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THE EFFECT OF DEPOSIT ZEOLITES ZSM-5 ONTO DATE PALM FIBERS ON CURING CATIONIC DYES DECOLOURIZATION

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ABSTRACT

This paper describes the removal of cationic dyes using modified palm date fibers. As it is defined as a linocellulosic fiber, the palm date can catch an important amount of dyes by either adsorption or absorption process. These fibers were physically modified by zeolites deposition on their surface. These zeolites are recognized as high porous minerals and are widely used as primordial materials in areas where sorptive, catalytic and rheological applications are required. Zeolites (ZSM-5)/Cellulose composites are synthesized from date palm cellulose fibers and zeolites powders. These natural cellulose fibers are pre-treated with NaOH and modified by deposition of zeolites. Several techniques such as diffuse reflectance, infrared spectroscopy and X-ray diffraction were used to characterize these materials.Then, we check for the first time the ability of the prepared composite palm fibre/zeolites to remove textile dyes from waste water. Furthemore, the adsorption and absorption mechanism of cationic dyes by zeolites ZMS-5 grafted onto palm fibers was discussed.

KEYWORDS

Date palm fiber; Zeolites ZSM-5; Binder; Hydroxide of sodium; Cationic dyes.

1. INTRODUCTION

Cellulose is the most abundant natural polymer that has been used as a renewable raw material in a wide range of applications, such as paper and textile manufacturing. With an increasing of environmental awareness, cellulose fibers such as cotton, flax, hemp, jute and henequen have recently received increased attention in both industrial and scientifical fields.

During the last 50 years, ion exchange membranes have evolved from a laboratory tool to industrial products with significant technical and commercial impact. Today ion exchange membranes are receiving considerable attention and are successfully applied for desalination of sea and brackish water and for treating industrial effluents. Cation exchange membranes contain negatively charged groups, fixed to the membrane backbone and allow the passage of cations but reject anions.

Many researches were developed in attempts to find an innovative waste water treatment technique that can resolve the problem of textile dyes effluent (Allen et al., 2005). Earlier studies have shown that many traditional methods of water treatment are inefficient to purify wastes. The modification of cellulose of palm date presented a solution for improving adsorption and absorption properties of these fibers. In our

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previous experiments, we investigated the physical modification by zeolites deposition on the surface of these fibers (Ben Marzoug et al., 2011).

Indeed, zeolites have been intensively studied in the last half century although attention has been concentrated mainly on synthetic zeolites and it is only in recent years that zeolites have started winning interest in wastewater purification.

Zeolites are microporous crystalline solids with specific structures. Generally, they contain silicon, aluminum and oxygen in their framework and cations, water and/or other molecules fixed within their pores. Zeolites have a porous structure that can accommodate a wide variety of cations such as Na^+,K^+,Ca^{2+},Mg^{2+}….(Erdem et al., 2004). Cation-containing zeolites are extensively used as desiccants due to their high affinity for water, and find application in gas separation, where molecules are differentiated based on their electrostatic interactions with the metal ions. Conversely, hydrophobic silica zeolites preferentially absorb only organic solvents. Zeolites can hence separate molecules based generally on differences of size, shape and polarity (Kokotailo et al., 1978). Due to their perfect porous properties, zeolites are used in a variety of application. The major uses are in petrochemical, ion-exchange for water softening and purification (Chena et al., 1977).

Zeolite/cellulose and cellulose acetate composites have already been proposed for numerous uses. For example, they have been tested for medical applications, filtrations, air purification, filtration membranes for aerated water, adsorbent filter for decaffeinating processes (Metin et al., 2004).

The shape-selective properties of zeolites are also the major reasons for their use in molecular adsorption. The ability to adsorb certain molecules, while excluding others, has offered a wide range of benefits for zeolites (Ozdemir et al., 2004). Sometimes it is simply a matter of the size and shape of pores controlling access into the zeolite. In other cases different types of molecule access to the zeolite, although some diffuse through the channels more quickly, leaving other molecules trapped behind. (Ahcène et al., 2004; Leiva et al., 2005).

The deposition of zeolite on the surface of palm date fibers improve ion exchange (Allen and al 2005) and gives new function to fix and adsorb dyes (Mintova et al,. 1996).

The present study reports the use of composite zeolite/date palm fiber as an alternative low cost absorbent system for the removal of cationic dyes from aqueous solution. By the qualities of zeolite and cellulosic fibers, this composite can provide several advantages. As also proved, fibers with zeolite can facilitate the sorption and the binding of this category of dyes with microporous structure (Ozdemir et al, 2004) and with great capacity of ion exchange.

This work aims to evaluate dye absorbency of modified palm date fiber. To check the deposition of zeolites successfully on the palm date surface, characterization of reinforced zeolite cellulosic fiber is done with effective techniques such as IR and DRX.

2. MATERIAL AND METHODS

2.1. Chemical composition of palm date fiber

The palm date used in this work belongs to the species of Dactylifera. The palm date fibers are mainly composed of 32-35,8% of cellulose, 24,4-28,1% of hemicelluloses, 26,7-28,7% of lignin. The date palm fibers were extracted with the same method used of esparto fibers (Ben Marzoug and al, 2011). The palm date leaf is treated in preheated solution at 90°C during 90min containing 30g/L of sodium hydroxide, 35mL/L of hydrogen peroxide, 3g/L of wetting agent (Subitol LSN BEZEMA) and 25mL/L of stabilizer of hydrogen peroxide (contavan GAL).

2.2. Pre-treatment of the cellulose of fibers with NaOH

The date palm fibers were suspended in this NaOH solution. The resulting suspension was stirred until it reached finally a macroscopically homogenous appearance. This NaOH-cellulose mixture was then removed from the reactor and washed with distilled water. All these successively washing cycles were necessary used to remove physically adsorbed NaOH from the date palm fibers. Then this mixture was placed in an oven with forced air circulation at 375K until a total evaporation of water. These fibers were rinced until they reached

the neutrality (pH=7). Finally, these fibers were again placed in an oven at 375K until they obtained a fixed mass surface and/or irreversible adsorption on the fiber palm date (Vu et al., 2003).

2.3. Zeolite deposition

The appropriate amount of fibers was placed in a round bottomed flask and stirred in a water solution containing an appropriate amount of liar agent. The reaction was already allowed to proceed in a preheated water bath at the desired temperature for 15 minutes. Then, the forming suspension was stirred until it reached a macroscopically homogenous appearance. Then, the appropriate amount of zeolite was added with stirring all the mixture for 30 minutes. When the grafting time was over, the grafted fiber was filtered and washed with distilled water. The grafted samples were then filtered and allowed to dry in an air oven at 60°C until constant weight (Ben Marzoug and al, 2011).

The binding percent was determined by the percent increase in weight as follows:

$$\mathrm{Tf}(\%) = \frac{\mathrm{Wi}-\mathrm{Wf}}{\mathrm{Wi}}\mathrm{x}100 \qquad (1)$$

Where Wi and Wf represent the weights of the initial and the grafted fibers respectively.

2.4. Dyeing procedure

Maxilon Yellow M3RL is a cationic dye whose λmax is about 582 nm. The fiber is grafted then was immersed separately in a dye bath composed of an amount of Maxilon Yellow M3RL dye. The dye liquor ratio (RdB =$\frac{1}{40}$) was always kept constant for all samples and the pH of the dye bath was adjusted by adding drops of 2% acetic acid at 80% to maintain pH of the dye bath between 4.5 to 5. An amount 1.5% of sodium acetate and 10% of sodium sulfate was added in the solution (sabaa 2002). The temperature of the dye bath was kept at 20°C over 90min then gradually raised to 90°C and was kept at this temperature for an additional 240 min .The temperature of the dye bath was then allowed to cool, the dyed fabric was squeezed, rinsed thoroughly with water and dried in air. The amount of the dye absorbed was measured by conventional colorimetric methods to measure the concentration of the dye remaining in the dye bath.

2.5. Infrared spectroscopy

In this study, a perkin Elmer 398 IR-Transmission Spectrometer ranging from 400 to 4000 cm^{-1} was used. The FTIR spectra were obtained with a perk in Elmer Paragon 1000 FT-IR Spectrometer working in diffuse reflectance mode (DRFIFT) with a total of 40 scans and with a resolution of $4cm^{-1}$. We mixed an amount of 5mg of fibers with 200 mg of analytical of grade KBr and the resulting ground and pressed in order to obtain pellets. All DRIFT, spectra were plotted according to the Kubelka-Munk Function. Table 1 reports the band assignments according to the cellulose.

Table 1: Band assignments according to the cellulose (Bessadok et al., 2008).

Band position (cm^{-1})	Functional groups
3200-3700	Stretching hydroxyl group (O-H alcohol)
2900-2970	Stretching CH
2853-2870	Stretching Elongation de CH_2
1635-1623	H_2O absorbée
455-1336-1205	OH (bending in the plan)
1420-1430	CH_2 symetric bending
1374-1282	CH (bending)
895	δ_{asy} CH pyranosic cycle
1317	CH_2(oscillation)
1114	υ C-O (des C-O-H), stretching of cycles
1060	υ C-O (cycle glucopyranose stretching)
1162	Pont C-O-C (antisymetric stretching)
1125, 1015, 1035,1058	Stretching of pyranosic cycle

2.6. X-Ray diffraction

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

3. RESULTS AND DISCUSSIONS

3.1 Effect of zeolite concentration on the relative binding rate

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

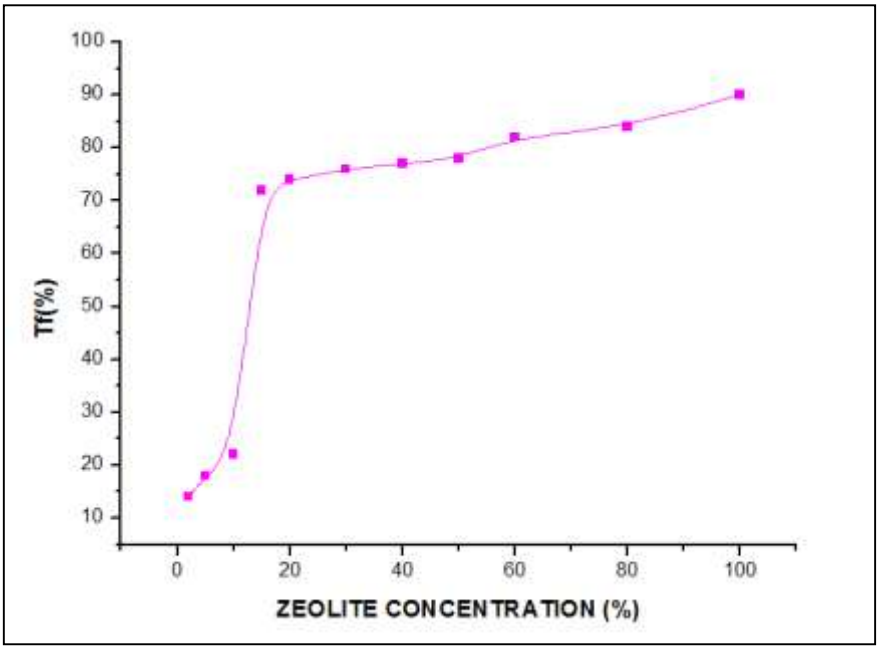

Figure1. Effect of zeolite concentration on the relative binding rate at T=20 °C,[binder] = 10ml/L.

The graft degree increases fast within the zeolites concentration of 20% and shows an attractive maximum at about 100% of zeolites.

3.2 Effect of temperature on the relative binding rate

The effect of temperature on binding degree is given in Figure 2. As it is observed, the graft degree initially increases and then passes through the maximum. This phenomenon can be attributed to the increased number of free radicals generated and to the increased mobility of the free radicals at higher temperatures. Indeed, a higher temperature increases, the spacing between the chains of the amorphous region is favored, which means that the free volume in the structure of the fiber increases.

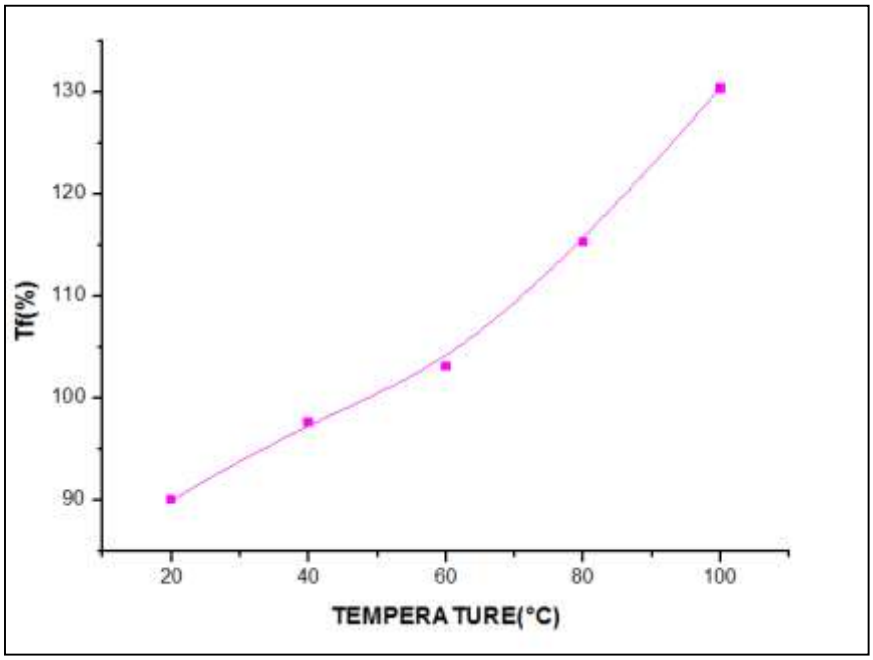

Figure2. Effect of temperature on the relative binding rate: [zeolite] =100%, [binder] = 10mL/L.

It is found that when the temperature increases, the binding yield increases progressively until it reaches its maximum at T = 100°C which corresponds to a maximum rate.

The temperature facilitates access to the support of the zeolite. Thus, as the temperature increases, the activation energy of the crystalline regions are improved because of the fiber structure swelling becomes more accessible to reactive species.

3.3 Effect of binder concentration on the relative binding rate

Figure 3 illustrates the effect of binding agent concentration on the binding degree. It can be observed from this figure that the relative binding degree increases with the rise of binder concentration.

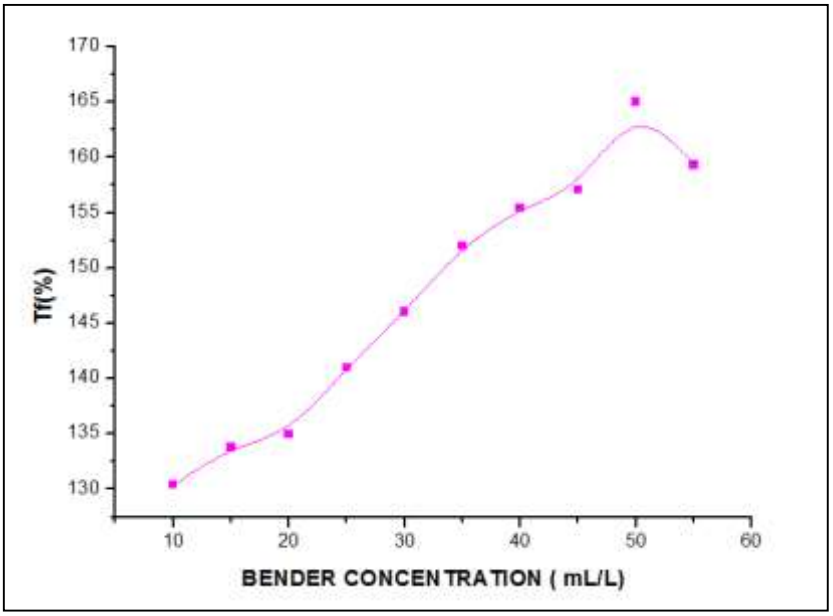

Figure 3. Effect of binder concentration on the relative binding rate: [zeolite] =100%, T=100°C.

There is not a real attraction between the date palm fiber and the zeolite. In fact, these zeolites are charged with negative charges and so is the cellulose in water. Thus, to occur an attractive link between zeolite and

palm date fiber, the binder is useful in this case because it's able to adhere cellulose and zeolites with an electrostatic bond.

It is noted that when binder concentration rises, the binding degree increases progressively to achieve its maximum for a concentration of 50 mL / L corresponding to a maximum rate. Beyond this binder concentration there is a decrease in the rate of binding.

3.4 Alkali treatment

Alkali treatment leads to the increase in the amount of amorphous cellulose at the expense of crystalline cellulose. The important modification occurring here is the removal of hydrogen bonding in the network structure. This activation step using sodium hydroxide can convert cellulose into alkali cellulose according to the following reaction:

$$\text{cell} - \text{OH} + \text{NaOH} \rightleftharpoons \text{cell} - \text{O}^{-}\text{Na}^{+} + \text{H}_2\text{O} \quad (1)$$

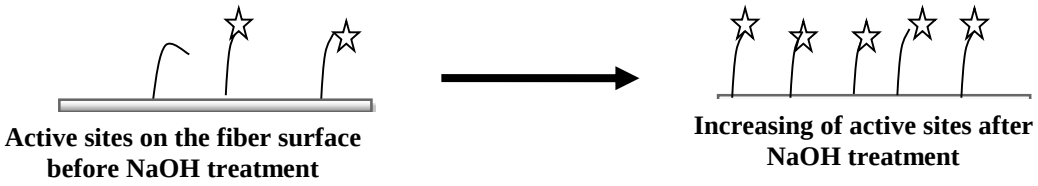

Figure 4. Activation fiber using an alkali treatment.

The alkali treatment (figure 5) provides the palm date fiber more negative charges on the surface so it is required to the use of additional amount of binder to consume all these charges created. After alkali treatment, the optimum conditions respectively zeolite concentration, binder concentration and temperature are 100%, 90mL/L and 100°C.

3.5 X-Ray Analyses

The XRD method was used to characterize palm date fiber reinforced zeolite. The aim of this study was to observe the amount of zeolite deposed on fiber and to identify the different peaks provided.
The variation in the degree of crystallinity of the treated cellulose fabric was studied by measuring the X-ray diffraction of the reinforced cellulose samples (figure 6).

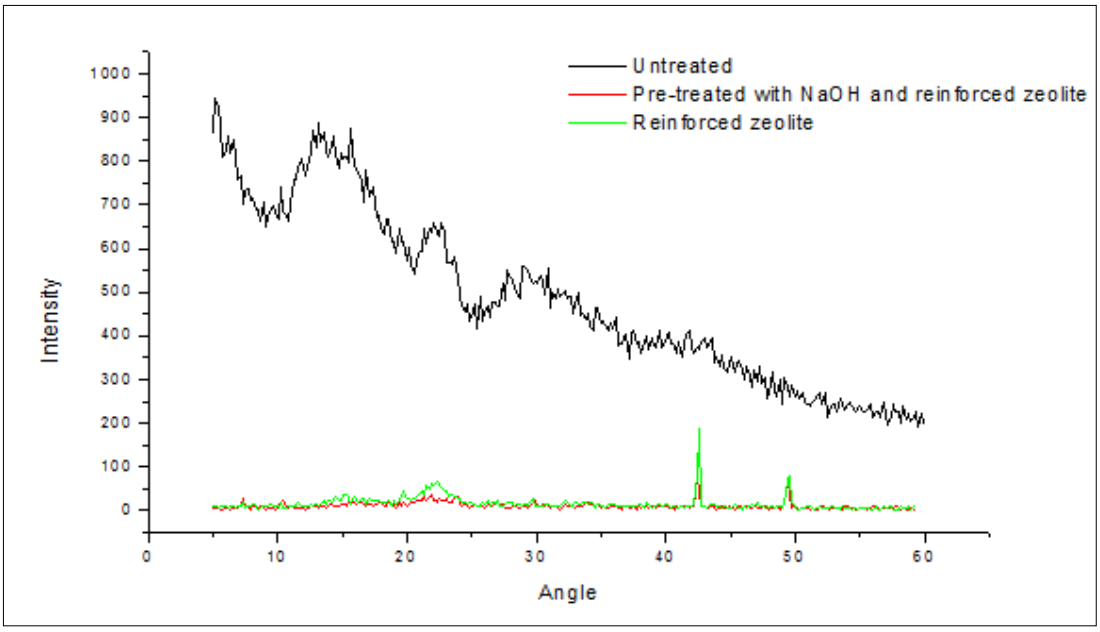

Figure 5. XRD diffractogram of modified date palm ultimate fibers

The peak ratio of the zeolite reflection mentioned above (2Θ= 6,19°) and that of cellulose (2Θ= 16,45°) was always used as a relative measure of the zeolite content on materials (Vu and al 2002)
It can be observed that the X-ray spectra for the inactivated palm date cellulose with alkali solution and treated shows an amorphous plateau at 11-19° (2Θ), indicating the presence of more amorphous material than that present in the treated cellulose. Deposition of zeolites increases band is at 23° (2Θ) which means it doesn't exist a change in structure of the fiber and a microstructural modification. This implies a change in the physical structure a modification in the morphology of the fiber surface as a result of zeolite deposition. The results clearly show a remarkable increase in the degree of crystallinity with the increase in the percentage of grafting (2Θ= 7°,10°,13°,16° and 25°). Moreover, the X-ray diffraction shows appearance of peaks in the position at 2Θ= 10°,26°,28°,30° for fiber alkali treated may reflect a change in the surface which drops the crystallinity of the fiber . The lowering in the degree of crystallinity is attributed to an increase in the intermolecular distance between the cellulosic chains during pretreatment, which consequently lowers the degree of H-bonding between chains and thus increases the amorphous regions due to the pretreatment.

3.6 FTIR Results

The IR spectrum of palm date fibers modified with different method of surface activation is illustrated in figure 6. Samples of the fibers are treated with zeolites ZSM-5 and NaOH are studied by infrared spectroscopy.

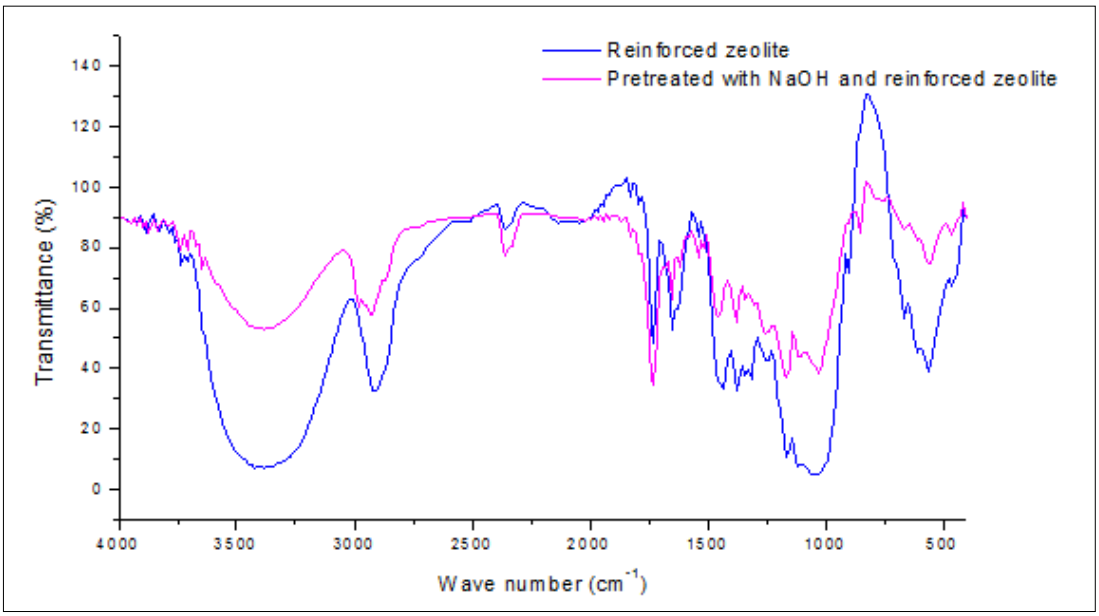

Figure 6. Infrared spectrum

The spectra in the 4000–400 cm-1 range, for grafted palm date are shown in Figure 6. These spectrogrammes show the presence of these relatives bands at 612, 1070, 1431,1320,1637,2915 and 3400 cm^{-1}. The results give a confirmation of the grafting process.

The treatment with sodium hydroxide eliminates lignin, pectin and hemicellulosic compounds, so they decrease polar character given by functional groups such as alcohols, aldehydes, carboxylic acids, ketone and phenolic hydroxides. These treatments can give homogenous surface and rise hydroxyl groups relative to cellulose (Mintova et al., 1996).

The spectrogram demonstrate the same peaks but with different intensities. As shown in fig.7, the intensity increases after each treatment. Treatment with NaOH then zeolite increases the vibration of hydroxyl groups indicated at 3400 cm^{-1}. The Existence of more hydroxyl groups can provide repulsion of ionic substances (Ben Marzoug et al., 2011).

3.7 Sorption studies

The sorption capacities of 500mg reinforced zeolite palm date fibers were determined by contacting 200 ml Jaune Maxilon M 3RL solution containing an amount of color (50mg to 500mg). The reactionnal middle contains 2% acetic acid to regulate pH between 4.5 to 5 and 1.5 sodium acetate. The choice of pH condition is related to the degradation of cellolosic fiber and the optimum condition for dye of these fibers with cationic dyes (Ben Marzoug et al). The temperature is related to maximum affinity of the Jaune Maxilon M 3RL dye.
The solution of dye and the fibers are agitated and the test is reproduced by varing temperature, duration, pH and quantities of salt. Date palm fiber and reinforced zeolite date palm fibers were separated from the solution by filtration. Residual concentration of Jaune Maxilon M 3RL in the dye solutions was determined spectrophotometerically using Schimatzu UV 2401 PC UV/VIS spectrophotometer.
Decolourisation efficiency was determined spectrophotometrically by monitoring the decrease in absorbance at 582 nm, and calculated according to the following formula:
percentage of decolorisation (%) :

$$\mathrm{E}(\%) = \frac{\mathrm{Ai}-\mathrm{Af}}{\mathrm{Ai}} * 100 \qquad (2)$$

3.7.1. Effect of color concentration on dye sorption

In this case, effect of color concentration was evaluated on untreated date palm fiber and palm date fiber reinforced zeolite. Samples were treated at 80 ° C during 90 minutes. To do this test, an amount of cationic dye is put in 200 ml of distilled water.
Fig. 7 presents the variation of absorption quantities by varying color concentration. The absorption of dyes quantities increases with rising of dyes quantities in the solution. This test shows that untreated fiber sorbs more than treated fiber.

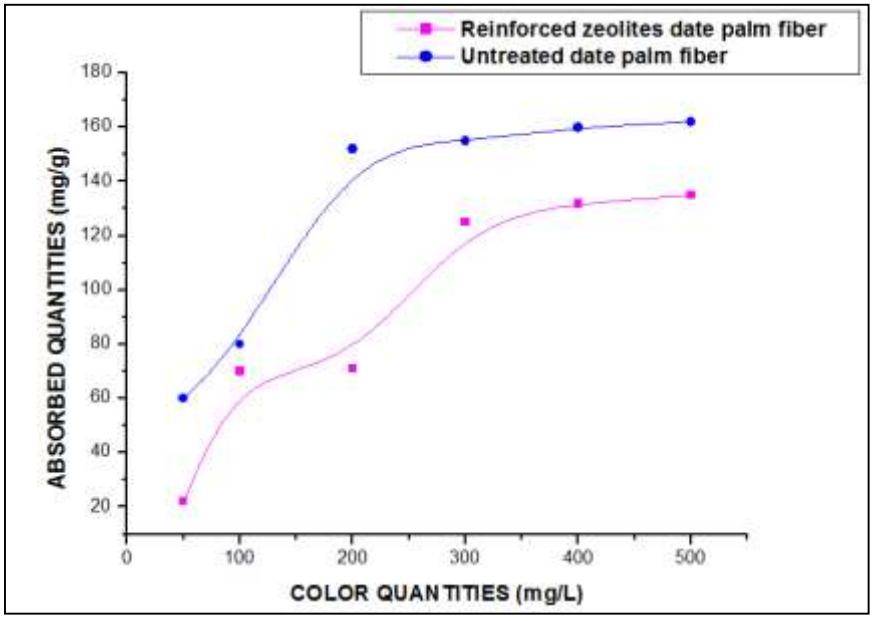

Figure 7. Effect of color concentration on dye sorption.

3.7.2. Effect of temperature on dye sorption

The effect of temperature on the sorption of Jaune Maxilon M 3RL by untreated date palm fiber and date palm fiber reinforced zeolites at equilibrium was investigated at temperature ranged between 40–80 ºC and an initial concentration of 500 mg/L.

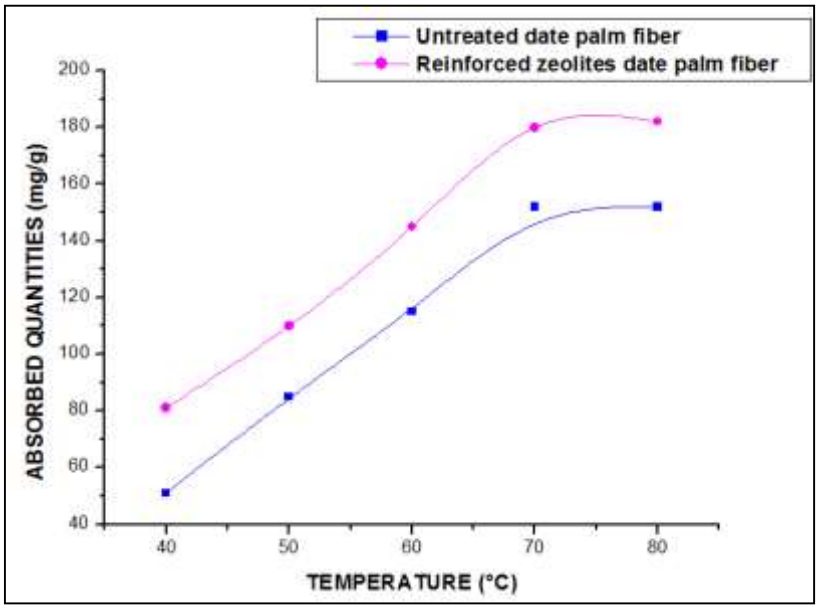

Figure 8. Effect of temperature on dye sorption.

Figure 8 demonstrates the variation of absorption quantities by increasing temperature.
The sorption of Jaune Maxilon M 3RL by both untreated dated palm fiber and date palm fiber reinforced zeolites was noted to increase with the increase in temperature up to 80 ºC (Figure 8). These results suggest that sorption of Jaune Maxilon M 3RL dye may not be only physical but also chemical sorption. The temperature can increase reactivity and the affinity of dyes toward the cellulosic materials. As known, 80 ° C is little greater than glass temperature of cellulosic fiber. At this temperature chains can really move and facilitate dyes diffusion and migration.

3.7.3. Effect of contact duration

In order to determine the effect of contact time on the dye sorption capacity of untreated date palm fiber and date palm fiber reinforced zeolites, both absorbents were exposed to aqueous Jaune Maxilon M 3RL dye solution (500 mg/L) for different times at the optimum temperature (80 ºC).

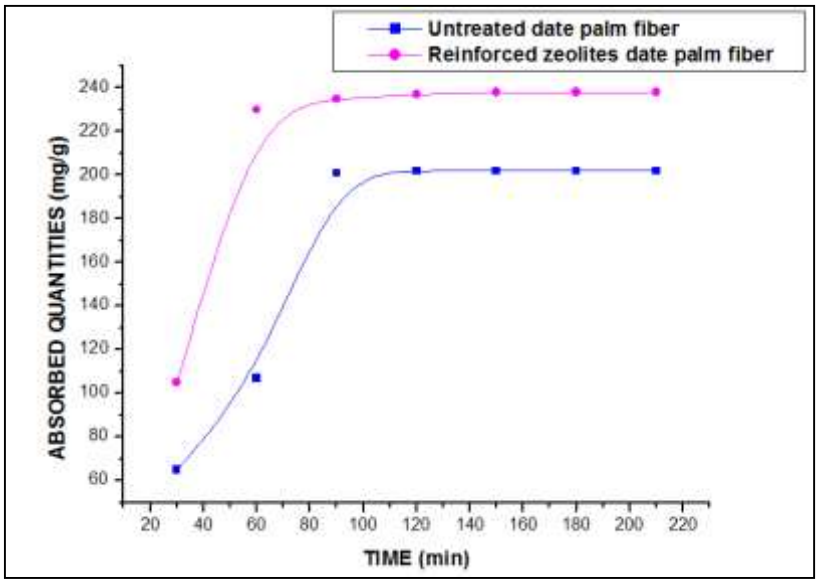

Figure 9. Effect of contact duration on the dye sorption.

Figure 9 presents the variation of absorption quantities by varying contact duration. Results presented in this figure show that the rate of dye uptake by date palm fiber was rapid, with maximum uptake occurring in the

first 90 min amounting to over 60 % and 52 % sorption for date palm fiber reinforced zeolite and untreated fiber respectively. The sorption rate after this initial fast phase, however, slowed or/and achieved a landing after having indicated the equilibrium of the system. The optimum duration relative to maximum sorption is 90 minutes.

4. Conclusion

To sum up, a reinforced zeolite date palm fiber is described and characterized using IR and DRX techniques. These analyses proved that zeolite is, successfully, deposed on the date palm fiber. This phenomenon can change the surface charge of the fiber and provide other properties. Indeed, zeolite with microporous structure and with great capacity as ion exchange can give other properties to cellulosic product. The applicability of the prepared composite was checked for cationic dye absorbency. The variation of experimental condition including temperature, color concentration and contact duration was studied. Results revealed that sorption of Jaune Maxilon M 3RL dye may not be only physical but also chemical process. The optimum duration relative to maximum sorption capacity of color was achieved after 90 minutes.

Refereeing to our finding data in terms of dye adsorption capacities, we prove that the present described technique can replace many other traditional waste water treatment processes such as coagulation, ozonation, oxidation, precipitation.

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