SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALIZED ZEOLITE REINFORCED LIGNOCELLULOSIC DATE PALM FIBERS

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Received March 16, 2015

This paper reports on the synthesis of (3-Aminpropyl triethoxylane) functionalized zeolites by binding silane coupling agent onto the surface of zeolites, using the silylation technique. The modification procedure was carried out using two different methods. Zeolite/cellulose composites with a well-defined structure were then prepared from date palm lignocellulosic fibers and the functionalized zeolite powders. The effect of chemical modification of zeolites was investigated. Also, the effect of zeolite concentration, reaction temperature and contact time on the binding percent was studied. The obtained samples were characterized by XRD, SEM, EDX and XPS. The results confirmed the deposition of treated zeolites onto modified date palm fiber. The work also aimed to characterize the reinforced date palm fiber, including its surface properties, degree of crystallinity and functional groups.

Keywords: zeolites, lignocellulosic fiber, XRD, XPS, SEM, EDX

INTRODUCTION

Recent ecological concern has resulted in a renewed interest in cellulosic fibers. In fact, many natural fibers, such as alfa, sisal, luffa, and date palm, are of interest because they are environmentally friendly and are not hazardous for the environment.[1-3] Hence, in the last few years, lignocellulosic fibers in general have been widely applied in many fields because of their renewability, biocompatibility, and natural abundance.

Date palm fiber is a useful lignocellulosic natural fiber and has been subjected to many chemical modifications. In fact, several works reported the study of chemical and physical modifications of date palm fibers.[4-11]

Several modification methods and agents have been used to improve the performance of lignocellulosic fibers. In this study, we focused on improving their adsorption capacities for waste water treatment. Many adsorbents, such as activated carbon, perlite, dolomite, lignite, pentonite and zeolite, have been exploited in order to increase adsorption and ion exchange properties. In addition, several studies have shown the role of zeolites in removing heavy metals and dyes. Zeolites are one of the most significant materials in chemistry, their application as adsorbent being especially important in relevant industrial processes.[12-14]

Thus, zeolites are microporous materials with regular pores and cavities of molecular dimensions (3-15Å) formed by heteroatoms in tetrahedral coordination (primary Si and Al) connected through oxygen atoms. These adsorbent materials have, in their internal structure, interconnected channels and cavities of molecular dimensions, where compensation cations, allowing ion exchange, exist. Moreover, zeolites can be modified by introduction of new functional groups in order to improve their activity and selectivity for the removal of many substances.[15-17]

Complete usage of the zeolite surface can be accomplished by zeolite deposition on lignocellulosic fibers. Many applications of zeolite-cellulose composite materials, essentially related to adsorption and absorption process, have already been proposed. Zeolite deposition can be also accomplished by using an adhesive substance. Many researches indicated that there are several disadvantages associated with this process: the most important is the weak

zeolite/cellulose interaction. In addition, incorporating a binder in the zeolite/cellulose composite is not efficient for certain applications, such as waste water treatment, especially if the polymer is unstable or soluble in filtration medium due to high temperature. Numerous problems of adhesion and wetting between an organic and an inorganic phase are encountered in many fields. One way to resolve them is to modify the surface properties of the zeolite to make it more compatible with cellulose surface.[16,18-23] This can be achieved, for instance, by binding some organic chains onto the inorganic surface by means of silane coupling agents. Among various procedures of chemical modification of zeolites reported in the literature, silylation was chosen due to its relative simplicity and flexibility to incorporate various functional groups. Silane coupling agents have been used to functionalize the surface of the zeolites to improve the adhesion at the zeolite particle/cellulose interface. Organosilane reacts with the hydroxyl groups on the surface of the zeolite particles *via* the silylation reaction to form covalent bonds. Furthermore, the silane coupling agents with second reactive functional groups on the cellulosic fiber chains form covalent bonds between the zeolite surface and the lignocellulosic fiber, promoting adhesion for the composite zeolite/cellulose.[24,17]

Zeolite/cellulose and cellulose acetate composites have already been proposed for numerous uses in many fields. For example, they have been tested for medical applications, filtrations, air purification, and filtration membranes. The deposition of zeolite on the surface of date palm fibers improves ion exchange and adsorbs dyes. The composite zeolite/date palm fiber is used as an alternative low cost absorbent system for the removal of dyes from aqueous solution. By the qualities of zeolite and cellulosic fibers, this composite can provide several advantages. As also proved, functionalized zeolite reinforced date palm fiber can facilitate the sorption and binding of dyes with microporous structure and has great capacity of ion exchange.

The aim is to provide stable zeolite/cellulose composite materials, and particularly to investigate a facile method for preparing such composite materials. Our approach consists in the development of a new composite based on zeolite and date palm fibers, two materials that permit achieving this objective.

The adsorption process provides an attractive alternative for the discoloration of dye wastewaters, and low-cost and readily available adsorbents have been used for various applications. The adsorption process onto cheap, high capacity and selective adsorbing materials appears to be an excellent alternative, especially when the exhausted adsorbent may be recycled or reused.[25,26]

In the present investigation, the modification and characterization of treated fibers and zeolites were performed. The work also focused on investigating the effect of zeolite concentration, reaction temperature and contact time on the binding degree of zeolite particles, as well as the properties of the reinforced date palm fiber, including its surface properties and crystallinity.

EXPERIMENTAL

Fibers

The date palm fiber used in the current work belongs to the species of Dactylifera. It is composed of 32%-35% cellulose, 25% hemicelluloses and 27% lignin.

Cellulose was extracted using a combined process based on sodium hydroxide and hydrogen peroxide; in a preheated solution at 120 °C containing 35 g/L sodium hydroxide, 55 mL/L concentration of hydrogen peroxide, 3 g/L of a wetting agent (Subitol LSN BEZEMA), and 25 mL/L of stabilizer (Contavan GAL), date palm leaves were treated for 90 min.[27,28]

Surface modification of zeolite: silylation

Surface modification of zeolite was performed using a silane coupling agent (3-Aminpropyl triethoxylane). The silylation of zeolite was performed in solution. Zeolite was added to solution of silane agent (0.5 wt%) in 50 %V aqueous ethanol solution. The zeolite to solution ratio was taken as 1:1 on weight/volume basis. The slurry was stirred for 2 h by a magnetic stirrer and then kept for 1 h at room temperature. The surface treatment of the zeolite with the silane coupling agent was completed after drying the slurry in an oven at 110 °C for 4 h.[17,24,27,29]

Surface modification of date palm fiber using silane coupling agent

The treatment of cellulosic fibers with 1 wt% of the chosen silane was carried out in water medium for 2 hours. In addition, 0.5 wt% of initiator sodium persulfate was added, and acetic acid was used to fix the pH between 2 and 3. Then, the fibers were filtered and dried at room temperature for 2 days and heated at 120 °C for 2 hours.[1,30]

Deposition of zeolites

The appropriate amount of date palm fibers was placed in a round-bottomed flask and stirred in a water

solution under the appropriate experimental conditions. The appropriate concentration of the zeolite (a type of zeolite from Aldrich, purified, in the form of grains from 45 μm) was added and the reaction was allowed to proceed in a preheated water bath at the desired temperatures for the required time. When the time was over, the treated fabric was washed thoroughly with distilled water and then was allowed to dry in an air oven at 100 °C, until it reached a constant weight.[27]

The binding degree is defined as the depositing zeolites percent, and was determined by the percent increase in weight as follows:

$$T_f\ (\%) = \frac{W_f - W_i}{W_i} \quad (1)$$

where T_f is the percent of zeolites deposited onto date palm fiber (%), W_i (g) and W_f (g) represent the weights of the initial and the modified fibers, respectively.

Characterization of date palm fiber-zeolite composite

X-ray diffraction (XRD)

X-ray diffractograms were obtained with an analytical X Pert PRO MPD diffractometer, having an X-ray tube producing monochromatic Cu Kα (λ= 1,789 A°) radiation.

Scanning electron microscopy (SEM)

SEM analysis of unmodified and modified zeolites and date palm fiber was performed using an XL30 ESEM model from SEI.

SEM-EDX

Qualitative SEM-EDX spectra were obtained on a Quanta 200 environmental scanning electron microscope from FEI, in the low vacuum mode (at a pressure of 1.0 Torr, *i.e.* 133 Pa).

X-ray photoelectron scanning (XPS)

The X-ray photoelectron spectroscopy (XPS) experiments were performed with an XR3E2 apparatus from Vacuum Generators, UK.

RESULTS AND DISCUSSION

Effect of zeolite concentration

Figure 1 shows that the binding degree increases to achieve its maximum with the increase of initial zeolite concentration. Gradually, as the zeolite concentration increases, the binding rate also increases and reaches its maximum. The binding degree increases fast at a zeolite concentration of 20% and shows an attractive maximum at about 100%. The binding rate reaches a maximum value for a concentration of up to 100% zeolite.

Effect of reaction temperature

Figure 2 shows the effect of temperature on the binding degree within the range of 40-100 ºC. As the temperature was increased, the binding degree also increased and reached a maximum value and then decreased. Thus, the optimum binding degree was calculated as 87.4% at 60 ºC. The initial increase in the binding degree may be attributed to the increase of the mobility and diffusion of zeolite molecules. Indeed, the higher the temperature, the more the spacing between the chains of the amorphous region is favored, which means that the free volume in the structure of the fiber increases, which explains the movement of the segments along the chains.

It is found that when the temperature increases, the binding degree increases progressively until its maximum at T = 60 °C. The temperature facilitates the access of the zeolite to the support. Thus, as the temperature increases, the activation energy of the crystalline regions is improved due to swelling of the fiber (the structure becomes more accessible to reactive species).

Effect of contact time

Figure 3 shows the effect of contact time on the binding degree of the zeolite, investigated by varying the time (from 30 to 240 min), while the reaction temperature and the concentration of zeolites were kept constant.

As shown in the figure, the binding degree decreases gradually with time. The optimum binding value is about 30 minutes. Due to mechanical agitation, the deposited zeolite on the surface of the fiber is eliminated gradually over time.

XRD results

XRD was used to characterize the date palm fiber reinforced with the zeolite. The aim was to observe any changes in the structure of the fiber, including changes in the chemical structure, rearrangements in the morphology of the polymeric chains as a result of zeolite deposition. To characterize the date palm fiber reinforced zeolite, XRD was used to determine the quantity of zeolite deposited on the fiber and to observe the different peaks provided by the zeolite.

XRD diffractograms of treated fiber illustrated the presence of these peaks: 6, 10, 12, 16… The peak ratio of the zeolite reflection mentioned at 2Θ = 6.19 to that of cellulose (2Θ = 16.901) was always used as a relative measure of the zeolite content on materials.[22]

In this study, this ratio is equal to 0.82 (Fig. 4). The deposition of zeolite decreases the band at 2Θ

= 26, which means a change in the structure of the fiber and reveals a microstructural modification as a result of zeolite deposition.

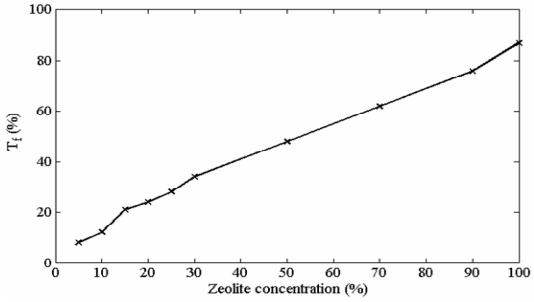

Figure 1: Effect of zeolite concentration on binding rate

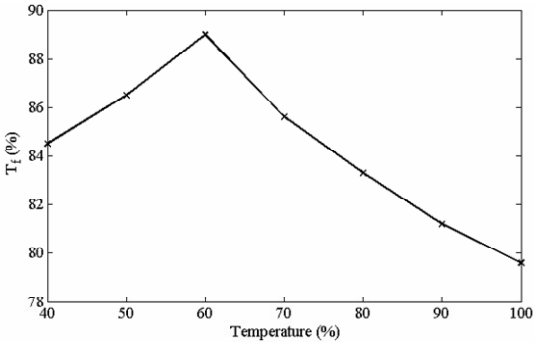

Figure 2: Effect of temperature on binding rate

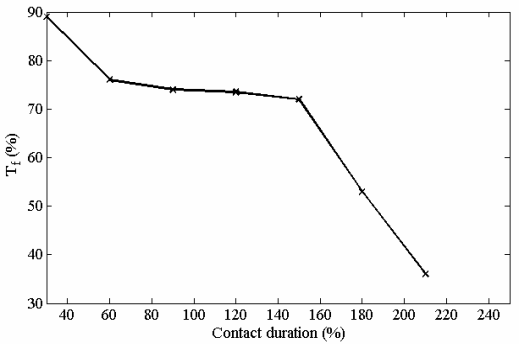

Figure 3: Effect of contact duration on binding rate

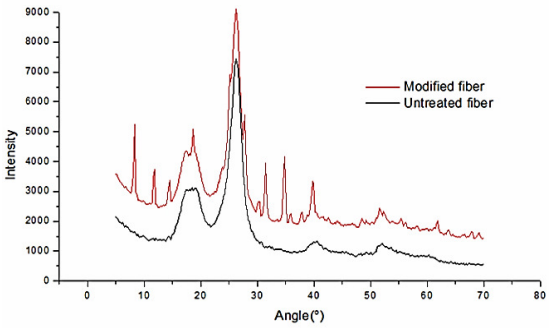

Figure 4: DRX diffractogram of untreated and reinforced date palm fiber

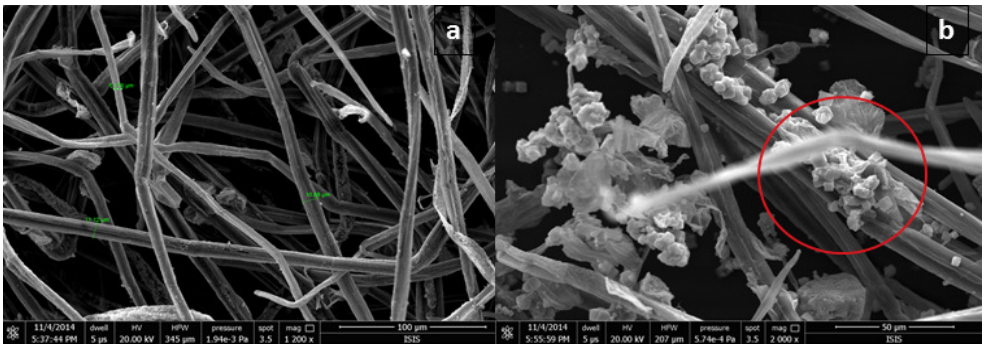

Figure 5: SEM results for (a) untreated date palm fiber and (b) zeolite reinforced date palm fiber

SEM results

The results of SEM analysis revealed the morphological properties of the modified date palm fiber. Figure 5 demonstrates clearly the presence of zeolite particles. Thus, SEM demonstrates the deposition of the zeolite on the fiber surface. However, the coating was not homogenous.

EDX results

Figure 6 shows the EDX results for the reinforced date palm fiber. The EDX spectra of cellulosic fibers consist predominantly of carbon and oxygen. The treated fiber exhibits the presence of silicon and aluminium atoms.

Table 1 reports the surface atomic composition of the studied fiber, as determined from the EDX measurements. However, the atomic composition

determined from the EDX measurements shows that the levels of silicon and aluminium are particularly low.

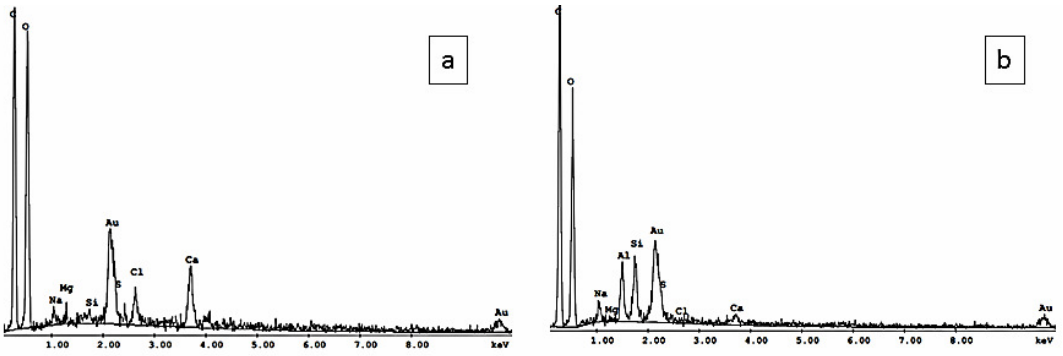

Figure 6: EDX results for (a) untreated date palm fiber and (b) zeolite reinforced date palm fiber

Table 1
Chemical composition of untreated and modified date palm fiber

Element	Untreated fiber: Wt%-At%	Modified fiber: Wt%-At%
C	39.97-58.66	44.97-64.94
O	32.74-36.07	26.44-28.67
Na	0.71-0.55	1.05-0.80
Mg	0.34-0.24	0.13-0.10
Al	0-0	2.17-1.39
Si	0.35-0.22	2.49-1.54
S	0.26-0.14	0.48-0.26
Cl	1.53-0.76	0.24-0.12
Ca	3.46-1.52	0.74-0.32

Wt%: weight percentage, At%: atomic percentage

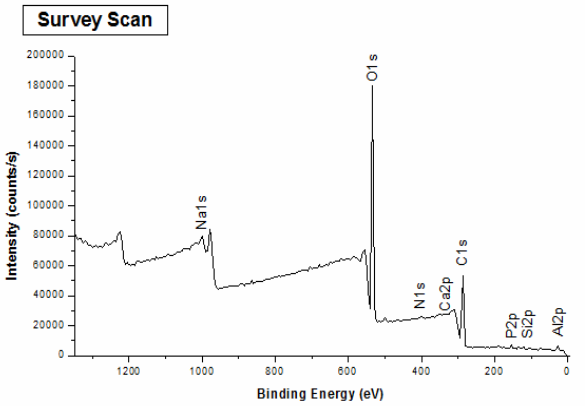

Figure 7: Survey scan XPS data of zeolite reinforced date palm fiber

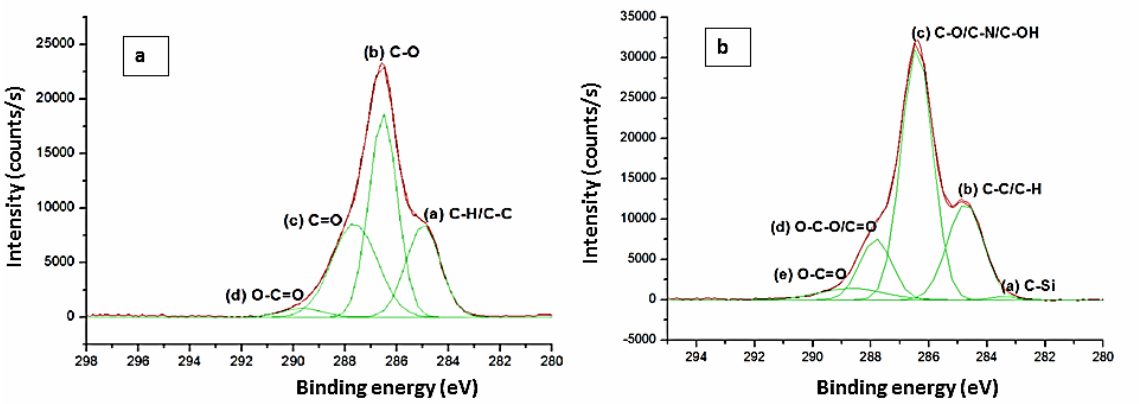

Figure 8: XPS results for (a) untreated date palm fiber and (b) zeolite reinforced date palm fiber

XPS results

XPS proved to be a very powerful technique when used to ascertain the efficiency of the deposition of zeolites, allowing the detection of various changes occurring on the modified fiber surfaces.

Figure 7 illustrates the presence of mainly two peaks situated at 285 eV and 531 eV, and attributed to carbon and oxygen atoms, respectively, in the spectra of the untreated and modified fibers. A small characteristic peak of N1s is present in the spectrum of the modified fibers. However, we observe that the modified fiber contains, in addition to carbon, oxygen and nitrogen, two additional signals, namely: at 102 and 150 eV, corresponding to Si2s and Si2p silicon atoms, respectively. The chemical composition of the untreated and treated date palm fiber surface was also evaluated by XPS. As presented previously in the literature, the XPS spectrum of untreated cellulosic fiber (Fig. 8), with deconvolution in the spectral region of carbon 1s line, contained four individual components with binding energies (Ebound), corresponding to the carbon in groups: C-H/C-C (Ebound = 285 eV), C-OH/C-O (Ebound = 286.6 eV), O-C-O/-C=O/CO-NH_2 (Ebound = 287.8 eV) and O-C=O (Ebound = 289.8 eV).

However, the XPS spectrum of the reinforced date palm fiber, with deconvolution in the spectral region of carbon 1s line, contained five different individual components (Fig. 8): C-Si (Ebound = 283.4 eV), C-H/C-C (Ebound = 284.7 eV), C-O/C-N/C-OH (Ebound = 286.4 eV), O-C-O/-C=O/CO-NH2 (Ebound = 287.8 eV) and O-C=O (Ebound = 288.6 eV). The treated fibers have 56% atomic concentration of carbon with C-O/C-N environment.

CONCLUSION

This work aimed to evaluate zeolite deposition on date palm fiber. A silane coupling agent was used to functionalize the surface of the zeolites to improve the adhesion at the zeolite particle/cellulose interface. The modification of the zeolite through the silylation technique induced microstructural modification and formed covalent bonds. This chemical structure promoted adhesion for the zeolite/cellulose composite.

The zeolite reinforced date palm fiber was characterized using XRD, SEM, EDX and XPS techniques. These analyses proved that the zeolite was successfully deposited on the date palm fiber.

It was determined by the XRD method that the zeolite was deposited on the fiber in a ratio equal to 0.82. SEM demonstrated inhomogenous deposition of the zeolite. EDX measurements showed the presence of silicon and aluminium atoms. XPS results revealed that the treated fibers had 56% atomic concentration of carbon with C-O/C-N environment.

To conclude, successful zeolite deposition was achieved on date palm fiber. Zeolite deposition can endow the fiber with new properties, such as adsorption capacity, ion exchange, anti-bacterial and flame retardant effects, thus making it suitable for a variety of applications.

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