Journal of Applied Sciences Research, 3(11): 1336-1342, 2007

Extensive Characterization of Raw Barley Straw and Study the Effect of Steam Pretreatment

[1]A.A.Amer, [2]Azza El-Maghraby, [3]G.F.Malash, [4]Nahla.A.Taha

[1]Alexandria Petroleum Company.
[2]Department of Fabrication Technology, Institute of Advanced technology and New Materials, Mubarak City for Scientific Research and Technology Applications, Alexandria, Egypt.
[3]Chemical Engineering Department, Faculty of Engineering, Alexandria University, Egypt.
[4]Institute of Advanced technology and New Materials, Mubarak City for Scientific Research and Technology Applications, Alexandria, Egypt.

Abstract: The properties of barely straw play a crucial role in some industrial applications. Despite that, there is a lack of its scientific data concerning thermal, mechanical and chemical properties of these fibers. To maximize their potential use it is necessary to understand their characteristic. In this work, barely straw was characterized by analytical techniques such as FTIR, X-ray, TGA and SEM. The straw treated with distilled water and compare the new analytical properties with the properties of the raw, which revealed that the adsorption properties improved with steam treatment due to increase of functional groups which can share in adsorption reaction.

Keywords: Agriculture waste, Barely straw, Characterization, Sorbents.

INTRODUCTION

Vegetable fibers are spread worldwide, as a renewable resource material mainly abundant in the tropics. Their biodegradability can contribute to a healthier ecosystem and their low cost and reasonable performance fulfill economic interest of various industries[1]. Agriculture wastes are composed of fibrils glued together with natural resinous materials of the plant tissue[2,4]. Some of these fibers have been extensively investigated and used in some industries as textile fabrics, composites and for some medical purpose. Many other less known fibers find limited applications. One of the handicaps for finding new uses for these natural fibers is the lack of available scientific data regarding their structure and properties[1]. Barely straw is a renewable substrate for production of cellulose, glucose, alcohol and other chemical compounds. Barley straw, being easily available, is often used during containment and clean up of oil spills[5,6]. Barely straw is also used as a biodegradable substance for oil removal from soil[7]. and for inhibition of algae and cyanobacteria growth in aquatic reservoir[8]. The production of barely straw in Egypt is about 300,000 ton/year which give as the importance for use this waste. When searching for new applications for a particular material, its through characterization is very useful. The knowledges of barely straw is very limited. The aim of this study is to investigate the structure and the stability of the straw.Important characteristics of the fibers will aid their increasing utilization in present and future applications such as polymeric biocomposities, clean up of oil spill or other uses. Also properties of steam treated fibers are obtained to investigate their use in removal of dye from wastewater.

MATERIALS AND METHODS

The research was conducted on the barely straw. Sun dried barley straw obtained from Egyptian farms harvests in May every year. Scanning electronic microscope, Model JSM 6360 LA Jeol, was used to study fiber surface morphology. Before examination, the fiber samples were sputter coated with a thin layer of gold in a vacuum chamber. Thermogravimetric analysis was carried out in (TGA-60A Shimadzu) at a heating rate of 10 °C/min from room temperature to 600 °C in a N_2 atmosphere. The fibers were also analyzed with FTIR-8400 S Shimadzu spectrophotometer in order to identify the function groups in the fiber structure. The degree of crystallinity of straw was shown from X-ray diffractograms

Corresponding Author: Azza El-Maghraby, Universities and Research Centers District, new Borg El-Arab City, P.O. Box: 21934 Alexandria.
Phone: + 0103087123, Fax: 002 03 4593423, Email: maghrabyazza@yahoo.com

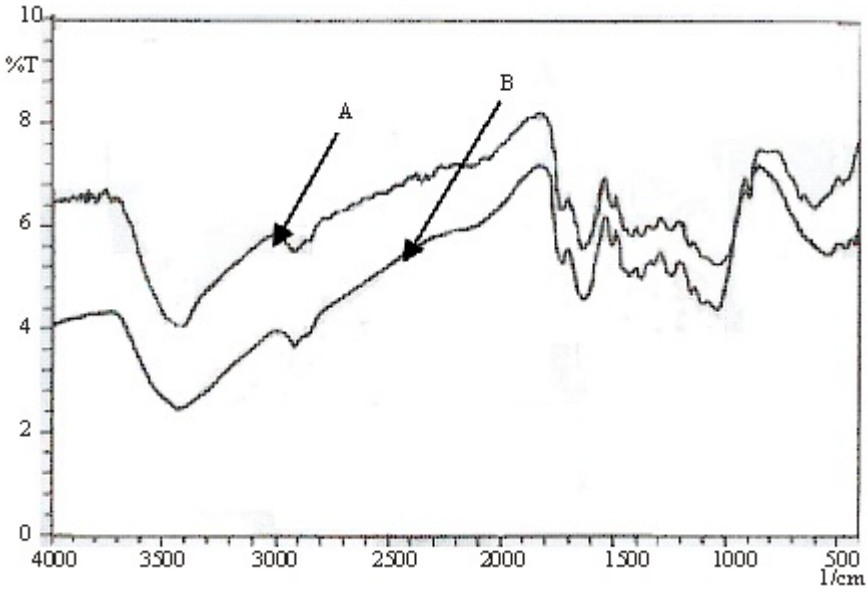
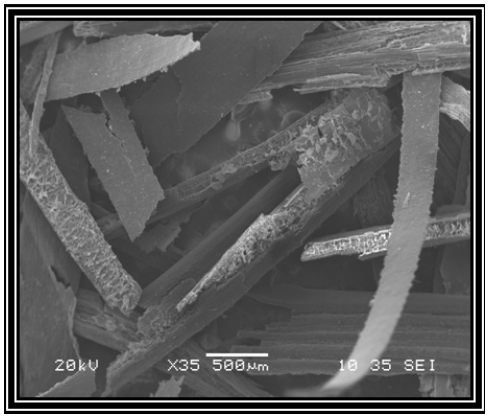
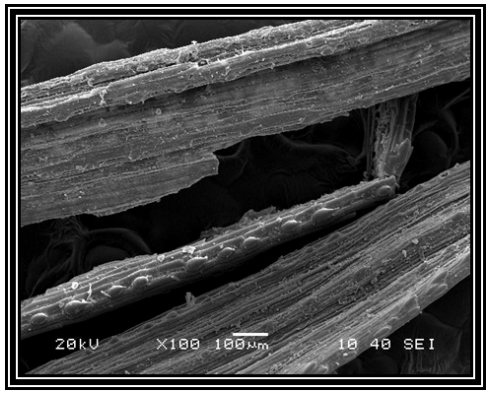


Fig. 1: (A) FTIR spectra of the raw barley straw- (B) FTIR spectra of the treated barley straw.

(X-ray 7000 Shimadzu). Barley is steam pretreated as 0.5 g of the dried cruched straw with particle size1000µm was mixed in 50 ml of distilled water autoclaved for 15 min at 121°C. The mixture, after cooling, was filtered using a muslin cloth. The residues were dried in an oven to constant weight at 80 °C[9]. The characteristics of the treated fibers were also studies by SEM, FTIR and study the thermal stability by TGA finally the crystalline degree of treated fibers were studied by X-ray diffraction. To examine the ability of straw to be used as sorption agent adsorption experiments for Methylene blue dye were carried out by agitating 10 mg of treated fibers in 100 ml glass beaker, at pH 5 for dye solutions was maintained and the beakers were agitated at 150 rpm at room temperature on arotary shaker (KIKA-WERKE,GMBH& Co.KG). This were done for raw barley and treated. For choosing the optimum condition for treating the straw, it was boiled with hot water to select the most suitable temperature for treating the fiber to obtain maximum adsorption Concentration of dye was estimated spctrophotometrically by monitoring the absorbance at 655 nm on UV/ Visible spectrophotometer (Ultrospec 2000"Pharmacia Biotech").



(a)

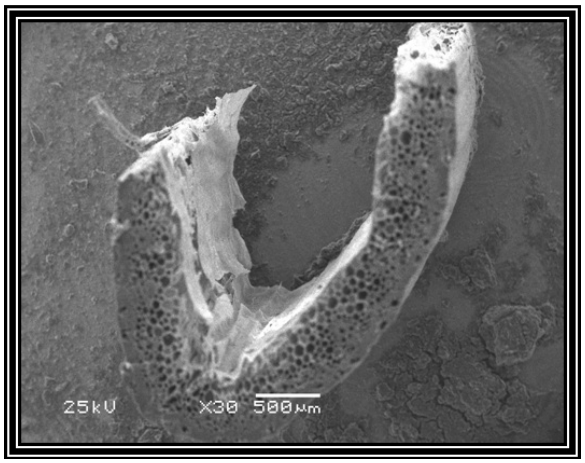


(b)

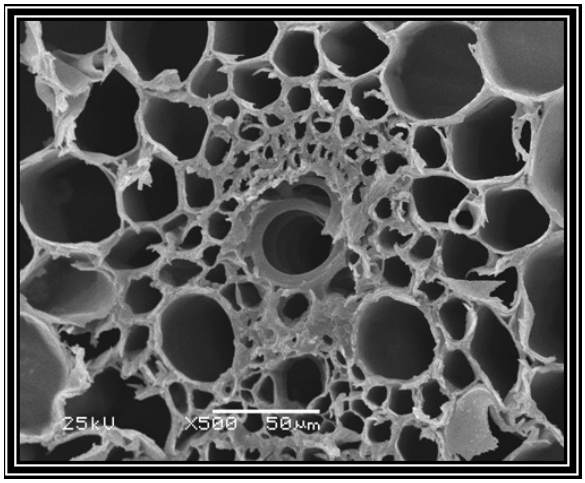
Fig. 2a, b: Surface of barley straw

RESULTS AND DISCUSSIONS

The FTIR analysis permits spectrophotometric observation of raw barely straw in the range 400-4000 Cm^{-1}, and serve as a direct means for the identification of the organic function on the surface. An examination

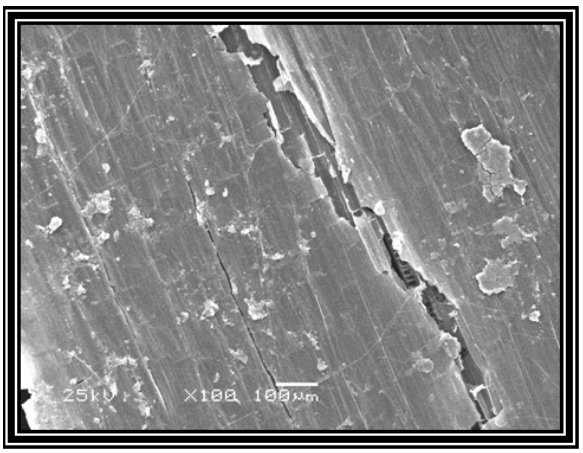


(a)

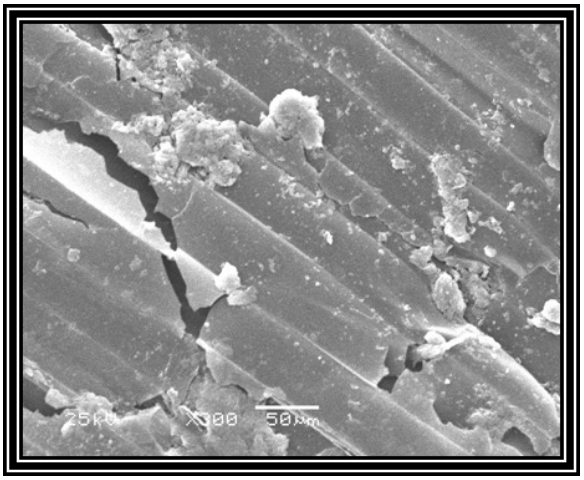


(b)

Fig. 3a,b: Cross section of barley straw



(a)

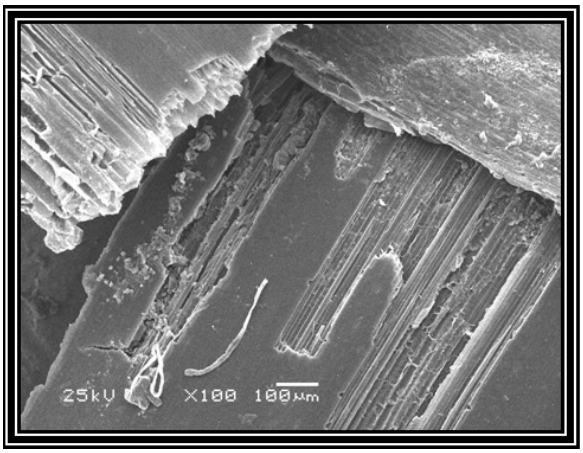


(b)

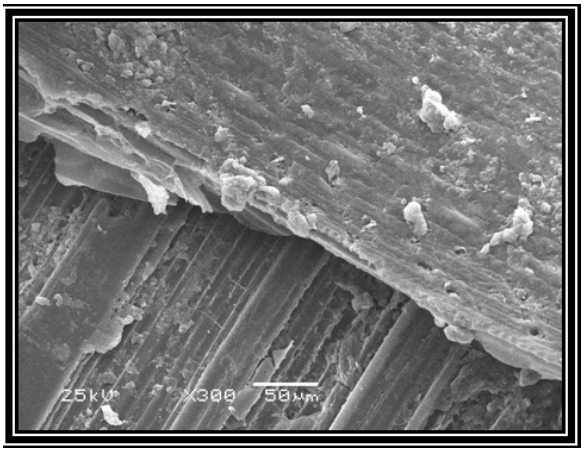
Fig. 4a,b: Dye on raw straw surface

of the barley straw surface and after treatment possibly provides information regarding the surface groups that might have participated in the adsorption reaction and also indicates the surface site (s) on which adsorption can take place. IR studies indicate the participation of the specific functional groups in adsorption interaction which indicates the possibility of using barley straw as adsorpent.

The IR spectrum of the raw barley straw (Fig. 1A) showed that the most prominent peaks in the spectrum originate from OH vibrations (3450 Cm^{-1}), CH_2 and CH_3 asymmetric and symmetric stretching vibrations (2935-2915 Cm^{-1}). Very intense peaks in region (1742-1620 Cm^{-1}) originate from the stretching mode of carbonyls mainly ketons and esters[10]. A very unique set of adsorption peaks originating from β-diketones, is observed in the spectrum: keto-Tautomer display a doublet at 1730 Cm^{-1}[10], at (1000-1500 Cm^{-1}) the aromatic region related to lignin[11,12]. Similar measurement were done for the treated barley (Fig. 1B). Both spectra are similar in terms of the most characteristics and intense peaks. However, in the (2400-2000) Cm^{-1} region, remarkable changes are observed in case of treated barley. For the external surface, absorption is detected. Therefore, it is possible that the spectra represent the thin wax layer. Cellulose, hemicellulose as well as lignin, having many OH groups in their structure, make the most absorbing layer.



(a)



(b)

Fig. 5a,b: Dye on steamed straw surface

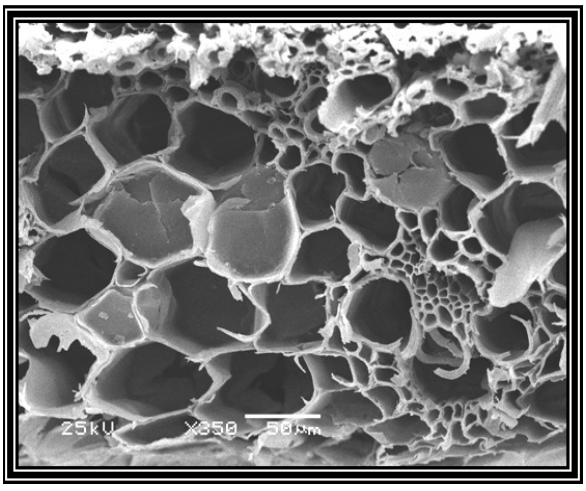


Fig. 6: Dye in cross section of barley straw

SEM images for the barley straw were taken in order to examine and classify the morphology of the fibers.(Fig. 2 a,b) presents SEM micrographs of the surface morphology of barley straw. It can be seen that the fibers consists of longitudinal tissue which make its surface rough this was also shown by increasing the magnification factor to see the roughness surface of the straw[13]. In the image of the external surface, many cylindrical wax rods of size up to 100µm, arranged at different angles can be seen (Fig. 2 a,b). The clusters of rods are distributed irregularly over the epidermal surface with a tendency to accumulate in the space between the straw veins. However, it can expected that there is a thin wax film covering barley surface, consisting of few layers of molecules only[10]. Unfortunately, this kind of coverage is hardly visible by SEM[10]. Cross section of barley straw showed hollow tubules (Fig. 3 a, b) which can be used for entrapping dye, oil and so on. It is described in literature that morphology and composition of plant waxes can change during plant development and later during storage[14]. Similarly, the chemical composition of the wax determines the shape and size of the crystals. It has been found that the tubular form of the wax crystalloids is related to the presence of β-diketones in the wax[10]. Based on knowledge about the straw wax composition, it can be concluded that during the growth process of the barley plant there is a tendency for an increase in crystalline zone caused by transformation of alcohols into ketones and at the same time a decrease in the number of hydrogen bond in wax. The morphology of the loaded adsorbent showed some important observations. Typical SEM photographs are shown in (figure 4,5) for raw and steam treated barley loaded. Coverage of the surface of the adsorbent due to adsorption of the dye molecules leading to formation of a monolayer of the adsorbate coverage. The above observation was further confirmed well with the batch mode adsorption studies. SEM studies visualized the formation of the molecular cloud of the dye over the surface. Figure 6 showed the entrappying of the dye into tubular structure of the barley which confirm that this structure can be used for removal of dye, oil and so on. Plant cell wall material is composed of there important constituents: cellulose, hemi-cellulose and lignin. TGA of barley straw and treated straw is shown in (Fig. 7a,b). The fiber mass decreased from about 91.2 % (at 100 °C) to 88.6 % (at 250 °C) and to 78.4 % at 350 °C. Different regions can be associated with the loss of retained water at 100°C, hemicellulose degradation at 200-260 °C and cellulose degradation at 240-350 °C and lignine degradation at 280-500 °C. Between 100and 250 °C,

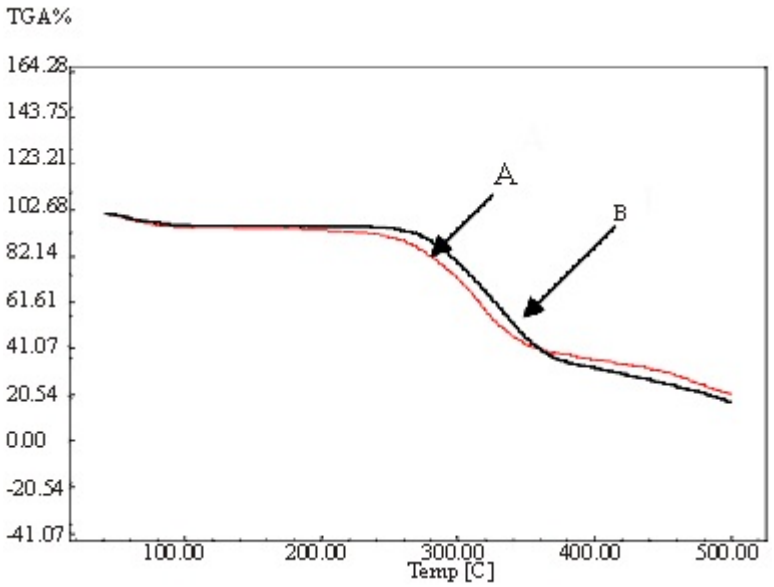


Fig. 7: (A) TGA for raw barley straw (B) TGA for steamed barley straw

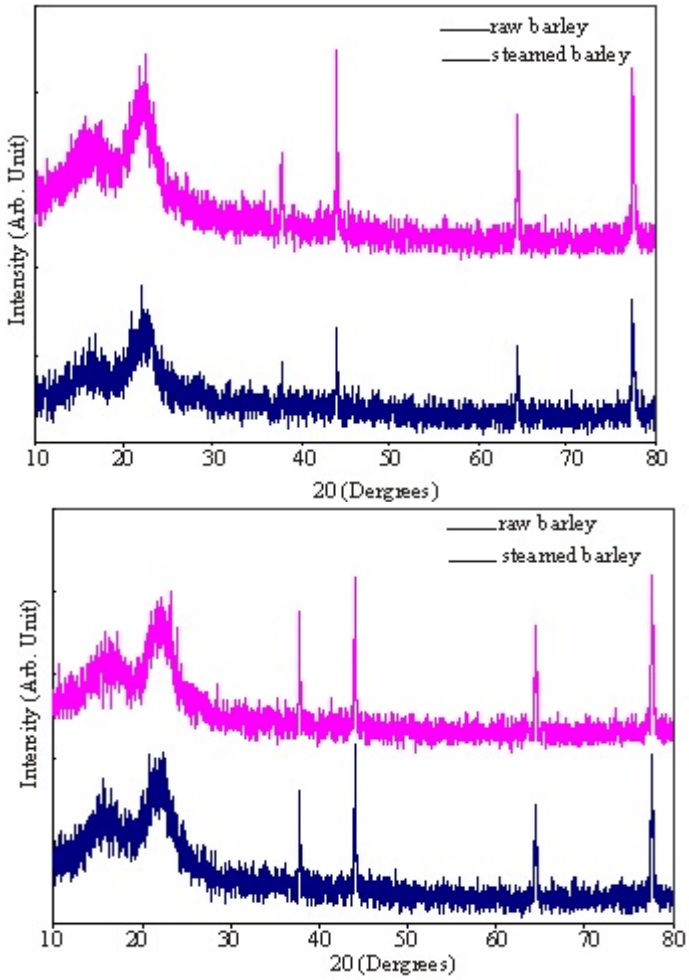


Fig. 8(a): X- ray diffraction of raw barley straw and steamed barley (b) X- ray diffraction of barley straw with dye.

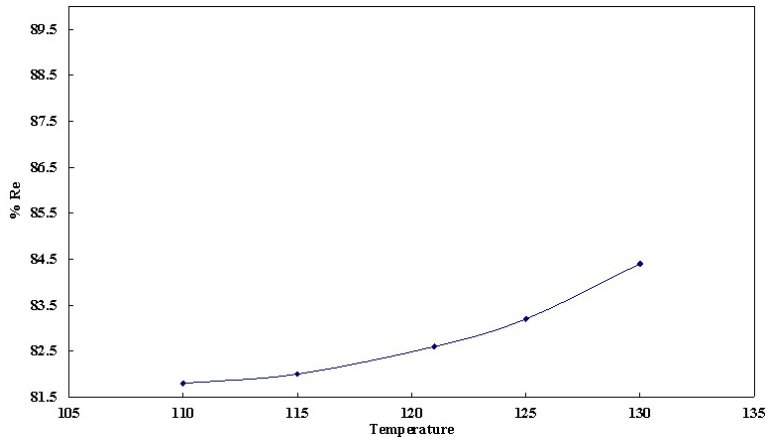


Fig. 9: Sorption capacity of the treated barley at different temperatures

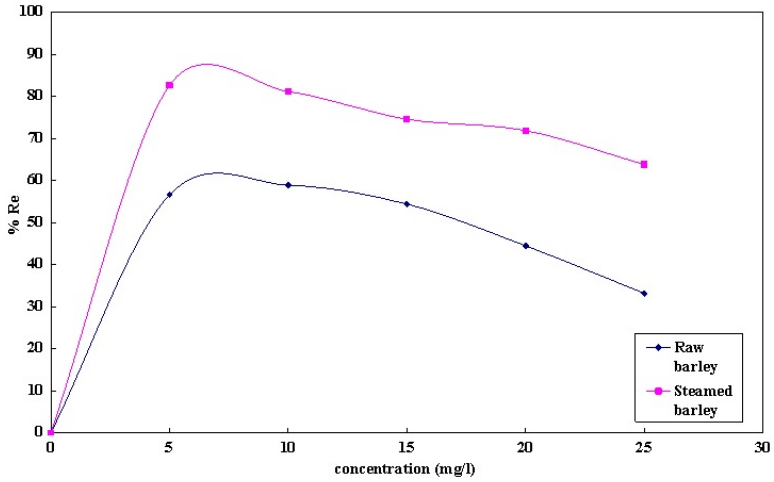


Fig. 10: Percentage removal for raw and treated barley straw at different concentrations

degradation turns the lignocellulosic fiber into a brownish color material, losing its strength, although this was not quantified. At higher temperatures, up to 500 °C, carbonization occurs with accentuated loss of material[15]. Treated fibers showed a slight increase in thermal resistance (figure 4 b). X- ray diffraction technique is a powerful tool to analyze the crystalline nature of the materials.If the material under investigation in crystalline, well- defined peaks are observed while non crystalline or amorphous systems show a hollow instead of well defined peak[13]. (Fig. 8a) shows X-ray diffraction pattern of the raw fibers which is compound in nature i.e., it has crystalline nature shown in sharp peaks corresponding to 2 ≈ 38, 45, 64 and 78 and also broad peak with low angle shown in 2 ≈ 16 and 22[16]. X- ray of treated straw (Fig. 8b) showed no change in the Crystallinity of the straw but the peak at 2 = 16, 38, 45 intensity increased due to dye incorporation.

Adsorption reaction may lead to change in molecular and crystalline structure of the adsorbent and hence an understanding of the molecular structure and crystalline structure of the adsorbent and the resulting changes would provide valuble information regarding adsorption reaction. The XRD patterns of the dyes adsorbents are presented in (figure 9 a,b). These diffractograms indicate increase in the crystallinity at 2θ = 38 and 45 after adsorption and this suggest that the dye molecule diffuse into micropores and macropores. The effect of boiling temperature of straw was studied by changing the temperature from 110 ºC-150 ºC. The sorption capacities were measured at 5 mg/l concentration. Figure (9) indicates that the sorption capacity of the treated barley increases with increasing the temperature and the corresponding pressure. The change of % removal from 120 ºC to 150 ºC is not too much so we choose the temperature of 121 ºC was chosen as[9] for economies the expense

of treating. Soaking of the fibers in hot water increases its affinity to water. The external surface area of the fibers due to its swelling by hot water increases, it also refers to the dissolving part of lignin included in the straw fibers. In general, this treatment must cause an increase in the fibers sorption capacity due to increase the external surface area, Figure (10) compared between the raw barley straw and the treated at 121 ºC which indicated increase in the sorption capacity occurs for the treated barley.

Conclusion: Extensive analytical effort to characterize this waste has been made in order to supply data would help valuing the by- product which may use in the future in different industries.Based on the experimental results, the morphological and chemical complexity of barley straw surface has been clarified. FTIR studies indicate the specific function groups which can introduced in different chemical treatment to modify the fibers to be effective in dye adsorption, oil removal from soil or oil spill cleanup and should allow us to improve understanding of the mechanism of oil adsorption at the straw surface. It was shown that the main constituents of the straw were β-diketons, alkenes and esters. While application of SEM techniques –allowed us to observe the morphological heterogeneity of the barley straw and visualized the hollow tubular structure of the straw. XRD studies shows increase in peak intensity due to adsorption reaction.

REFERENCES

1. Valcinede Tanobe, O.A., H.D. Thais Sydenstricker, Marilda Munaro, C. Sandro Amico, 2005. A comperhensive Characterization of chemically treated Barazilian spongegourds (Luffa Cylindirica). Polymer Testing, 24: 474-482.
2. Chand, N., S. Sood, P.K. Rohatgi, K.G. Satynarayana, 1984. Resources structure, Properties and uses of natural fibers of Madhya- Pradesh. J. Sci. Ind. Res. India, 43(9): 489-499.
3. Amin, M.B., A.G. Maadhah, A.M. Usmani., 1985. Natural Vegetable revisited.Proc. Am. Chem. Soc (ACS) Div. Polym. Mater., Florida, 52: 19-23.
4. Sen, K.K., S.S. Reddy, Carbohydrate analysis of some natural fibers. Res. Ind, 39(4): 258-260.
5. Hupka, J., 1979. The sorption capacity of sorbents in oil spill clean up. Symposium on the Application of physics in controlling the oil pollution effects in the Marine Environment. Gdańsk, 1-10.
6. Hupka, J., P Paczkowski,, 1981. Ochronabrzegu morskiego przypomocy sorbent Ó w. Studia i Materialy Oceanologiczne, 35: 279-289.
7. Edyta. Witka-Jezweska, Jan Hupka, Piotr Pieniazek, 2003. Investigation of Oleophilic nature of straw sorbent conditioned in water, 8: 561-564.
8. Witka, E., J. Jezewska, Hupka, 2000. in: Proceeding of the seventh polish- Danish workshop on biomass for energy, starbienion, December 7-10, pp: 25.
9. Saddler, J.N., L.P. Ramos, C. Breuil, 1993. In: Bioconversion of forest and agricultural plant residues. CAB International, Walling Food, UK, 73-91.
10. Sylwia K. Wisńiewska, Jakub Nalaskowski, Edyta Witka- Jezewska, Jan Hupka, Jan D. Miller, 2003. Surface Properties of barley straw. Colloids and Surfaces B: Biointerfaces, 29: 131-142.
11. Ali, M., A.M. Emsley, H. Herman, R.J. Heywood, 2001. Spectroscopic studies of the ageing of Cellulosic paper. Polymer, 42(7): 2893-2900.
12. Colom, X., F. Carrasco, P. Pagès, J. Cańavate, 2003. Effects of Different treatments the interface of HDPE/lignocellulosic fiber composites.Compos. Sci. Technol, 63(2).
13. Cullity, B.D., 1978. Elements of X-ray Diffraction. Addison-Wesley, Reading, MA.
14. B.E. Juniper, C.E., 1983. Jeffree.Plant Surfaces. Edward Arnold, London.
15. Browning, B.L., 1963. The Chemistry of Wood. Interscience, New York.
16. Biscoe, J., B.E. Warren., 1942. An X-ray study of carbon black. J. Appi. Phys, 13: 364-371.