SURFACE STUDIES OF A BIOMATERIAL FOR THE DEVELOPMENT OF A BIOSENSOR FOR THE DETECTION OF TRACE METALS

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Abstract
Polymeric mediators have been used in biosensor development. However, the synthesis of the polymeric mediators is tedious. To reduce the cost of biosensors organic polymer constituents, there is a search for low cost alternatives. Maize tassel (MT) has shown its potential to adsorb trace metals from aqueous solution. But before MT can be put into use in biosensor development, its characteristics properties need to be known. In this study, we report the surface characterization of maize tassel with respect to the morphology, dispersion, elemental composition and adsorption trends. The BET results indicate that the powdered material is mesoporous with specific surface area (S_{BET}), of 2.52 m^2/g. Functional groups, $-NH_2$, -C=O and -COOH were identified by FTIR analysis. Zeta potential study indicates that maize tassel possesses positive Zeta potential at pH<5.5 and negative Zeta potential at pH >5.5, and these amount to Zeta potential of 0 to ±5mV. High-resolution scanning electron microscopy (HRSEM) reveals a microstructure showing predominantly flattish rod like particles. Energy dispersive x-ray (EDX) shows high percentage levels of Al, Mg and Si with potential to form organometallic compounds. The presence of amino groups would form a linkage entry of the enzyme into MT.

Introduction

Conventional analytical techniques, although highly precise, suffer from the disadvantages of high cost and are laboratory bound. Electrochemical techniques have been widely recognized as powerful techniques for trace metal detection. The recognition is as a result of remarkable sensitivity that allows detection at very low levels as well as it can be coupled very easily to inexpensive and easy-to-use instruments. In a number of enzyme-based sensors, biomaterial polymeric mediators have been used for the purpose of immobilization with the ability to transfer electrons [1]. However, the synthesis of the polymeric mediators is tedious and difficult. To reduce the cost of biosensors low cost organic polymer constituents have been suggested and used.

Maize tassel is the 'male' flower of the maize plant that forms at the top of the stem. Once the useful nutrient rich portions of maize plants have been harvested, the remaining portion of the plant is usually either ploughed back into the land or is discarded as agricultural waste. Little is known about the chemical composition of tassel. However, there is anecdotal evidence, that tassel may contain amino acids, polypeptides chains and some simple sugars as it attracts insects. Being plant material, it is postulated that tassel contain cellulosic surface hydroxyl groups. Maize tassel (MT) has shown its potential to adsorb trace metals from aqueous solution [2-4]. But before MT can be put into use in biosensor development, its characteristics properties such as morphology, dispersion and adsorption trends need to be known. In the current study, we present the aforementioned properties of MT. It is anticipated that these factors would enhance the integration and coordinated participation of the enzyme during catalysis

Experimental

Nitrogen adsorption-desorption was determined at an analysis bath temperature of -197^oC and at a maximum manifold pressure of 925 mmHg. 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 analyzed 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.

A Perkin-Elmer GX2000 FTIR spectrometer adapted with Perkin-Elmer Auto Image Microscope System was used in the identification of the functional groups that may be responsible for adsorption of metal ions on tassel surface. The pure tassel and tassel with Pb(II) samples were first dried at 105 248°C for 16 h and then stored in a desiccator. The dry samples were then diluted to 5% in KBr and cast into disks before FTIR analysis. The Zeta potential was determined using a Zeta-Plus4 instrument (Brookhaven Corp., USA). Ground fractions of tassel powder in their natural state with sizes ranging from 45-750 µm were morphologically characterized by high resolution field emission-scanning electron microscopy. EDX analysis of tassel powder was carried out on JSM 5800LV, Vantage 6, Analytical Systems with 130 eV detector (JEOL, Tokyo, Japan). The EDX was carried out in order to characterize the metal distribution on the surface of the tassel. A small amount of powder was spread on the sample stage coated with gold. The sample was then bombarded with electrons accelerated by 20 keV power supply at a takeoff angle of 35° in order to get an EDX spectrum.

Results

Figure 1 shows the nitrogen adsorption-desorption isotherm measured at -196^oC. 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 confirms MT adsorbent is mesoporous in nature.

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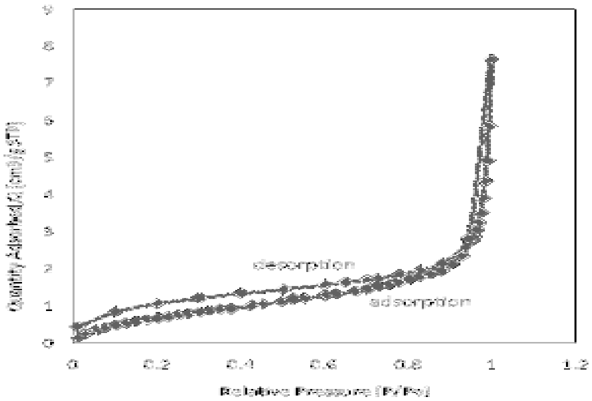

Figure. 1. Adsorption–desorption curves for the 45-50 µm fraction

The FT-IR spectrum of tassel is shown in Figure 2. The spectrum of the adsorbent was measured within the range of 40000-600/cm wave number. The absorption peak around 3466/cm indicates the existence of O-H groups. The peaks observed at 2921/ cm can be assigned to stretching vibration of the C-H group. The absorption peaks at 1734, 1643 and 1036/cm are associated with the presence of C=O, C=C and C-O, as indicated by [5-6].

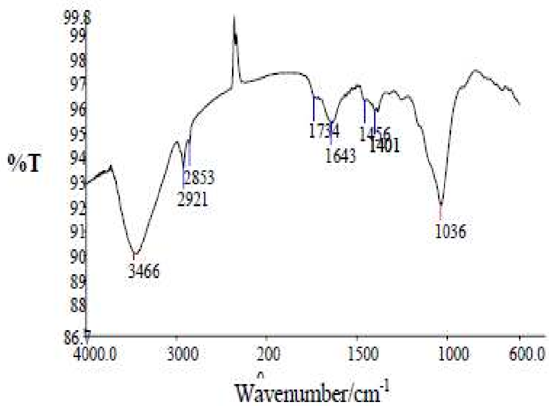

Figure 2 FTIR spectrum of maize tassel

The result of Zeta potential measurement of maize tassel is shown in Figure 3. As can be seen in Figure 3, there is a positive Zeta potential between 0-5mV at pH >5.5, 0, and this amounts to Zeta potential of 0 to ±5mV and negative Zeta potential at pH >5.5. The positive Zeta potential between 0-5mV indicates probably rapid coagulation or flocculation properties; while negative Zeta potential of -20mV indicates some moderate stability.

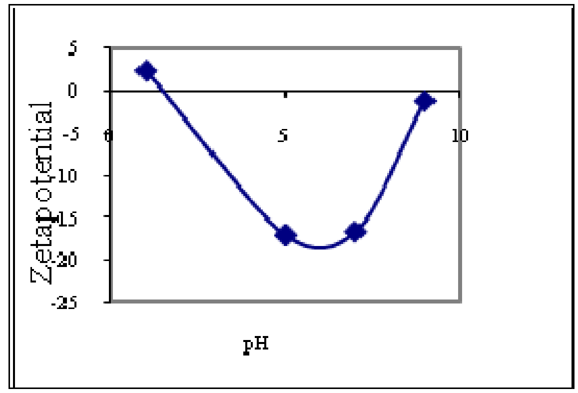

Figure 3 Zeta potential measurement of maize tassel

The micrograph of maize tassel in Figure 4 exhibits flattish shapes originating from the fibrous nature of tassel material. No porosity is observed from the particles hence its adsorption behavior can be linked to its surface morphology.

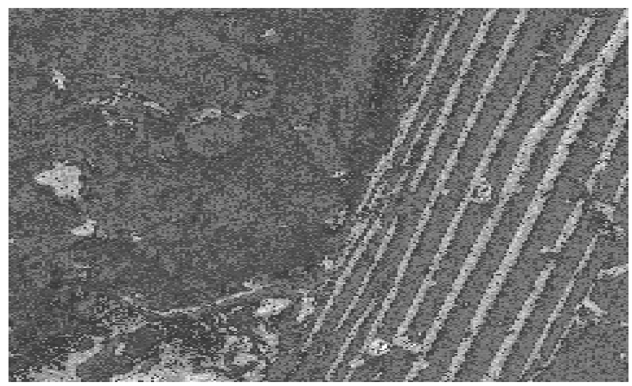

Figure 4 Micrograph of maize tassel powder

The EDX spectrum obtained for tassel is shown in Figure 5. The elemental distribution of tassel shows high percentage levels of Al, Mg and Si elements with potential to form organometallic compounds which might be responsible for the tough elastic properties exhibited by the tassel powder.

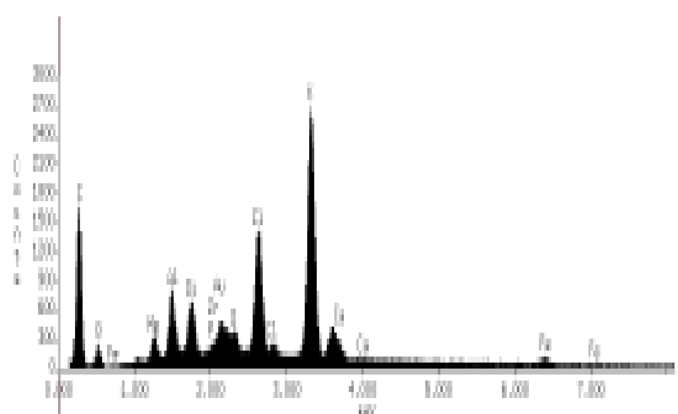

Figure 5 EDX spectrum of pure tassel powder

Conclusions

Maize tassel adsorbent has mesoporous morphology according to the BET result. Hence the mode of adsorption exerted by tassel could be ascribed to physisorption. The Zeta potential measurement suggests that the material could coagulate very rapidly. The HRSEM shows that the material is generally flattish with no porosity. On the basis of the FTIR result, the functional groups on the surface of the MT, MT may have the ability to conduct electrically. This is important since the MT itself must mediate the transfer of electrons between the immobilized enzyme and the electrode surface. In addition, the presence of the amino groups would also form a linkage entry of the enzyme into the MT. As a bifunctional agent, glutaraldehyde will be used to cross-link enzymes to their support through covalent binding. Chaubey [7] and Avramescu [8] employed the same technique to immobilise L-lactate dehydrogenase via glutaraldehyde on the surface of conducting polymers covering the electrode and developed a biosensor for L-lactate.

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References

1. Abia A.A., Asuquo E.D., "Pb^{2+} and Ni^{2+} adsorptions kinetics from aqueous metal solutions using chemically modified and unmodified agriculture adsorbents". *Agric. J. of Biotechno*. 5 (16), (2006), pp. 1475-1482.

2 Zvinowanda, C., Okonkwo, J.O., Shabalala, P.N., Agyei N.M. "Physicochemical characterisation of maize tassel adsorbent: Part I. Surface texture, microstructure and thermal stability". *J Polymer Sci* 111, (2009), pp. 1923-1930.

3 Zvinwanda, C., Okonkwo, J.O., Agyei N.M. Shabalala P.N. "Preparation and characterisation of biosorbents made from Tassel". *Canadian J Pure & Appl Sci:* 2 No: 3, (2008), pp. 483-488.

4 Zvinowanda, C., Okonkwo, J.O., Shabalala, P.N., Agyei , N.M. "Application of maize tassel for the removal of Pb, Se, Sr, U and V from borehole water contaminated with mine wastewater in the presence of alkaline metals". *J Haz. Mat.* 164, (2008), pp. 884-891.

5 Cardenas, G., Mirand, S.P., "FTIR and TGA studies of chitosan composite films". *J. Chil. Chem. Soc*., 49(4), (2004), pp. 291-295.

6 Chauhan, G. S., Jaswal, S., Verma, M., "Post functionalisation of carboxtmethylated starch and acrylonitrile based networks through amidoximation for use as ion sorbents". *Carbohydrate*. *Poly*. 66 (4), (2006), pp. 435-443.

7 Avramescu A., Noguer T., Magearu V., Marty J. L. . "Chronoamperometric determination of D-lactate using screen-printed enzyme electrodes". *Anal. Chim. Acta* 433, (2002), pp 81-88.