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Cellulose from *Tamarix aphylla*'s stem via acetocell for cadmium adsorption



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KEYWORDS

Tamarix aphylla; Acetocell; Cellulose; Adsorption; Cadmium **Abstract** This study emphasized the efficiency of unconventional delignification treatment "Acetocell" as a basic pretreatment to isolate cellulose fiber from *Tamarix aphylla*'s stem. Chemical proprieties of obtained cellulose were determined and its efficiency for cadmium ions adsorption was evaluated subsequently. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction analysis, thermogravimetric analysis (TGA), Scanning Electron Microscopy (SEM), fluorescence microscope and Morfi were used to analyze the thermochemical and morphological characteristics of the fibers before and after treatment. Cellulose was used as a biosorbent to remove cadmium ions from polluted water. The effects of many parameters on the efficiency removal of cadmium were investigated; the amount of cellulose, the contact time, pH and the initial concentration of cadmium ions. The optimum conditions were 45 mg of adsorbent, 45 mg L⁻¹, 1200 min and pH 8 which provide best adsorption capacity equal to 44.21 mg g⁻¹. The energy value E = 6.65 kJ mol⁻¹ which confirm the physical interaction between cellulose-cadmium ions.

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Then Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models were followed for modeling adsorption. Langmuir isotherm and the pseudo-second order model seems the most suitable which describe better the adsorption of cadmium ions with best R^2 values which equal to 0.9937 and 0.9979, respectively.

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1. Introduction

Noteworthy water pollution threatens flora and fauna these days, industries devastatingly release products that are harmful to the environment, threatening rivers and water tables. It is therefore imperative to resolve the industrial effluent's problem and its ensuing pollution. Dyes, poisonous organic materials and especially heavy metals discarded currently by the industry's discharge. The release manner of these heavy metals in polluted water is major problem for the industry and it accounts for a sort of real threat to the environment. Countless metals such as copper, cadmium, lead, chromium, zinc are noxious metals in addition to its non-biodegradability, thus it is necessary to adjust the water treatment processes. Therefore, its removal from the contaminated water is an obligation for both environment and human health safety (Nordberg et al., 2015; Wang et al., 2019). In this regard, significant research efforts have been made to optimize the cadmium ions retention processes, with a view to maximize energy and environmental recovery. With this in mind, during the last decades, many sorbents were used for this purpose. Indeed there are a huge number of studies on the potential of biosorbents for removal of cadmium ions from aqueous solution, such as; Pin sawdust biomass and some vegetable plants as Peganum harmala seeds (Khosravi et al., 2014; Liu et al., 2019), activated carbon from plants (Bohli et al., 2015; Khosravi et al., 2018) and biopolymer as chitosan (Vilela et al., 2019) and also cellulosic materials (Hokkanen et al., 2016). However many researchers have focused on the adsorption technique by adapting the preparation of certain adsorbents from vegetable biomass, to use it as adsorbents as a surrogate in order to replace activated carbon. Indeed, cellulose was used already as biosorbent to get ride out different dye (Putro et al., 2019), and heavy metals removal such as silver (Zhu et al., 2015) and cadmium (Widyayanti et al., 2021; Zheng et al., 2019) which is the main concern of this presented research work. In the beginning, cellulose is replying as well to various industries needs, paper making, composite, textiles, and as well in the medical and pharmaceutical field (Gatenholm and Klemm, 2010; Park et al., 2008) owing to its outstanding characteristics. Cellulose considers as one of the most natural demanded polymers worldwide (Belgacem and Gandini, 2008). It is widely available, accessible and inexhaustible. Its worldwide availability as well attracted the research's attention and encouraged them to use it as basic material for research study and industry application. In fact, cellulose could be extracted from various sources; some agricultural wastes, vegetable biomass, forestry residues (Martin et al., 2007).

For this work, we interested to isolate cellulose fiber from the stem of a woody plant "*Tamarix aphylla*". This plant was never been used as biomaterial for cellulose fiber. So, it is promising plant to work with. Firstly, this plant belongs to the family of *Tamaricaceae*, adapts simultaneously in the desert, sand, and alluvial saline (Orabi et al., 2011). *Tamarix aphylla* has a wide geographic distribution in the entire world (Hayes et al., 2009) and it has been considered as medicinal plant thanks to its interesting biological proprieties (Orabi et al., 2011). The structural and morphological properties of the isolated cellulose were determined. Subsequently, its role as adsorbent for cadmium ions from the contaminated water was achieved. Hence, this is the concern of our research work, the methodology proposed in this paper for the adsorption of Cd^{2+} ions on cellulose extracted from the stem of *Tamarix aphylla*. For the best of our knowledge, currently there is no research that pursues the cadmium ions adsorption using, as a biosorbent, the cellulose isolated from *Tamarix aphylla* stem via acetocell treatment. This process is one of the organosolv delignification methodology which is well-known by its efficiency for plant pulp extraction, as well its low cost comparing by others mechanical or chemical process (Marques et al., 2021). Acetocell is not frequently employed for cellulose extraction, thus its using for this reported scientific paper for cellulose isolation from plant not used previously is a significant novelty. Besides, the important efficiency of this extracted cellulose for cadmium retention comparing by sundry cellulose adsorbent and even some other biosorbent was emphasized by this present study.

2. Experimental section

The stems of *Tamarix aphylla* were used as raw materials. The plant was harvested from a swamp in Gafsa in southwestern Tunisia. After that, it was washed and cut into small pieces, and then ground into powder, washed again, and dried at room temperature in the dark.

Glacial acetic acid (Reagent Plus, $\geq 99\%$), sodium chlorite (Technical grade, 80%), sodium hydroxide (BioXtra, $\geq 98\%$), sulfuric acid (ACS reagent, 95.0–98.0%), hydrochloric acid (ACS reagent, 37%), cadmium chloride (99.99% trace metals basis) were supplied by Sigma-Aldrich. All chemical reagents were used without further purification.

2.1. Tamarix aphylla's composition

According to the method reported by the Technical Association of Pulp and Paper Industry (TAPPI), the chemical composition of *Tamarix aphylla* is determined. The insoluble lignin is determined according to the Klason method (T222 om-06). The percentage of soluble compounds in both hot water and cold water, and 1% sodium hydroxide aqueous solution and ethanol-toluene mixture were determined according to the TAPPI standard methods (T207 cm-08, T212 om-07, T204 cm-07). Then, following to the standard method (T211 om-07), the ash content was determined by calcination of *Tamarix aphylla*'s stem at 525 \pm 25 °C for 4 h.

2.2. Cellulose obtainment

The acetocell process was followed to pretreated *Tamarix aphylla* stem's powder with acetic acid. The biomass powder was transferred with an aqueous acetic acid into a round bottom flask. Different samples were synthesized by varying the concentration of this solution; 20, 40, 80 mg L⁻¹, with the treatment time extent between 2 h and 8 h. Then the mixture was filtered and washed with distilled water (Marques et al., 2021).

The previous pretreated sample has undergone a bleaching process by adding an aqueous sodium chlorite solution 1.7% (w/v), was assisted by a buffer solution (2.7 g NaOH in

50 mL of water with 7.5 mL of acetic acid and the addition of water to a volume of 100 mL). The liquid ratio NaClO₂/buffer acetic solution/ H_2O was 1:1:3 (Nabili et al., 2016).

The last step of the treatment was the differential solubilization, which was achieved according to the standard method TAPPI (T203 cm-99) using 15 mL sodium hydroxide (17.5%) at 25 °C for 40 min with stirring. The cellulose obtained was filtered and washed vigorously with distilled water until a neutral pH was reached.

2.3. Characterization

Fourier transform infrared spectra were recorded using a Perkin-Elmer FTIR spectrophotometer between 400 and 4000 cm^{-1} .

The X-ray diffraction analysis was performed on DS and CDS powder. The samples were placed in a 2.5 mm deep cell and the measurements were performed with a PANalytical, X'Pert PRO MPD diffractometer (PANalytical, Massachusetts) equipped with an X'celerator detector.

The elemental distribution was evaluated through SEM assisted by energy dispersive EDX in a Joel JSM 400 equipment with a silicon drift detector. Scanning electron microscopy (SEM) (model Philips 30) was used to observe the surface morphology of the treated fibers in each stage of treatment.

Florescence optic microscope where performed using the Axio. ImagerM1m, the pictures were obtained by a high resolution camera 3-CCD (1360x1024 pixels) JVC KY-F75U and it were extracted through Axion Vision Relase 4.8 software.

The analyzer MORFI LB-01 (Techpap, France) was used to determine the suspended fibers (weighted length, width and of fine elements).

The thermal stability of the samples was determined by a thermo-gravimetric analyzer STA 6000 (Perkin Elmer Instruments, Buckinghamshire), which measures the weight loss of the samples during the temperature's increase.

The cellulose's degree polymerization was determined from the intrinsic viscosities [η] of cellulose solutions in cupriethylenediamine/water at 25 °C.

The Brunauer–Emmett–Teller surface area (SBET) and pore structure parameters of the cellulose were obtained from nitrogen adsorption desorption measurements at 77 K using a Micromeritics ASAP 2020 instrument.

2.4. Batch adsorption experiments

Initial cadmium aqueous solution was prepared 100 mg of cadmium chloride per 1L of deionized water. Then various concentrations from 10 to 45 mg L^{-1} were gotten from the initial solution through dilution. Various samples were prepared by varying different parameters.

The removal of cadmium ions from an aqueous solution onto prepared cellulose was carried out by batch method. After the adsorption experiment, the equilibrium adsorption capacity Q_{ads} (mg g⁻¹) was calculated according to equation below

$$Q_{ads} = \frac{(C_0 - C_e) \times V}{m}$$
(1)

where C_0 and C_e (mg L⁻¹) are concentrations of cadmium ions in aqueous solution at the initial and equilibrium time, respectively; V (L) is the volume of the solution; and m (g) the biosorbent weight.

For the absorbent amount evaluation on the adsorption procedure, assays were performed at the same temperature and contact time used in the previous experiments with conserving the (pH = 6) except we varied the adsorbent dose; 10, 15, 20, 25, 30, 35, 40 and 45 mg.

To test the effect of the pH of the solution, the adsorption process was carried out at 25 °C using 10 mg of biosorbent with 10 mL of the aqueous solution contaminated with cadmium (45 mg L⁻¹), the pH was adjusted from 2 to 12 using HCl and NaOH solutions (0.1 mol L⁻¹). The different solution samples were subjected to magnetic stirring for 1200 min. Then, the samples were filtered and cadmium ion concentration was determined by Flame Atomic Adsorption Spectroscopy (FAAS) Fisher Scientific iCE 3000.

In purpose of evaluation of concentration of cadmium, ions Cd^{2+} on aqueous solution effect, various concentrations from 10 to 45 mg L^{-1} with respecting the followed conditions earlier as cellulose amount (10 mg), contact time (1200 min), pH = 8.

In order to describe the kinetic of the cadmium adsorption onto cellulose, time extent from 60 to 1200 min were evaluated in this step while retaining the used previously conditions with cadmium ions concentration of 45 mg L^{-1} .

2.5. Adsorption isotherms and kinetic models

The Freundlich, Langmuir, Dubinin– Radushkevich and Temkin isotherms were followed to evaluate the experimental points for cadmium adsorption (Table 1). The pseudo-firstorder (Eq. (2)) and pseudo-second (Eq. (3)) order model were used for kinetic adsorption estimation (Ho and McKay, 1999; Lagergren, 1898; Saad et al., 2014).

$$ln(Q_{ads} - Q_t) = lnQ_{ads} - k_1t \tag{2}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_{ads}^2} + \frac{t}{Q_{ads}} \tag{3}$$

where, " Q_{ads} " and " Q_t " (mg/g) are the quantities of adsorbate at equilibrium and at the instant "t", respectively. k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the adsorption rate constant respectively for the first and pseudo-second-order adsorption.

3. Results and discussion

3.1. Tamarix aphylla's composition

The chemical composition of *Tamarix aphylla* and other plants from the literature were summarized on Table 2. The percentage of the isolated cellulose from *Tamarix aphylla* (39.0%) was similar to that of Mechi's work (Mechi et al., 2017) and comparable to that of *Nitraria retusa* (41.0%) (Ferhi et al., 2014a), moreover, found to be lower than cellulose content for some annual plants namely *Pituranthos chloranthus* (46.6%) (Ferhi et al., 2014a), *Stipagrostis pungens* (44.0%) (Ferhi et al., 2014b) and *Opuntia ficus-indica* (53.6%) (Mannai et al., 2016). The ash's percentage was around 3.5%, which is lower

Table 1 Mathematical models and their linear forms.							
Isotherm	Non-Linear Form	Linear Form	Plot				
Langmuir (1918)	$Q_{ads} = \frac{C_e Q_{max} K_L}{1 + (K_L C_e)}$	$\frac{1}{Q_{ads}} = \frac{1}{K_L Q_{max}} \frac{1}{C_e} + \frac{1}{Q_{max}}$	$\frac{1}{Q_{ads}} VS \frac{1}{C_e}$				
Freundlich (1906)	$Q_{ads} = K_F C_e^{1/n}$	$\ln\left(Q_{ads}\right) = \ln(K_F) + \frac{1}{n}\ln(C_e)$	$\ln(Q_{ads})vs\ln(C_e)$				
Temkin (Temkin and Pyzhev, 1940)	$Q_{ads} = \frac{RT}{B} \ln(A_T C_e)$	$Q_{ads} = \frac{RT}{B} \ln(A_T) + \frac{RT}{B} \ln(C_e)$	$Q_{ads}vsln(C_e)$				
Dubinin-Radushkevich (1947)	$Q_{ads} = Q_{max} e^{-\beta \varepsilon^2}$	$\ln\left(Q_{ads}\right) = \ln(Q_{max}) - \beta\varepsilon^2$	$\ln{(Q_{ads})vs\epsilon^2}$				

 Q_{ads} -the amount adsorbed (mg/g), K_L -Langmuir constant (L/mg), Q_{max} -the amount adsorbed at equilibrium (mg g⁻¹), C_e -the concentration of the solution at equilibrium (mg L⁻¹), K_F -Freundlich constant (mg^(1-1/n)L^(1/n)g⁻¹), (1/n) -Freundlich coefficient, *B*-Temkin constant relating to heat of adsorption (L g⁻¹), A_T -Temkin constant relating to adsorption potential, *R*-universal gas constant (kJ/kg mol K), *T*-temperature (K), β -constant related to the mean free energy of adsorption (mol²/kJ²), ϵ -Polanyi potential.

 Table 2
 Chemical composition of Tamarix aphylla compared with some plants.

	Ash	Lignin	CW	HW	NaOH (1%)	E.T	Hol	Cell	Hemi
Tamarix aphylla	3.5	30.0	12.8	19.0	18.5	4.5	50.0	39.0	11.0
Tamarix aphylla (Mechi et al., 2017)	10.0	19.8	22.3	25.4	16.8	3.3	58.0	39.0	19.0
Pituranthos chloranthus (Ferhi et al., 2014a)	5.0	17.6	25.0	26.7	49.0	9.5	61.9	46.6	15.3
Nitraria retusa (Ferhi et al., 2014a)	6.1	26.3	23.0	25.5	40.0	3.1	51.8	41.0	10.8
Retama raetam (Ferhi et al., 2014a)	3.5	20.5	32.0	31.5	47.0	10.0	58.7	36.0	22.7
Stipagrostis pungens (Ferhi et al., 2014b)	4.6	12.0	19.3	20.5	42.9	4.8	71.0	44.0	27.0
Opuntia ficus-indica (Mannai et al., 2016)	5.5	4.8	24.0	36.3	29.6	9.8	64.5	53.6	10.9
Astragalus armatus (Moussaoui et al., 2011)	3.0	16.7	26.2	33.0	32.7	13.0	54.0	35.0	19.0

CW (%) -cold water solubility; HW (%) -hot water solubility; E.T (%) -solubility in mixture Ethanol/Toluene; NaOH(1%) -solubility in 1 % aqueous sodium hydroxide; Lignin (%) -Klason lignin. Hol (%) -holocellulose; Hem (%) -Hemicellulose; Cell (%) -cellulose.



Fig. 1 SEM-EDX spectra of Tamarix aphylla's ash.

Table 3	Quantification of the	spatial element distribution	obtained by SEM-EDX	from algorithm ZAF in ash.
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Element	0	Ca	S	Na	K	Mg	Р	Si	Al	Cu
Mass fraction (%)	48.03	17.40	14.70	8.80	4.90	3.50	1.04	0.85	0.69	0.19

than that presented by Mechi's work (10%) (Mechi et al., 2017). However, it was similar to other plants such as *Retama raetam* (Ferhi et al., 2014a) and *Astragalus aramtus* (Moussaoui et al., 2011). In contrast, *Tamarix aphylla* has an important lignin percentage of 30%, which was higher than that of annual plants listed in Table 2 and particularly for that

of *Opuntia ficus-indica*, which not exceeds 4.8% (Mannai et al., 2016). This difference on composition distribution from one biomass to another can be explained by the variance of botanical source of the raw material (Sukumar et al., 1991).

Tamarix aphylla was rich in mineral compounds (Fig. 1, Table 3). The calcium and sulfur were present with a signifi-

cant mass ratio on *Tamarix aphylla*, which were respectively 14% and 17%. The swamp sol was rich with sulfur (Driese et al., 2021), thus it provide an important amount of this last to *Tamarix aphylla*, in which it was grown. Other elements such as sodium, magnesium and potassium were present with modest percentages, moreover traces of aluminum and copper were observed as well.

3.2. Effect of temperature on delignification efficiency

Generally, temperature is a kinetic factor that speed the chemical reaction. Indeed, the diagram of Fig. 2 illustrates the effect of temperature on cellulose bleaching. The rise up of temperature to 100 °C during the bleaching allowed the decomposition of sodium chlorite NaClO₂ into ClO⁻, which reacted subsequently with the aromatic ring of lignin to destroy it. Thus, the split-up of the ether bonds that linked hemicelluloses and lignin was taken place resulting on the elimination of noncellulosic compounds (Hornsby et al., 1997; Yue et al., 2015). At 100 °C, the bleaching lasted eight hours. However, at 75 °C, the reaction requires more than ten hours to get the pure white color of holocellulose and more than 24 h with a lower temperature of 50 °C.

3.3. Characterization and chemical proprieties of cellulose

The color of the raw material is brownish-yellow then changes from brown after acetocell pretreatment to pure white cellulose after bleaching. This color change is due to the removal of non-cellulosic compounds mostly lignin. The pure white color of the final fiber clearly shows the success of the delignification process. The cross-section of *Tamarix aphylla*'s stem (Fig. 3.a) shows a homogeneous morphology on the surface, a tegument shape, it was made from several cellular strads arranged perpendicular to the albumen cells. The longitudinal section (Fig. 3.b) shows clearly that the albumen consists of hexagonal oblong cells juxtaposed of 30 μ m with thick walls and wellbuilt. At the cross-sectional level, short, tight cells have the shape of a bee's beehive (Fig. 3.c); clear pores are observed on the surface of raw material (Fig. 3.d).

During the delignification process, some morphological changes have been observed owing to the exclusion of non cellulosic fibers (Fig. 3.e, f, g). After acetocell pretreatment, the fiber surface becomes detached, which indicates the partial removal of the non-cellulosic materials such as lignin. This elimination cause some morphological changes for cellulose,



Fig. 2 Effect of temperature on bleaching process.



Fig. 3 Scanning electron micrographs of raw material shape: Transversal section (a), tegument (b), albumen (c), longitudinal section (d), pretreated fiber (e), holocellulose (f) and cellulose (g).

such as broken ends that its percentage is around 18.62% (Table 4). According to previous reports (Hornsby et al., 1997; Yue et al., 2015), lignin forms a bridge bond with the cellulose bond so it acts as a binder in the fiber components. Hence, the preserving of the organized form after delignification treatment cannot be possible and the destruction of the combined structure is a predictable consequence. Indeed, the disjointing of the cellulose fibers which appear and became more and more obvious after each step of treatments due to the progressive removal of cemented material (Yue et al., 2015). The formation of cellulose fibers was not newly produced but they were existed but they mainly appeared after

Table 4 Morphological proprieties of cellulose fiber	s.		
Fibers (million/g)	4.112		
Average arithmetic length (µm)	364		
Diameter (µm)	21		
Linear mass (mg/m)	0.64		
Angle of cubits (%)	129		
Portion of angled fibers (%)			
Curvature (%)	3.8		
Macro-fibrilla length rate (%)	0.77		
Percentage of broken ends (%)	18.62		
Fine elements (% in length)	76.6		
Fine element rate (% at the surface)	43.36		

gotten ride off the lignin and extractible and other compounds of *Tamarix aphylla*.

The separation of the cellulose fiber was confirmed by the Florescence optical microscopy observation (Fig. 4) and it was accompanied by a diameter reduction from raw material (32 μ m) to cellulose (21 μ m). This size reduction was mainly attributed to the elimination of lignin and hemicelluloses (Yue et al., 2015), and it causes, as a result, an increase in the fiber aspect ratio (length/diameter), which improve the reinforcing ability of the fibers for composite applications.

The cellulose polymerization degree was estimated at 598 according to Mark-Houwink equation (Kasaai, 2007; Paul and Lodge, 2007). This value was in an average of cellulose degree of polymerization's scale, it was higher than the polymerization degree of cellulose extracted from Posidonia oceanic, which was 153 (Khiari et al., 2010), and it is lower than the fiber extracted from annual plants namely Nitraria retusa, Pituranthos chloranthus, Stipagrostis pungens, Retama raetam, Astragalus aramtus and Opuntia ficus-indica (Ferhi et al., 2014a; 2014b; Mannai et al., 2016), with a polymerization degree higher than 1000. In addition the Specific surface area of the isolated cellulose was around 1 $m^2 g^{-1}$, which almost matching to that of cotton cellulose film $(0.72 \text{ m}^2 \text{ g}^{-1})$ reported by Rowen and Blaine (1947) and to that described one by Emmett and Dewitt (0.60 m² g⁻¹) (Emmett and Dewitt, 1941). Nevertheless, it is much lower than other biosorbent such as activated carbon from date palm petiole which was around 655 m² g⁻¹ (Khadhri et al., 2019).



Fig. 5 FTIR spectrogram of raw material (a), pretreated fiber (b), holocellulose (c) and cellulose (d).

The obtained infrared spectra of raw material, pretreated, bleached sample, and cellulose were illustrated in Fig. 5. The band near 3400 cm⁻¹, observed in all spectra, was attributed to stretching vibrations of a hydroxyl group (O-H). The raw and pretreated sample shows a band around 1720 cm^{-1} relative to the C=O bonds of the carbonyl group which are corresponding simultaneously to the ester groups in hemicellulose and carboxylic acid groups in lignin (Hornsby et al., 1997; Yue et al., 2015). The disappearance of this band in the spectrogram (Fig. 5.d) confirms the full missing of C=O groups in the obtained cellulose so its purity from any trace of other polysaccharides (Alemdar and Sain, 2008). All spectra present a band at 1640 cm^{-1} that corresponds to the absorbed water. The band around 1500 cm^{-1} assigned to the lignin aromatic ring, was present in the raw material spectra and disappeared in both holocellulose and cellulose (Fig. 5) (Sun et al., 2005). The band in 890 cm⁻¹ observed in all spectra refers to stretching vibration of C-O-C assigned to glycosidic bridges of cellulose (Alemdar and Sain, 2008).

The crystallinity index (CrI) of the different samples was determined based on the reflected intensity data following the method reported by Segal et al. (1959).

$$CrI(\%) = (I_{002} - I_{am}/I_{002}) \times 100$$
 (4)



Fig. 4 Florescence optical micrographsof cellulose.



Fig. 6 X-ray diffractogram of raw material (a), pretreated fiber (b), holocellulose (c) and cellulose (d).

where, I_{002} was the maximum intensity of the (002) lattice diffraction peak which was located at a diffraction angle around $2\theta = 22^{\circ}$ and I_{am} was the intensity scattered by the amorphous part of the sample which was measured as the lowest intensity at a diffraction angle around $2\theta = 16^{\circ}$.

The results reveal an increase in the crystallinity index through the chemical treatment of *Tamarix aphylla*'s stem (Fig. 6). The cellulose crystallinity index (52%) was higher compared to the holocellulose, pretreated and untreated fibers, which were respectively 48%, 42% and 32%. After each treatment, the crystallinity index of sample increase due to the remove of amorphous compounds such a hemicelluloses and lignin. These observations are accorded to those of Alemdar and Sain (2008) and Sun et al. (2005) whose work has shown that after chemical treatment the crystallinity index of fiber must be definitely increase.

The TGA curves (Fig. 7) show some common masses' losses and different other ones. The decomposition starts slightly later especially in the case of raw material and pre-treated sample. All TGA curves show a slight common mass loss at 100 °C. It is all obvious an evaporation of moisture;



Fig. 7 TGA curves of raw material (a), pretreated fiber (b), holocellulose (c) and cellulose (d).

corresponding to the fiber dehydration by releasing the absorbed water. At temperature range 250–310 °C, a significant mass loss corresponding to the hemicelluloses decomposition. The decomposition of hemicelluloses has decreased after each step of treatment from the raw material 30% until the cellulose 10%. The hemicellulose was progressively eliminated after treatments. Due to its quasi-crystalline and cohesive structure, cellulose requires a high temperature for the breakdown of glycosidic bonds and hydrogen bonds. Therefore, its decomposition was observed at a temperature; from 330 to 400 °C. The cellulose curve shows a quasi total mass loss at this range of temperature (Alemdar and Sain, 2008; Hornsby et al., 1997; Sun et al., 2005; Yue et al., 2015).

The lignin's aromatic rings started decomposing at 200 °C and continued to 600 °C since it has required an elevated temperature to break the strong aromatic ring bonds. The TGA curves of the untreated (Fig. 7.a) and treated (Fig. 7.b) samples show mass losses of 30% and 20%, respectively, at 200 °C. Contrary, there is no mass degradation at that specific temperature of lignin decomposition (600 °C) in both holocellulose and cellulose curves (Fig. 7.c and Fig. 7.d). This confirms the absence of lignin so to the effectiveness of the delignification process "acetocell" and the followed step of treatment to cellulose fiber isolation.

3.4. Adsorption outcomes

Within increasing the pH, tending from acidic to alkaline one, the capacity of Cd²⁺ adsorption onto cellulose is increasing. The influence of pH on cadmium adsorption capacity was significantly presented 3 levels in the Fig. 8.a. From 2 to 4 pH, the adsorption capacity recorded its lowest values which were respectively 24.50 and 28.01 mg g⁻¹. Up to 6 pH, the Cd^{2+} adsorption capacity was more promising with 42.21 mg g^{-1} and it remain increasing to reached the peak with 44.21 mg g^{-1} at 8 pH. Nevertheless, the adsorption capacity was decreased to 35 mg g^{-1} at pH 12. The cadmium uptake decreased at 10-12 pH range but it is still higher than at acid solution (Ozel, 2012). In fact, the pH_{PZC} of cellulose was 4.8, at pH below than pH_{PZC}, the surface of cellulose was positively charged. Thus, the Cd²⁺ uptake was inhibited due to the possibility of the competition between H⁺ ions and cadmium on the surface of the cellulose at low pH values. This is explanation was admitted by earlier works of Ozel (2012) and Zamani et al. (2013). However, at pH above pH_{PZC}, the cellulose surface is negatively charged. Consequently, the Cd²⁺ was well adsorbed by the O⁻ ions of cellulose at pH $> pH_{PZC}$. Indeed, the adsorption was very privileged at pH 6-8, this is justified by the natural of the electrostatic interaction link between Cd²⁺ and cellulose O⁻ which enhanced the adsorption process. The obtained result was accorded to earlier work on the efficiency of adsorption process of heavy metal at alkaline medium especially around this range of pH (Ozel, 2012; Udoetok et al., 2016; Zamani et al., 2013).

Once we increase the cellulose amount from 10 mg to 45 mg, the elimination rate of Cd^{2+} increasing toward reach the highest value (0.983) (Fig. 8.b). This last almost equal to 1 which present the total of cadmium's elimination rate. Axiomatic, more cellulose quantities along the adsorption process provide extra liber O⁻ ions of cellulose which improve the creation of chemical interactions with the Cd^{2+} ions, which lead



Fig. 8 Effect of pH (a), cellulose amount (b), time (c) and cadmium concentration (d) on adsorption of cadmium ions onto cellulose.

then for their removal subsequently the cadmium uptake increasing (Gueye et al., 2014; Khosravi et al., 2014; 2018; Wang et al., 2010). These results are coherent with those obtained by Khosravi et al. (2014) and Gueye et al. (2014).

Since we have worked at room temperature (25 °C), the cadmium uptake was increasing progressively with more adsorption process time extent (Fig. 8.c). We needed the largest period of time; 1200 min to reach the maximum of cad-

mium's elimination rate (0.978). Therefore, we fix this temperature for the rest of the experiment steps.

Moreover, the cadmium ions concentration influence on its uptake on cellulose. The adsorption capacity increases proportionally with cadmium concentration (Fig. 8.d). Best cadmium uptake recorded with the highest concentration value 45 mg L^{-1} . More cadmium ions released on the treated solution enhance the chemical links creation with the cellulose ions which improve subsequently the removal of cadmium (Wang et al., 2010). This finding is in line with the results of the study of Khosravi et al. (2014).

Adsorption capacities of sundry adsorbents, cellulosic and non cellulosic ones were illustrated in the Table 5. Comparing with others adsorbent, the cellulose from Tamarix aphylla reported in the present study displayed a significant cadmium adsorption capacity 44.21 mg g⁻¹ at pH 8 which was higher value than those obtained using mesoporous silica and cellulose/chitin beads (20 wt% chitin) which were only 3.62 mg g^{-1} (Lalchhingpuii et al., 2017) and 35.9 mg g^{-1} (Zhou et al., 2021), respectively. Nevertheless, Zeolite-supported nanoscale zerovalent iron (Z-NZVI) (Li et al., 2018), Zeolite-supported microscale zerovalent iron (Z-mZVI) (Kong et al., 2017), HMO-P(HMAm/HEA) hydrogel (Zhu and Li, 2015) and orange peel (Tran et al., 2016) were revealed Q_{max} values of 62.02 mg g^{-1} , 63.14 mg g^{-1} , 93.86 mg g^{-1} , and 59.5 mg g^{-1} , respectively, which were higher than that of cellulose from Tamarix aphylla. However, comparing with raw α-cellulose, the surface-modified cellulose and Sulfur-chelating cellulose, the cellulose presented in this work have a Q_{max} much higher than that correspond to α -cellulose which was around 7.47 mg g^{-1} (Widyayanti et al., 2021) but it was slightly lower than that of Sulfur-chelating cellulose (54.71 mg g^{-1}) (Zheng et al., 2019). The cellulose obtained from Tamarix aphylla was privileged for cadmium adsorption than modified celluloses from pineapple (Cell -EDTA and Cell-CM) (Daochalermwong et al., 2020), which provide only a value of Q_{max} of 33.2 mg g⁻¹ and 23 mg g⁻¹, respectively.

To sum up all the outcomes stated above, we can conclude that unmodified cellulose from *Tamarix aphylla*, exhibited a significant capacity for cadmium adsorption and better than

Table 5Comparison of cadmium adsorption capacities ontodifferent adsorbents.

	pН	$\begin{array}{c} Q_{max} \ (\mathrm{mg} \ \mathrm{g}^{-1}) \end{array}$
Mesoporous Silica (Lalchhingpuii et al., 2017)	6	3.62
Zeolite-supported microscale zerovalent iron (Z-mZVI) (Kong et al., 2017)	6	63.14
Zeolite-supported nanoscale zerovalentiron (Z- NZVI) (Li et al., 2018)	6	62.02
Orange peel (Tran et al., 2016)	7	59.5
HMO-P(HMAm/HEA) hydrogel (Zhu and Li, 2015)	5.5	93.86
Sulfur –chelating Cellulose (Zheng et al., 2019)	5	54.71
cellulose/chitin beads -20 wt% chitin (Zhou et al., 2021)	5	35.9
Cellulose (Widyayanti et al., 2021)	6	7.47
Modified Celluloses Prepared from Pineapple (Daochalermwong et al., 2020)	7	23-33.2
Cellulose from Tamarix aphylla (This study)	8	44.21

Table 6 Kinetic constant for batch adsorption of cadmium ions onto cellulose.								
	Pseudo-first-order			Pseudo-second-ord	er			
$Q_{ads} \ (\mathrm{mg \ g}^{-1})$	$Q_{cal} (\mathrm{mg \ g}^{-1})$	$k_I (\mathrm{min}^{-1})$	R^2	$Q_{cal} \ (\mathrm{mg \ g}^{-1})$	$k_2 (g mg^{-1} min^{-1})$	R^2		
44.03	29.77	0.0035	0.9758	45.87	0.0003	0.9979		

Table 7	Isotherm	model	constants	for	batch	adsorption	of
cadmium	ions onto	cellulos	se.				

Langmuir	$Q_{max} (\text{mg g}^{-1})$	47.393
	$K_L (\mathrm{L} \mathrm{mg}^{-1})$	26.375
	R_L	0.0008-0.0037
	R^2	0.9937
	χ^2	0.7720
Freundlich	K_F	54.773
	$1/n_F$	0.2951
	R^2	0.822
	χ^2	7.9735
Temkin	$A_T (\mathrm{L} \mathrm{g}^{-1})$	607.3839
	$B (\text{J mol}^{-1})$	7.3724
	R^2	0.9319
	χ^2	2.8859
Dubinin- Radushkevich	β	0.0113
	$Q_{max} (\text{mg g}^{-1})$	48.74
	R^2	0.9674
	χ^2	1.7546



Fig. 9 Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms fitted to experimental sorption of Cd^{2+} onto cellulose.

other celluloses, this is mainly the originality approach of our work.

3.5. Kinetic study and adsorption isotherms

Origin 6.0 software was used to estimate kinetics and equilibrium parameters using nonlinear regression 6.0 software. The kinetic study was performed through pseudo-first-order and pseudo-second order model, which were calculated using the previous described equations. As shown on Table 6, the value of R^2 (0.9979) corresponding to the pseudo-second-order was higher than that of pseudo-first order (0.9758). Therefore, the adsorption process follows the pseudo-second order which determines the nature of adsorption. The chemical interaction occurred to get rid of the cadmium ions, which confirmed the interpretation obtained previously; that at assortment of pH (6–8), an electrostatic interaction take place between the available cellulose anions and free cations in the aqueous solution.

Similarly, adsorption isotherms were modeled using the models of Dubinin-Radushkevich, Freundlich, Langmuir and Temkin. The obtained parameters were illustrated in Table 7. According to these values of R^2 and γ^2 , the Langmuir seems as the best model to describe the adsorption process since its R^2 is equal to 0.9937, which was higher than that of the other three isotherms, Freundlich, Dubinin-Radushkevich and Temkin (Fig. 9). Langmuir isotherm describes more appropriately the adsorption process, which consists to a monolaver adsorption of cadmium onto cellulose (Foo and Hameed, 2010). Cellulose as a polymer with identical monomers chain, allowed the retention of Cd^{2+} on the same sites. This actively demonstrates that the cadmium ions adsorbs at sites identical of cellulose with same energy through formation of a molecular monolayer (Langmuir, 1916). The adsorption energy, E, was obtained from the relationship in below (Araissi et al., 2020; Faghihian et al., 2013):

$$\mathbf{E} = 1/\sqrt{(2\beta)} \tag{5}$$

The obtained E value for adsorption of Cd^{2+} was 6.65 kJ/mol < 8.0 kJ/mol, indicating that the sorption process is done through physical sorption (Araissi et al., 2016; 2020; Faghihian et al., 2013).

4. Conclusions

To sum up everything that has been stated so far, cellulose was isolated successfully from *Tamarix aphylla*'s stem via a non-classical process in which we used acetic acid and a buffer solution. This treatment was efficient in fully eradicating of non-cellulosic compound. Infrared spectroscopy, X-ray diffraction, thermogravimetric analysis and morphology examination were used to figure out the cellulose's characterization. Even though it's low surface area, this not obstruct cellulose from get rid of the cadmium ions from contaminated water through the chemi-physical interaction which was taken place. The best capacity cadmium adsorption onto cellulose amount, 45 mg L^{-1} for cadmium concentration and 1200 min.

Langmuir model confirm that the sorption of cadmium ions was carry out onto monolayer since it was considered as the most appropriate one to describe this adsorption with the best value of R^2 0.9937. In addition, the pseudo-second-order was the suitable model for this adsorption by recording the highest R^2 0.9979. A physical aspect was described for the cadmium uptake onto cellulose with a mean free energy of 6.65 kJ mol⁻¹.

Bring to a close, cellulose has an important potential as biosorbent for cadmium ions removal and the achieved results were very encouraging.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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