methodology of estimating percentage yield is presented in Section 2.3. The percentage yield of Corn Stalk Cellulose and Peanut Shell Cellulose was 77.1% and 78.4%, respectively. This value for peanut shells cellulose is relative with the findings of Masenda *et al* [4] whose values for cellulose from peanut shells was 65.3%-79%. The corn stalk values were significantly higher than several researches [13, 16], whose value for sorghum stalk was 47.36%. However, the slight variations could be as result of the effect of land quality of soil that the different groundnuts were grown or experimental error.

During the Acetylation process, a fraction of approximately 20 % of the extracted Cellulose was further dissolved yielding a total of 15.5 g of Cornstalk and 15.7 g of peanut Shell cellulose acetate from 20 g of alpha cellulose. This was due to residual hemicellulose which dissolved in acetic acid [23]. Table 1. presents the yield obtained in this study.

Table 1.: Percentage yields through experimental processes

EXPERIMENTAL PROCESSES	CORN STALK			PEANUT SHELLS		
	Initial weight (g)	Final weight (g)	Percentage weight (%)	Initial weight (g)	Final weight (g)	Percentage weight (%)
Bleaching	50	31.4	62.8	50	36.1	72.2
Alkaline Hydrolysis	31.4	24.2	77.1	36.1	28.3	78.4
Acetylation	20	15.68	78.4	20	15.47	77.35

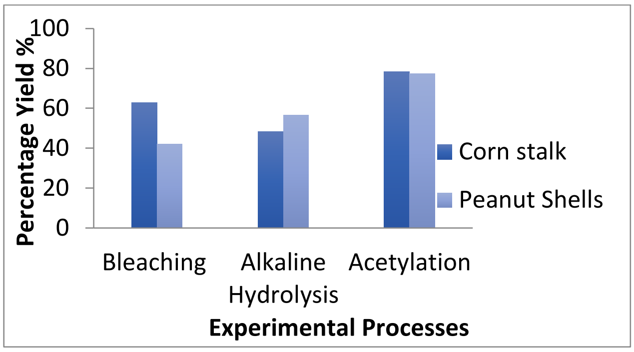

Figure1. Percentage yields through experimental processes

3.3 FTIR Spectroscopy

The most convenient and effective method of studying the structural characteristics of cellulosic experiments is the FTIR Spectroscopy [24,28]. The following FTIR spectra Figures 2, 3, 4 and 5, depict the spectrum of Peanut Shells (PSC) and cornstalk (CSC) celluloses, Peanut Shells (PSCA) and cornstalk Cellulose Acetate (CSCA).

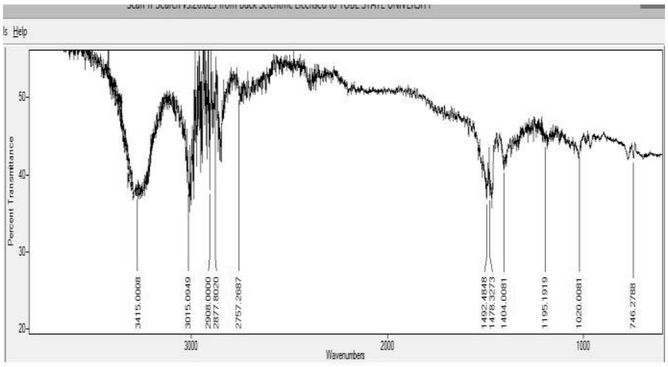

Figure 2. FTIR Spectrum of Corn Stalk Cellulose (CSC)

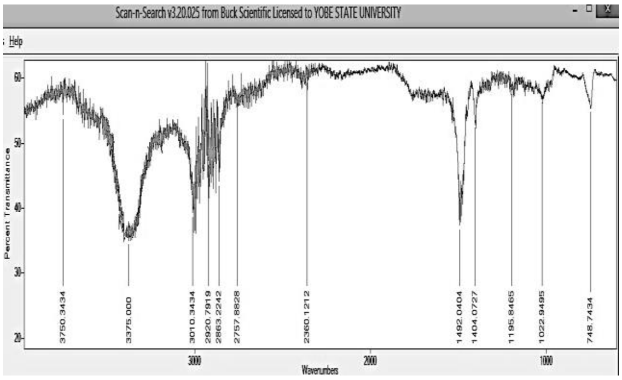

Figure 3. FTIR Spectrum of Peanut Shells Cellulose (PSC)

The spectra on figures 2 & 3 exhibit functional groups related to pure celluloses[25]. The broad band at 3415 and 3375cm-^{1} are due to the presence of hydroxyl groups -OH. The peaks at 3010 and 1490 cm^{-1} displays –C-H stretch and bending bond vibrations[26]. The peaks at 1492 to 1404 cm^{-1} indicate C-O stretching confirming the presence of lignin[27].

Table 2.: Lead Concentrations (mg/L)

S/N	Sample Name	Sample Conc (mg/L)	Sample Conc. (mg/L)	Sample Conc. (mg/L)	Mean Conc. (mg/L)	Standard Deviation
1	PSC	0.228	0.228	0.226	0.227	0.001
2	CSCA	0.228	0.224	0.231	0.228	0.004
3	CSC	0.602	0.595	0.605	0.601	0.005
4	PSCA	0.126	0.122	0.128	0.125	0.003

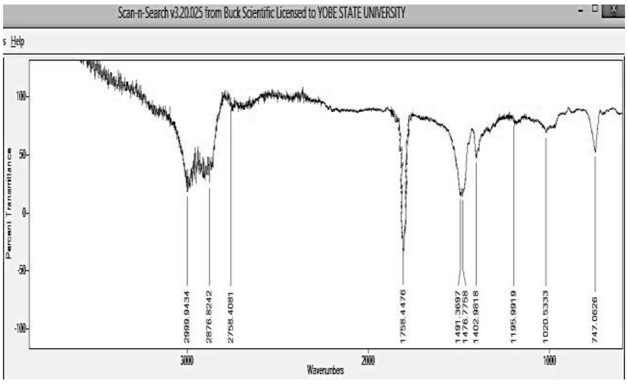

Figure 4. FTIR Spectrum of Corn Stalk Cellulose Acetate (CSCA)

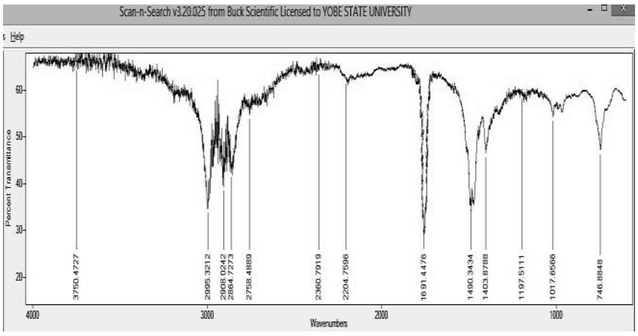

Figure 5. FTIR Spectrum of Peanut Shell Cellulose Acetate (PSCA)

Both Peanut shells and corn stalk Cellulose Acetates spectra in figures 4 & 5, shows that acetylation has taken place through peaks appearing at 1758 & 1691 cm^{-1} depicting Carbonyl groups **–C=O** and 1195 cm^{-1} for **–C-O** stretch by acetyl groups [29]. Although the **O-H** peaks have completely diminished in the acetyled cellulose, Peanut shells cellulose and cellulose acetate appear to have sharper peaks than modified corn stalk. This leads to the conclusion that modified peanut shells have a higher potential for more active binding sites and would therefore be better adsorbents than the modified cornstalk[30].

3.2. Adsorption:

3.2.1. Adsorption Capacities

The efficacy of the pure cellulose and modified cellulose samples for the adsorption of lead was determined using the AAS.

Table 3. Adsorption Isotherms

Adorbents (g)	Pb^{2+} Conc, (mg/L)	
	Initial C_i	Final C_f
Peanut Shell-Cellulose	20	0.227
Corn Stalk-Cellulose	20	0.601
Peanut Shell-Cellulose Acetate	20	0.125
Corn Stalk-Cellulose Acetate	20	0.228

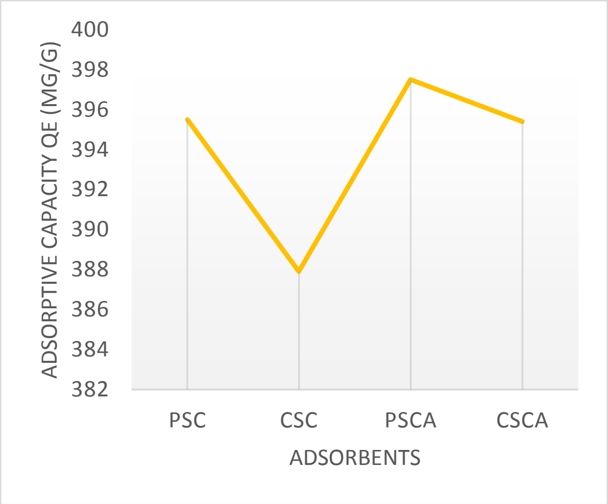

Figure 6. Adsorption capacity with respect to Concentrations of lead Pb $^{2+}$

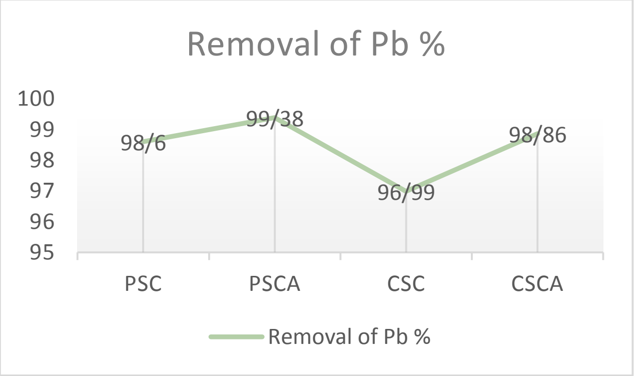

Figure 7. Percentage Removal of Pb^{2+} by Adsorbents

The four adsorbents all exhibited high removal percentage of Lead from the solutions as presented in the

Table 2 and Figure 6. However, surface acetyled Cellulose of peanut shells exhibited the highest adsorption capacity of 397.5 mg/g with final lead concentration of 0.125 mg/L, the removal of Lead from solution amounted to 99.3% as compared to the other adsorbents. This is as a result of the morphological and structural change of the Peanut Shells fibres through acetylation[31]. As the FTIR had shown higher peaks in the peanut shells cellulose and cellulose acetate appearing to have more active binding sites than the cornstalk cellulose acetate and non-modified cellulose[30,32].

3.2.2. Effect of adsorption on adsorbents

The dried samples of adsorbents were weighed after the adsorption process to analyse any change in weight due to deposition of Lead compound [$Pb(NO_3)_2$] on adsorbent surface.

Table 4.: Weight gains on Adsorbents after adsorption process

Adsorbents	Initial weight of adsorbent (g)	Final weight of adsorbent (g)	Weight gained By adsorbent (g)
Corn stalk cellulose acetate	1.0	1.06	0.06
Peanut shell Cellulose acetate	1.0	1.05	0.05
Corn stalk Cellulose	1.0	1.03	0.03
Peanut Shell cellulose	1.0	1.01	0.01

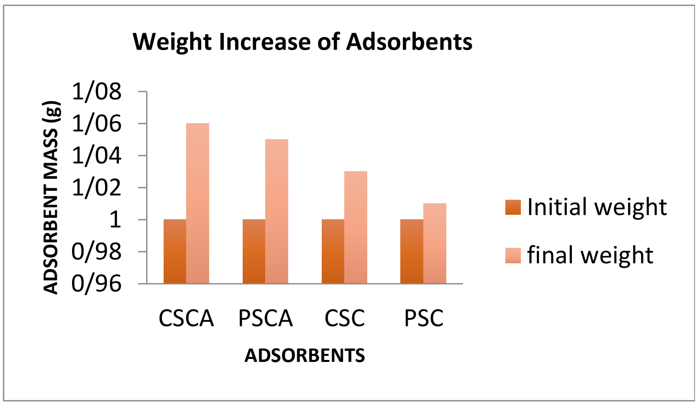

Figure 8. Weight gains on Adsorbents after adsorption process

There is an evident increase in weight of all adsorbents but a significantly higher increase in weight of the cellulose acetates which proves the theory of more active binding sites leading to higher deposition of lead (Pb) ion on the adsorbents[33. However, PSCA should have the highest in correspondence to the results of the Removal of Pb in Figure 7, but CSCA appears to have higher weight in Table 4 and Figure 8 above. This could be as a result of error during weighing[34].

4.Conclusion

The processes of isolation of Cellulose from peanut shells and corn stalk have proven effective as it resulted to attainment of medium grade cellulose acetate, which was successfully used as an adsorbent of Lead Pb^{2+}. Although, the Cellulose acetates exhibited higher absorption capacities as compared to the alpha or pure celluloses, Peanut shells cellulose acetate provided the best result for adsorptive capacity with removal of about 99.3% of Pb ions from the solution. The significant weight loss during the alkaline hydrolysis and delignification indicated that the soluble sugars amount up to half of the fibre weight. Acetylation process further dissolved 20% of the two different cellulose fibres. The quick adsorption of Pb ions by the cellulose acetates, within 10 to 15 minutes is the most remarkable breakthrough of this research. This research provides another source to be used as cheaper alternatives of adsorbents, for pollution control, as well as industrial separation of precious metals.

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