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PREPARATION AND CHARACTERISATION OF BIOSORBENTS MADE FROM MAIZE TASSEL

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ABSTRACT

Preparation and characterisation of biosorbents from maize tassel were studied. The Brunauer-Emmett-Teller (BET) isotherm was used to model experimentally obtained N_2-adsorption data (up to P/P_o= 0.30); the results indicated that the powdered material is mesoporous with specific surface area (S_{BET}), total pore volume (up to P/P_o= 0.98) and average pore width (4V/A BET) values of 2.52 m^2/g, 0.0045 cm^3/g and 7.2 nm, respectively, for the 150-300 μm particle size fraction. High-resolution scanning electron microscopy (HRSEM) revealed a microstructure showing predominantly flattish rod like particles. The material exhibited stability to thermal decomposition up to about 230 ºC, as evidenced by the results obtained from simultaneous thermogravimetry-differential thermal analysis (TG-DTA) and differential scanning calorimetry (DSC).

Keywords: Maize tassel, porosity, surface area, microstructure, thermal stability.

INTRODUCTION

Research efforts in water, wastewater and effluent treatment have focused to a large extent on the removal of heavy metals due to their well-known toxicity. Technologies that have been developed for the removal of these metals from aqueous solution involve processes such as ion exchange, reverse osmosis, membrane filtration, sludge leaching, electro-winning, solvent stripping, precipitation and adsorption. Adsorption is the predominant process, and commercial activated carbon (CAC) has been the most successful adsorbent investigated and used for this purpose (Netzer and Hughes, 1984; Reed and Arunachalam, 1994; Han *et al*., 2000; Daorattanachau *et al*., 2005; Ayotamuno *et al*., 2007). However, the adsorptive removal process is relatively expensive when a pure adsorbent such as CAC is used. This fact has led to on-going research into the feasibility of using lower cost adsorbents as alternatives to CAC for removing heavy metals and other pollutants from aqueous solution. Materials that have been investigated in this regard include, chitosan (McKay *et al*., 1989), clays (Srivastava *et al*., 1989), natural oxides (Joshi and Chaudhuri, 1996), sawdust (Ajmal *et al*., 1998), coal fly ash (Agyei *et al*., 2002), rice husks (Wong *et al*., 2003), zeolites (Kazansky and Pidko, 2005) and lignite (Mohan and Chander, 2006).

The material that can be considered an ideal candidate should be of low cost, locally available in large quantities and easily regenerated or discarded thereafter with minimal environmental impacts. Tassel, the male inflorescence of the maize plant that forms at the top of the stem, evidently meets these requirements. It is discarded by local communities in South Africa and elsewhere in large quantities with the rest of the plant once the cobs have been harvested. The authors have not yet found any information in the literature regarding the physical characteristics or chemical composition of tassel. Being a fibrous part of a plant that is rich in carbohydrates it is expected to contain a high proportion of polysaccharides with cellulosic surface hydroxyl groups and residual aromatic compounds which gives it some scent during its vegetative stage. The possibility of hydroxyl, carbonyl, conjugated bonds and amine functional groups on its surface could provide binding sites for metal cations and oxoanions.

Characterisation of a candidate adsorbent material is a fundamental step in its development because how efficiently an adsorbent can performance is influenced significantly by its inherent physicochemical characteristics. Furthermore, the sorption capacity of natural biosorbents often require enhancement through physical and chemical modification and successful modification requires knowledge of their morphology (texture and microstructure and its thermal stability) and surface chemistry. Researchers in the field characterise the texture of adsorbents by evaluating parameters such as porosity and surface area/particle size; techniques such as N_2 sorptiometry (Jaroniec and Madey, 1990; Gomez-Serrano *et al*., 2001; Figueiredo *et al*., 2005;) and laser diffraction analysis (Synytsya *et al*., 2004; Giuliano *et al*., 2007) have been used in this respect. SEM is the method of choice that has been commonly used to characterise adsorbent microstructure (Pollard *et al*., 1992; Baraka *et al*., 2007). Thermal analysis and calorimetry often yield information on properties which impact on surface

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morphology and sorptive behaviour such as thermal stability, hydroscopic water, volatiles, and phase transitions during pyrolysis (Rouquerol *et al*., 1989; Sarbak *et al*., 2004) and can, therefore, be used in adsorbent sorption capacity optimisation.

This study was aimed at determining various physicochemical characteristics of maize tassel, an agro-waste material which has exhibited a very commendable potential not only for the adsorptive removal of heavy metals from aqueous systems (Zvinowanda *et al*., 2007), but also for possible utilisation as a filler material in polymer industry. The porosity and specific surface area were determined by obtaining N_2-adsorption data and modelling it using the BET isotherm. The surface microstructure and the thermal behaviour of the adsorbent were characterised by HRSEM and TG (DTG)-DTA and DSC, respectively.

MATERIALS AND METHODS

The tassel was sampled from a hybrid cultivar SC71105, a maize variety bred by SEED-CO: Zimbabwe. The material was first air dried for 7 days and then thoroughly rinsed with copious amounts of distilled water. The material was then placed in an air powered drying hood to remove dripping water. Finally the tassel was dried in an oven with the temperature set at 105^{o}C for 24 hours to remove any moisture present. The dried material was then milled by a hammer mill model Laboratory Mill 3100 with stainless steel blades mounted with a ≤500μm sieve. A course powder of variable particle size was generated which was further fractionated into particle size ranges: 45-50, 50-150, 150-300, 300-500, 300-560, 560-630 and 630-750 μm. Stacks of analytical sieves of specification ISO3310-1 were used to accomplish the fractionation. The second, third and fourth fractions were the most abundant.

A Surface Area and Porosity Analyzer (ASAP2020 V3. 00H, Micromeritics Instruments) was used to perform textural analysis. The nitrogen used for this purpose was instrument grade. Microstructure was determined using a TSM-6000F (TEOL, Japan) scanning electron microscope. A simultaneous TGA/sDTA 851 (Mettler Toledo Star System) thermal analyser linked to a TSO 801 robotic sampler and a TSO 800 GCI gas control unit, and a DSC Q20 V23.10 Build 79 (Universal V4.4A TA Instruments) scanning calorimeter were used for thermal analysis.

Nitrogen adsorption-desorption isotherms

Textural characteristics of the tassel powder were determined by nitrogen adsorption-desorption at an analysis bath temperature of -197^{o}C. A sample mass of 0.200 g was placed in a cold free space holder of 52.6 cm^3 and the adsorptive properties of nitrogen were analysed at a maximum manifold pressure of 925 mmHg. The adsorption-desorption isotherm, the BET surface area, single point adsorption total pore volume of pore and desorption average pore width were determined.

HRSEM

Various fractions of tassel powder in their natural state with sizes ranging from 45 to 750 μm were morphologically characterised by high resolution field emission-scanning electron microscopy.

TG (DTG)-DTA and DSC analyses

Samples and reference material were heated in a 70.0 μl alumina pan made of aluminium oxide. Simultaneous TG (DTG)-DTA analysis in air was performed by placing 15.5 mg sample or material into the sample pan which was then heated in a dynamic mode from 25 to 900^{o}C at a heating rate of 10^{o}C/min and an air flow rate of 50 ml/min. In the DSC analysis a sample of 2.00 mg was placed in an aluminium pan and heated with a ramp of 10^{o}C/min and a nitrogen flow rate of 50ml/min over a temperature range of 25 to 450^{o}C. The DSC analysis was repeated after drying the tassel powder for 24 hours at 105^{o}C in an oven.

RESULTS AND DISCUSSION

Surface texture

Surface area and porosity are some of the most important properties of a material being developed into an adsorbent. Textural characterisation of the following carbonaceous materials prepared from natural adsorbents has been reported: cotton stalk (Bansal *et al*., 1988), olive stones (Wu *et al*., 1999), peanut hulls and nutshells (Wu *et al*., 2001), corncob (Juang *et al*., 2002), bagasse (Girgis *et al*., 2002) and plum kernels (Gupta and Ali, 2003). Generally, the more porous the material is the larger surface area there is and hence the greater the adsorption capacity. The adsorptive capacity of an adsorbent depends also on its surface chemistry functionality, a property which is usually predominant in cationic removal from aqueous systems.

Figure 1 shows the nitrogen adsorption-desorption isotherm measured at -196^{o}C. The isotherm of the tassel adsorbent is characteristic of materials without micropores since the adsorption hysteresis present indicates mesoporosity characteristics. The adsorption-desorption curve of tassel is a typical type IV linear plot because it exhibits a hysteresis loop as the desorption curve lags behind the adsorption curve. The plot further corroborates the evidence that this adsorbent is mesoporous in nature. The hysteresis loop exhibited during adsorption-desorption indicates that the tassel adsorbent is a type IV isotherm which means that this material is mesoporous (Gregg and Sing, 1982). The adsorption behaviour of mesoporous materials with

respect to trace metal removal from wastewater has been reported (Zvinowanda *et al*., 2007). The adsorption capacity of these materials which are still under development is highly promising.

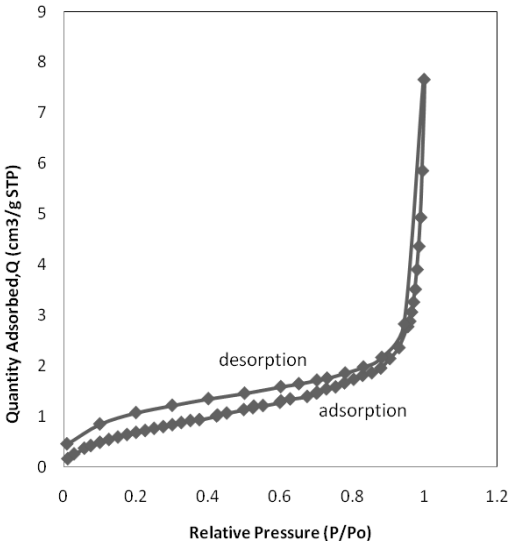

Fig. 1. Adsorption–desorption curves for the 45-50 µm fraction.

The plot of relative pressure as a function of inverse of mole fraction adsorbed gives a linear curve with a regression (R^2) of 0.9987(Fig. 2). This region signifies the monolayer adsorption of the sorbate giving a linear curve. The regression value obtained shows that the adsorption of nitrogen on the adsorbent was in agreement with theoretical work where the relative pressure is expected to be proportional to the mole fraction of adsorbed nitrogen for relative pressure between 0 and 0.30. Above 0.30 relative pressure, the pores are filled up and development of adsorbate multi layers on the surface adsorbent occurs resulting in the sigmoid shape of isotherms (Fletcher *et al*., 2006).

Table 1 show the summary of the physical parameters of the two tassel fractions which were analysed for textural characteristics. The monolayer and S_{BET} surface area of tassel found in this investigation is almost comparable. These figures are very low compared to other known microporous adsorbents (Wu *et al*., 1999; Elizade-Gonzalez *et al*., 2007[a,b]; Fletcher, 2006). However the performance of tassel as an adsorbent is highly comparable to other established materials. BET textural properties of natural adsorbents such as fly ash (Agyei *et al*., 2002; Ozao *et al*., 2006) carbonised avocado AGAP (Elizade-Gonzalez *et al*., 2007[a]) has been determined. The avocado adsorbent had very large S_{BET} (143-1069 m^2/g) and pore volumes (0.073-1.053 cm^3/g) as compared to fly ash with S_{BET} (2.5-19.0 m^2/g). Evidently, the high sorption capacity of tassel (Zvinowanda *et al*., 2007 In Press) can now be attributed more to chemisorption than physisorption. The pore width is used to classify adsorbent materials either as microporous (2 nm), mesoporous (2 to 50 nm) and macroporous (more than 50 nm) (Gregg and Sing, 1982; Guo and Lua, 2000). The two maize tassel fractions analysed in this study had average pore sizes of 7.2 and 8.5nm. The monolayer surface area and the BET surface area for both particles analysed are of the same range. The results show that there was insignificant multilayer formation. Other materials which have been analysed, such as silica (300 m^2/g) and carbon black (960 m^2/g) (Fletcher, 2006), had significantly large S_{BET} surface area. Furthermore, this elaborates that tassel adsorbent is a mesoporous solid. Mesoporous materials are known to have lower pore volumes than microporous materials.

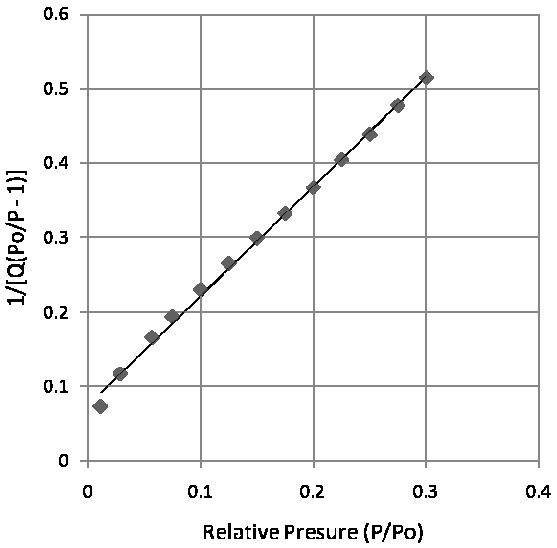

Fig. 2. BET surface area plot for the 45-50 µm fraction (R^2 = 0.999).

Microstructure

The micrographs in figure 3 exhibit flattish shapes originating from the fibrous nature of tassel material. Minimum porosity is observed from the particles hence its adsorption behavior may be linked to its surface chemical morphology. The particles in the three micrographs exhibit random morphology associated with the method of preparation. The finer particles (A) show some degree of porosity (most probably pseudo pores) compared to the courser ones (B) and (C).

Thermal stability

A thermal stability study of an adsorbent is very critical during product development stages. Its activity can be improved by subjecting it to an optimum heating program which improves its porosity and surface functionality. Thermal stability studies of cellulose have shown that it undergoes at least four thermal events when subjected to

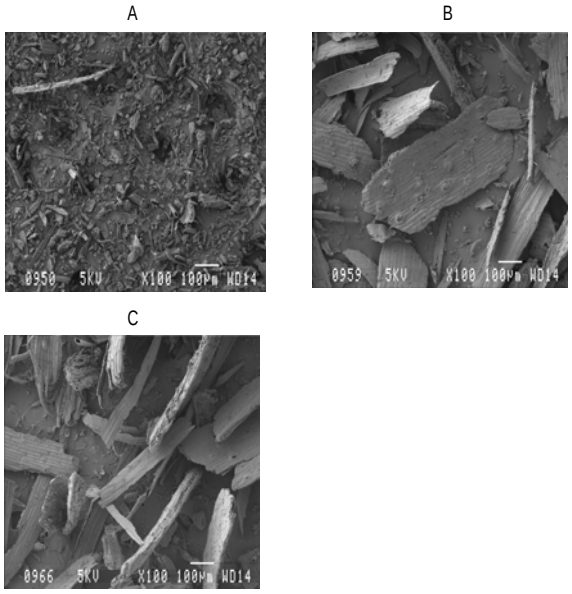

Fig. 3. Micrographs of tassel fractions (50-150 (A), 150-300 (B) and 300-500 (C) μm).

heating up to temperatures above 500°C. Endothermic and exothermic peaks and plateaus have been interpreted as follows. Endotherm 95 to 100°C: evaporation of hydroscopic water. Plateau 155 to 259°C: heating of cellulose without bond breaking. Exotherms 259 to 389°C: splitting of cellulose macromolecules. Plateau 452 to 500°C: formation of stable substances. Endotherm 500 to 524°C: completion of reaction (Shinogi and Kanri, 2003).

Simultaneous TG/DTG- DTA analysis of tassel powder gave the curves shown in figure 4. From the data obtained the endotherms, exotherms and plateaus may be interpreted as follows. The endotherm from 32 to 122°C should be associated with loss of volatiles and hydroscopic water. The bimodal exotherm with peaks at 303°C and 429°C and a plateau in between can be attributed to mixed reactions. These reactions include pyrolysis of various cellulosic macromolecules which will be forming stable substances. On further heating to temperatures above 405°C they begin to char off releasing combustible volatile gases which ignite to leave the ash. Analysis of the TG data for this study yielded an ash residue of about 9%. Similar materials such as wood cellulose have been reported to give a residue of about 10 % (Shinogi and Kanri, 2003), which is in good agreement with the results obtained in this study.

Figures 5 and 6 show the DSC curves for the non-dried and dried material. Non-dried tassel gave a larger endotherm with maxima at 89°C than dried powder which gave a poorly resolved endotherm with maxima at 67°C. The larger endotherm observed in Figure 5 is due to the energy required to remove both the volatiles and water adsorbed by the adsorbent. Most hydroscopic water and

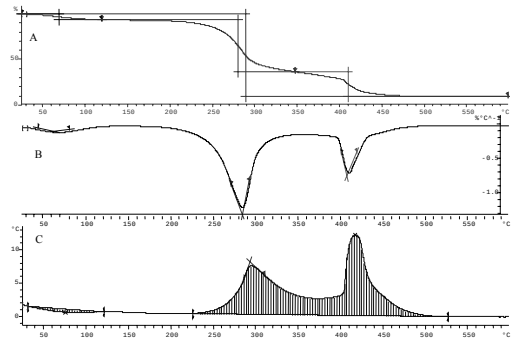

Fig. 4. TG (A), DTG (B) and DTA (C) curves for tassel powder in air.

volatiles are lost during drying thus a lower energy hump is observed for the oven dried material. Exotherm peak maxima at 331°C are observed for both the non-dried and dried adsorbents. This energy hump is associated with internal rearrangements of bonds in the polymeric materials of tassel resulting in the releasing of energy as more rigid cross linked structures are formed during thermal activation. This exotherm has been linked to internal rearrangement of bonds in the cellulosic macromolecules during pyrolysis (Wu *et al*., 1999; Elizade-Gonzalez *et al*., 2007[a]). It is this internal arrangement which results in the formation of new functional groups on the surfaces of an adsorbents resulting in increased sorption capacity after exposure to controlled heating programs (Wu *et al*., 1999). Data obtained by DTA and DSC give complementary information on the test material.

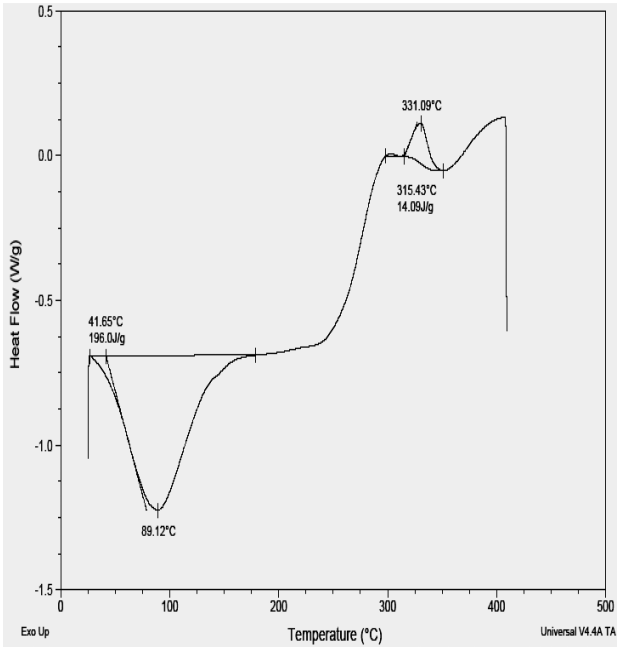

Fig. 5. DSC curve for non-dried tassel powder.

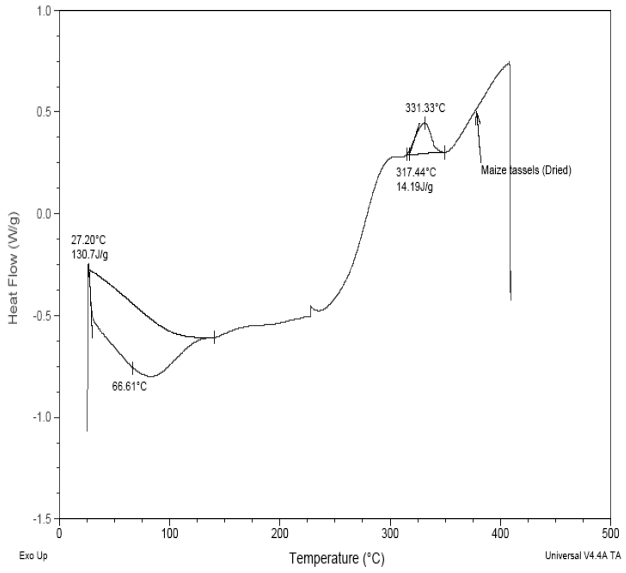

Fig. 6. DSC curve for oven dried tassel powder.

CONCLUSIONS

Tassel adsorbent has mesoporous morphology according to BET N_2-adsorption results. The specific surface area and the pore volume of adsorbent particles were significantly smaller compared to other known adsorbent material such as charcoal, activated carbon and zeolites. Hence the mode of adsorption exerted by tassel could be ascribed to physisorption and probably chemisorption of metal cations by various functional groups present on its surface. Thermal studies of tassel indicated that this material, because of its fibrous nature, could resist thermal decomposition up to 250^{o}C in air. The behaviour of tassel when subjected to a heating program was found to closely follow that of other cellulosic materials such as wood. These materials undergo pyrolysis at temperatures above 300^{o}C before undergoing decomposition. The microstructure of the adsorbent produced by HRSEM showed that the material was generally flattish with very minimal porosity being observed. This observation was corroborated by the BET N_2-adsorption results.

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