

Surface Functionalization of Cellulose Fibers Extracted From *Juncus Acutus L* Plant: Application for the Adsorption of Anionic Dyes from Wastewaters

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ABSTRACT

New amine-functionalized adsorbent was prepared by chemical modification of cellulose fibers extracted from *Juncus acutus L* (Smar) plants in order to be used as chelating support for the removal of copper ions (Cu (II)). Evidence of grafting DiEthyleneTriamine (DET) onto the raw Smar fibers was provided by nitrogen analysis and Fourier Transform Infrared (FTIR) spectra study. The ability of the binary system [Cu(II)/DET-Smar] for binding Acid Blue 25 (AB25) was then investigated in batch process. Equilibrium data were analyzed by Langmuir, Freundlich and Jossens models. The obtained results reveal that the adsorption of AB25 onto [Cu (II)/DET-Smar] complex show good compliance with the Jossens isotherm. Various thermodynamic activation parameters were estimated and it was found that the adsorption was spontaneous and follows an exothermic process.

Keywords: *Juncus acutus L*, cellulose isolation, adsorption, modeling, thermodynamics.

INTRODUCTION

Several industries such as dyeing textiles consume large amount of water and consequently generate a considerable amount of polluted wastewater. Since a very small quantity of dye in water is highly visible and cause allergic dermatitis, skin irritation, carcinogenic and mutagenic to human and aquatic organisms, the removal of these contaminants from effluents becomes environmentally very important. Among several chemical and physical techniques, the adsorption process is one of the most effective methods that have been successfully employed for the removal of dyes from aqueous solutions. This can be attributed to many factors such as simplicity of design, ease of operations, wide choice of adsorbent materials, and effectiveness [1]. Activated carbon has been widely investigated for the adsorption of dyes from effluents, but its high cost limits its commercial application. Therefore many attempts have been pursued toward the use of effective and low-cost adsorbents prepared from naturally occurring

materials for the removal of textile dyes from aqueous solutions [2]. Following this trend, cellulose-based substrates are considered as promising scavengers for the removal of different types of pollutants from wastewater. Cellulose, one of the most abundant, renewable and cheap natural polymers, is a semicrystalline polysaccharide made up of D-glucosidic bonds. By itself, cellulose is not able to adsorb aromatic pollutants [1]. Thus, the incorporation of new functional groups in cellulose materials provides a significant route to enhance their adsorption properties towards a large kind of pollutants [3-6]. In this field and in our previous studies [7, 8], we have demonstrated that Ethylenediamine grafted cotton fibers loaded with copper ions were highly effective for the removal of anionic dyes from aqueous solutions under batch and continuous flow rate conditions.

Finding alternative sources for cellulosic fibers is an interesting route in current application. *Juncus Acutus L* plant is a perennial rush that grows in waterways and saline areas. It is native to western and southern Europe, Africa, and North and South America [9]. In spite of its abundance, this plant is almost exclusively used by artisans. As with all plants, *Juncus acutus L* has three principal constituents, namely cellulose, hemicellulose, and lignin. In this study, the exploitation of this plant was assessed by the removal of cementing materials around the cellulosic fiber-bundles. The later have been successfully used, for the first time, for the removal of toxic contaminants from aqueous solutions.

The purpose of this work was to ascertain the feasibility and the characterization of a ternary complex formation between a model ligand (AB25), Cu (II) ions and DET grafted *Juncus Acutus L* extracted fibers, using a batch mode under several conditions. Adsorption isotherms were investigated and different adsorbent models (Langmuir,

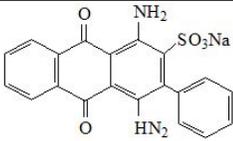
Freundlich and Jossens) were used to estimate the experimental data and to elucidate the possible adsorption mechanism. Thermodynamic studies were also assessed to determine the standard free energy (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0).

EXPERIMENTAL

Materials and Methods

All reagents [DiMethylFormamide (DMF), Thionyl chloride (SOCl_2), DiEthylenTriamine (DET), potassium hydrogen phthalate (for the Clark-Lub's buffer solutions) [10] and copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$)] were purchased from Sigma-Aldrich Company (Sigma-Aldrich Chimie Sarl, Saint-Quentin Fallavier, France) and used without further purification. The Acid Blue 25 (referred as AB25) used in the adsorption tests was also supplied by Sigma-Aldrich Company and was employed in its technical grade. The chemical structure and characteristics of the selected dye are given in Table I.

TABLE I. Chemical and physical characteristics of AB 25.

λ_{max} (nm)	Molecular weight ($\text{g}\cdot\text{mol}^{-1}$)	Brut formula	Developed formula
600	416.39	$\text{C}_{20}\text{H}_{13}\text{N}_2\text{NaO}_5\text{S}$	

Extraction of Cellulose Fibers from Juncus Acutus L

The cellulose fibers used in the present study were generated from *Juncus acutus* L plants (Smar) by a chemical treatment route. These plants were collected at Monastir in the east of Tunisia during the period of March-April. The isolation of cellulose fibers from *Juncus acutus* L required the removal of the non cellulosic materials such as lignin, hemicelluloses and pectin. This was achieved by the use of an alkaline treatment followed by a hydrogen peroxide bleaching as was described in our previous study [11]. The alkaline treatment was essentially performed to solubilise the pectin and the hemicelluloses substances [12]. In this work, the sheets of leaves were treated with 7M NaOH, at 100°C, for 3 h by using a liquid to plant ratio of 10:1. The solubilised components were then removed by washing several times with distilled water. Subsequently, the alkaline treated fibers were reacted with 10 mL.L⁻¹ H₂O₂, at 95°C, for 45 minutes. The

bleaching treatment was carried out to break down phenolic compounds or molecules having chromophoric groups present in lignin and to remove the by-products of such breakdown [12]. The extracted fibers were then thoroughly washed until neutral pH was reached and finally dried to constant weight.

Preparation of DET-Smar Grafted Adsorbent

DET-Smar grafted adsorbent was prepared at two stages: (1) preparation of CDC-Smar according to the method previously reported by Tashiro et al [13], and (2) subsequent amination of the CDC-Smar with DET. The incorporation of amine groups onto CDC-Smar was performed as follows. A sample of 1 g CDC-Smar, 20 mL of distilled water and 5 mL of DET were introduced into a round bottomed flask. The mixture was stirred for 3 h at reflux. At the end of the reaction, the product (namely DET-Smar) was separated from the liquid through filtration, rinsed first with methanol/acetone (50/50 v/v) mixture, then with water and finally dried under vacuum at 40 °C for 72 h.

Characterization of the Modified Materials

Nitrogen Content

The nitrogen amount of DET-Smar was evaluated using elemental analysis. The corresponding value was equal to 2.47%. The number of coordinating sites per gram of support, $C_a = 0.587 \text{ mmol}\cdot\text{g}^{-1}$, was calculated based on this nitrogen content value. It was determined using the following equation:

$$C_a = \frac{(\%N)}{3.M_N} \frac{1}{100} \times 10^3 \quad (1)$$

Where %N is the nitrogen content of the DET-Smar and M_N is the molecular weight of nitrogen.

Fourier Transform-Infrared Spectroscopy

FTIR spectra were examined to indicate the chemical modification of *Juncus acutus* L fibers via chlorination and amination reactions. The IR analysis were performed using Fourier Transform Infrared Spectrometer (Nicolet® 510M). For such characterization, 1 mg of the sample was blended with 100 mg of KBr, ground and pressed into small tablets. IR spectra were recorded in a transmittance mode and scanned in the range of 500-4000 cm^{-1} .

Figure 1 exhibits the infrared spectrum of untreated fibers (Figure 1(a)), CDC-Smar (Figure 1(b)) and DET-Smar (Figure 1(c)). The characteristic bands of virgin *Juncus acutus* L fibers are listed in Table II.

TABLE II. Summary of peaks in FTIR spectra observed for virgin *Juncus acutus* L fibers.

Band position (cm ⁻¹)	Band assignments	Reference
3424	O-H stretching vibration (hydrogen bonded)	[14]
2921	C-H stretching vibration	[14]
2851	-OCH ₃ methoxyl C-H stretching	[14]
1424	CH ₂ symmetric bending	[15]
1376	symmetric C-H bending from methoxyl group	[14]
1161	C-O-C stretching at the β(1,4)- glycosidic linkage	[16]
1059	C-OH stretching vibration of the cellulose backbone (v C-O secondary alcohol)	[15]
895	β-glycosidic linkages	[17]
670	C-OH bending deformation	[18]
1615	C-O stretching of lignin	[19]

The obtained results reveal that: (1) the extracted fibers were effectively free from hemicelluloses proved by the lack of the band at 1731 cm⁻¹ which characterize the C=O stretching of the acetyl groups of this materials [20], (2) the removal of lignin was assessed by the absence of the majority of the characteristic peaks of this component, and (3) the quantity of cellulose is high confirmed by the presence of many bands characterizing this material.

Comparing with the IR spectrum of untreated fibers, the ones of CDC-Smar and DET-Smar exhibit some changes. Indeed, the CDC-Smar spectra (*Figure 1 (b)*) reveal the appearance of new bands at 1729 and 752 cm⁻¹ that could be assigned to the bending and stretching vibrations of the C-Cl bond, respectively [21]. In addition to that, the band at 895 cm⁻¹ observed in the virgin fibers (*Figure 1 (a)*) spectra was reduced and shifted to 889 cm⁻¹ after chlorination (*Figure 1 (b)*) and disappeared after reacting with DET (*Figure 1 (c)*). These results confirm the substitution of hydroxyl groups by chlorine atoms.

For DET-Smar, the spectrum shown in *Figure 1(c)* exhibits the appearance of new three peaks at 1643, 1555 and 1471 cm⁻¹ which are attributed to the deformation vibration of N-H in primary amine (-NH₂), N-H in secondary amine (>NH) and C-H in -N-CH₂- groups, respectively [22].

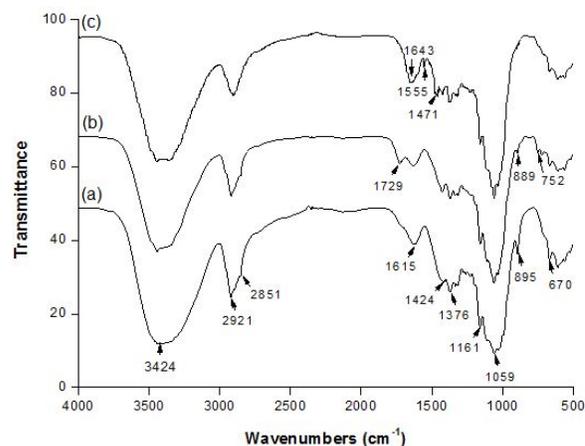


FIGURE 1. FTIR spectra of: (a) Smar fibers, (b) CDC-Smar, and (c) DET-Smar.

Loading of DET-Smar with Cu(II) ions

The effect of pH, initial metal concentration and contact time on the removal of Cu (II) ions by DET-Smar was evaluated by the batch adsorption experiments. The pH was ranged between 2 and 8 and adjusted to the desired value with a Clark-Lubs's buffer solutions [10]. For this, DET-Smar (0.1 g) was added to 100 mL of the different buffered metal ions solutions. The mixture was stirred in a 250 mL glass bottle for 24 h at room temperature (20°C).

The rate of copper uptake by DET-Smar fibers was performed at three different initial metal concentrations (0.695, 0.893 and 1.859 mmol.L⁻¹). Experiments were carried out at pH 7, at room temperature and similar procedures as above described were repeated. The sorption time was varied between 4 and 48h. At different time intervals, samples were withdrawn, filtered using a 0.45 μm membrane filter and the remaining Cu (II) concentration was measured using a Janway 6100 Spectrometer at the maximum absorption wavelength of the metal ion-phthalate complex.

The amount of metal bound by the DET-Smar was calculated using the following Equation:

$$q_t = \frac{(C_0 - C_t) \times V}{W} \quad (2)$$

Where C₀ and C_t (mmol.L⁻¹) are the initial concentration and the concentration of metal ions remaining in the solution at a given time, respectively, V (L) is the volume of the solution and W (g) is the weight of the DET-Smar used.

Adsorption of AB25 onto DET-Smar loaded with Cu(II) ions

Studies on the adsorption of AB25 measurements were carried out by batch procedure. For this purpose, 0.1 g of [Cu (II)/DET-Smar] and 100mL of the dye solution were stirred in an Ahiba Nuance® laboratory machine at pH 7. After the equilibrium was reached, the final concentration of AB25 in the solution was determined using a 6100 Janway® spectrophotometer at a wavelength of 600 nm. The adsorption isotherms experiments were performed at four different temperatures ranging between 20 and 80°C. The dye concentration retained in the adsorbent phase was calculated using the following relationship:

$$Y_e = \frac{(C_0 - C_e) \times V}{W} \quad (3)$$

Where C_0 and C_e (mmol.L^{-1}) are the initial and the equilibrium dye solution concentrations, respectively, V (L) is the volume of the solution, and W (g) is the weight of the adsorbent.

RESULTS AND DISCUSSION

Loading of DET-Smar with Cu(II) ions

Effect of the pH Solution

The pH of aqueous solution is one of most important factors for adsorption control. *Figure 2* shows the effect of the initial pH on the adsorption of Cu (II) onto DET-Smar. As can be noted, the adsorption capacity of the heavy metal ions increased with increasing pH, reaching a maximum value at around pH 7 and then decreased. The decline of adsorption capacity at strongly acidic pH can be ascribed to the electrostatic repulsion between the protonated adsorbent chains and the positive copper ions species. When the pH exceeded a value of 7, copper precipitation was observed due to the increase of the OH^- ions in the adsorption medium that induced a decrease in the removal efficiency.

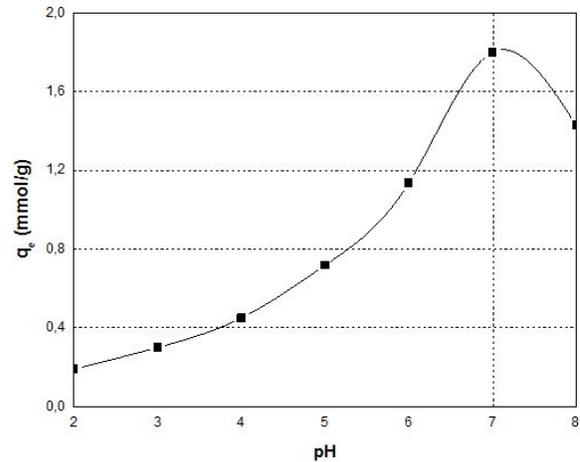


FIGURE 2. Effect of solution pH values on adsorption of Cu(II) ions onto DET-Smar.

Effect of Initial Copper Concentration and Contact Time

Figure 3 shows the contact time dependence of DET-Smar for the removal of Cu (II) ions at different initial copper concentrations.

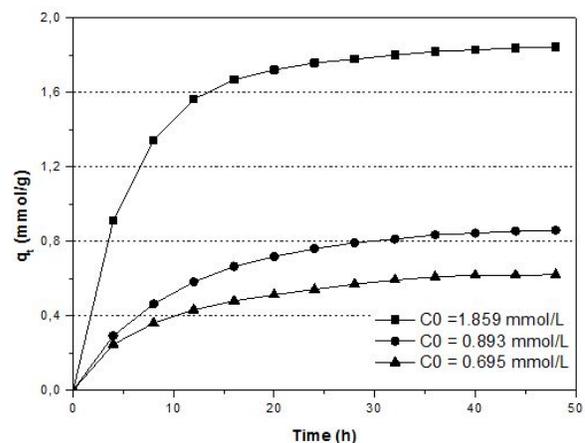


FIGURE 3. Effect of contact time on adsorption of Cu(II) ions onto DET-Smar.

The uptake of Cu(II) onto the used adsorbent is quite fast at the initial stages compared to the final one in which the adsorption capacity is gradually decreased until reaching equilibrium. This can be explained by the fact that a large number of vacant surface binding-sites are available for adsorption during the initial stage. However, after a period of time, the availability of active sites onto the surface of DET-Smar decreased as well as the pore diffusion of the solute into the adsorbent became slow.

Figure 3 also reveals that equilibrium capacities increased with increasing initial Cu(II) concentration. This could be attributed to the fact that the rise in initial copper concentration will cause an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass transfer at a high initial copper concentration. Therefore, a complete utilization of adsorption surface and available active sites was allowed which is not possible in low concentration.

It should be noted that when the initial Cu(II) concentration exceeds a value of 1.859 mmol.L⁻¹, there is no further increase in adsorption capacity revealing that all reactive sites are saturated with the copper ions. In this case the maximum amount of the solute adsorbed onto DET-Smar support was 1.845 mmol.g⁻¹. This leads to the formation of a binary complex system of the type [Cu (II)/DET-Smar] with a $\left[\frac{22}{7}:1\right]$ stoichiometry.

Kinetic Study of Cu (II) Adsorption

Various kinetic models have been suggested for the adsorption process, and two well-known models, pseudo-first order and pseudo-second order kinetic equations, are selected in this study.

The linearized form of the pseudo first-order model is represented by:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (4)$$

Where q_e and q_t (mmol.g⁻¹) are the amounts of Cu (II) adsorbed at equilibrium and at time t , respectively, and k_1 (min⁻¹) is the Lagergren rate constant of adsorption.

The values of k_1 and q_e for the adsorption of Cu (II) onto DET-Smar were determined from the plot of $\log(q_e - q_t)$ versus t . The obtained straight line yields k_1 as the slope and $\log q_e$ as the intercept.

The pseudo-second-order kinetic equation is given as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Where k_2 (g.mmol⁻¹.min⁻¹) is the pseudo-second-order rate constant. The constants of pseudo-second-order model, k_2 and q_e , can be obtained from the slope and intercept of the plot of t/q_t versus t .

Table III lists the simulated parameters by aforementioned kinetic models. The analysis of correlation coefficients revealed that adsorption kinetics of DET-Smar were in excellent agreement with the pseudo-second order kinetic model. Moreover, values of $q_{e,cal}$ calculated from pseudo-second-order equation were nearer the experimental values, $q_{e,exp}$, than those calculated from pseudo-first-order one. Hence, these results indicate that adsorption phenomenon belongs to the pseudo-second-order model during all period of adsorption. This supports the model presupposition that the adsorption is controlled by a chemical process involving valence forces through sharing or exchange of electrons between adsorbent and sorbate at different initial copper concentrations [23].

TABLE III. Pseudo-first-order and pseudo-second-order kinetic parameters of Cu (II) adsorption onto DET-Smar at different initial copper concentrations.

C ₀ (mmol .L ⁻¹)	Pseudo first order				Pseudo second order		
	q _{e,exp} (mmol.g ⁻¹)	K ₁ .10 ³ (min ⁻¹)	q _{e,cal} (mmol.g ⁻¹)	R ²	K ₂ .10 ³ (g.mmol ⁻¹ .min ⁻¹)	q _{e,cal} (mmol.g ⁻¹)	R ²
1.859	1.845	1.842	1.417	0.987	2.225	2.005	0.999
0.893	0.860	1.842	0.990	0.970	1.913	0.955	0.998
0.695	0.620	2.072	0.823	0.905	2.693	0.738	0.999

Adsorption of AB 25 onto DET-Smar loaded with Cu(II) ions

To perform such experiments, it was first necessary to saturate the DET-Smar support with Cu (II) ions at a $\left[\frac{22}{7}:1\right]$ ratio. Afterwards, the loaded support was

introduced into the dye solution and maintained until equilibrium was reached. All experiments were carried out at a pH value of 7, where the highest uptake of Cu(II) ions onto DET-Smar was obtained.

At first, we tested the adsorption efficiency of the selected dye onto untreated Smar fibers at 20°C. Experimental results (Figure not shown) revealed that the virgin fibers displayed some affinity towards AB25. This could be attributed to the eventual presence of phenolic groups onto the chemical structure of the extracted fibers [2]. However, this affinity remains always feeble ($Y_{ref} = 0.059$ mmol.g⁻¹) and could be probably improved by the use of the animated fibers loaded with copper ions. This was accomplished by studying the effect of temperature on the adsorption of AB 25 onto [Cu (II)/DET-Smar] complex.

According to Figure 4, it was found that the adsorption capacity of the binary system decreases with increasing temperature from 20 to 80°C. This reveals that the removal of the selected dye was unfavorable at high temperatures indicating the

exothermic nature of the adsorption process. The obtained results can be attributed to a tendency for AB25 molecules to escape from the solid phase to the bulk phase with the increment of the solution temperature. In this case, the rise of this parameter affects the solubility and the chemical potential of the adsorbate, the latter being a controlling factor for the adsorption [24]. *Figure 4* also shows that the equilibrium uptake of AB25 onto [Cu (II)/DET-Smar] at 20°C and pH 7 was about twenty eight times greater than that onto virgin Smar fibers. Indeed, at 20°C, the adsorbed quantity reached a value of 1.647 mmol per gram of [Cu (II)/DET-Smar]. In addition to that, we found that under the studied experimental conditions (pH = 7 and T = 20°C), the DET-Smar support revealed a lower affinity towards AB25 dye with an adsorption capacity of 0.1282 mmol.g⁻¹.

The obtained results indicate that the incorporation of Cu (II) ions onto the chemical structure of DET-Smar increased significantly the number of sorption sites, which greatly enhanced the adsorption capacity of the selected dye. This revealed that AB25 can act as efficient ligand in the metal-coordinating process.

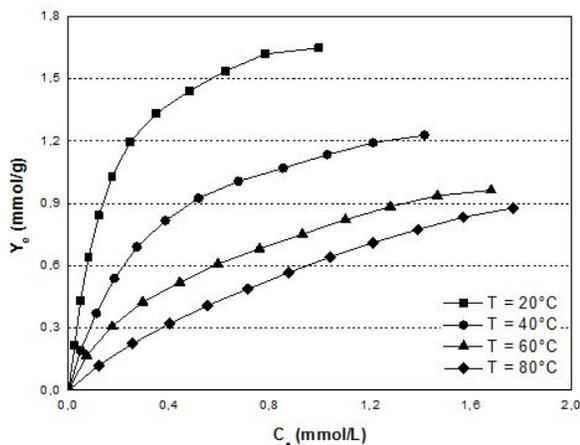


FIGURE 4. Effect of temperature on the adsorption of AB25 onto [Cu(II)/DET-Smar], pH= 7.

An additional presentation of the acquired results is shown in *Table IV* that gives a comparison between the capacity of the adsorbent C_a , the maximum amount of Cu (II) coordinated to DET-Smar support and the maximum quantity of dye adsorbed at the equilibrium onto [Cu (II)/DET-Smar] complex.

Results show the formation of ternary complex [AB25/Cu (II)/DET-Smar] with a $\left[\frac{14}{5} : \frac{22}{7} : 1 \right]$

stoichiometry at 20°C. The obtained stoichiometry reveals the presence of a particularly adsorption process which can be explained as follows. A number of four Cu (II) ions are adsorbed by two lateral chains, and each of Cu (II) is chelated by the bidentate ligand (-NH-CH₂-CH₂-NH-). In addition to that one Cu (II) is fixed by the NH₂ terminal groups of the two grafted chains. As a result, five Cu (II) ions could be adsorbed by two grafted DET chains, elucidating thus the obtained stoichiometry earlier mentioned.

TABLE IV. Maximum quantity of Cu (II) ions adsorbed at pH 7 (q_{ref} at 20°C) and Maximum Solid-phase Dye Concentration (Y_{ref} at different temperature).

Adsorbent	T (°C)	q_{ref} (mmol.g ⁻¹)	Y_{ref} (mmol.g ⁻¹)	Y_{ref}/C_a	Y_{ref}/q_{ref}
Cu(II)/DET-Smar $C_a = 0.587$ mmol.g ⁻¹	20	1.845	1.647	2.805	0.892
	40	1.845	1.227	2.090	0.665
	60	1.845	0.963	1.640	0.522
	80	1.845	0.876	1.492	0.475

A possible complex structure of [AB25/Cu (II)/DET-Smar] is presented in *Figure 5*.

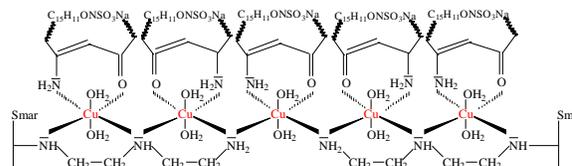


FIGURE 5. Proposal of associative structure between AB25 and Cu(II)/DET-Smar complex.

The present phenomenon was not observed in our previous study [7] where the AB25 was adsorbed by EthyleneDiamine cotton fibers loaded with copper ions. This could be attributed to the fact that the length of EthyleneDiamine chain is smaller compared to that of DiEthyleneTriamine (DET) one, which prevent in this case the linkage of grafted chains. Results presented in *Table IV* also reveal that the saturation limit corresponding to the molar quantity of adsorbed dye, at 20°C, is slightly lower than the maximum amount of Cu (II) chelated to DET-Smar. This could be attributed to the steric hindrance of the voluminous AB25 molecules which cannot reach all the reactive sites of the [Cu (II)/DET-Smar] complex, and/or to the fact that the grafted chains are not in front of each others as can be seen in *Figure 6*.

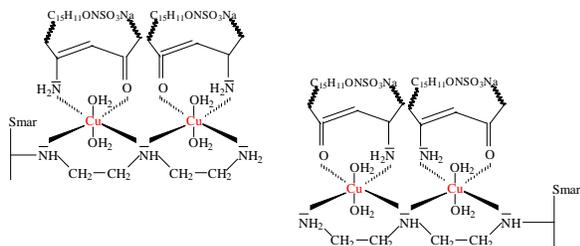


FIGURE 6. Proposal of associative structure between AB25 and Cu (II)/DET-Smar complex when the grafted chains are not in front of each other.

Adsorption Isotherms

The equilibrium adsorption isotherm is one of the most important data to understand the mechanism of the adsorption system. Therefore, it is necessary to establish the most appropriate correlation for the equilibrium curves. In this research, three adsorption isotherm models, Langmuir, Freundlich and Jossens, were applied to evaluate the adsorption experimental results.

Langmuir Model

The Langmuir model assumes that the adsorption occurs on a homogenous surface and there is no interaction between adsorbates in the plane of the surface [25]. It can be represented by the following expression:

$$\frac{C_e}{Y_e} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (6)$$

Where C_e (mmol.L^{-1}) is the liquid-phase concentration of the adsorbate at equilibrium, Y_e (mmol.g^{-1}) is the amount of adsorbate adsorbed at equilibrium, Q (mmol.g^{-1}) is the concentration of adsorbate in the adsorbent corresponding to complete coverage of the available site or the limiting adsorption capacity, and b (L.mmol^{-1}) is the Langmuir constant related to the affinity of binding sites.

Q and b values were computed from the slopes and intercepts of the straight lines of the plots of C_e/Y_e versus C_e , and are reported in Table V. As can be seen, the constant b decreased with increasing temperature, which indicates that, at lower temperatures, the adsorption density was higher and the adsorption energy was lower [26].

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L , also known as the separation factor, given by:

$$R_L = \frac{1}{1 + b \times C_{ref}} \quad (7)$$

Where C_{ref} (mmol.L^{-1}) is the highest fluid-phase concentration. This parameter indicates the isotherm is unfavorable ($R_L > 1$), favorable ($R_L < 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$) [27]. The values of R_L were observed to drop into the range 0-1 in all experimental systems as given in Table V, confirming that the ongoing adsorption process is suitable. Smaller R_L values at 20°C express greater affinity between AB25 and [Cu(II)/DET-Smar] complex [28].

TABLE V. Langmuir Constants of Adsorption of AB25 onto [Cu(II)/DET-Smar] complex.

T (°C)	Y_{ref} (mmol.g^{-1})	Q (mmol.g^{-1})	b (L.mmol^{-1})	R_L	R^2
20	1.647	2.000	5.904	0.145	0.998
40	1.227	1.500	3.122	0.184	0.999
60	0.963	1.263	1.715	0.257	0.987
80	0.876	1.714	0.578	0.492	0.988

In order to examine the thermodynamic behavior of the adsorption of AB 25 onto [Cu (II)/DET-Smar] complex, the enthalpy change (ΔH°), the entropy change (ΔS°) and Gibbs free energy change (ΔG°) were evaluated in this study. These thermodynamic parameters were calculated using the following equations:

$$\Delta G^\circ = -RT.LnK_L \quad (8)$$

$$K_L = Qb \quad (9)$$

$$\Delta G^\circ = \Delta H^\circ - T.\Delta S^\circ \quad (10)$$

Where R ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$) is the gas constant, T (K) is the solution temperature in Kelvin, and K_L is Langmuir equilibrium constant. The plot of ΔG° versus T yields a straight line from which ΔS° and ΔH° were calculated from the slope and intercept, respectively.

The values of the thermodynamic parameters recorded from this work are given in Table VI.

TABLE VI. Thermodynamic Parameters of Adsorption of AB25 onto [Cu (II)/DET-Smar] complex.

T (°C)	ΔG° (kJ.mol^{-1})	ΔS° ($\text{J.K}^{-1}.\text{mol}^{-1}$)	ΔH° (kJ.mol^{-1})
20	-6.016		
40	-4.021		
60	-2.143	-99	-35.23
80	0.001		

The negative ΔG^0 value indicates that the process is feasible and spontaneous at 20, 40 and 60°C. More negative value of ΔG^0 at lower temperatures, as was observed in this study, implies greater driving force for adsorption process. The inverse trend was shown by Ngah et al. [29]. The negative value of ΔH° confirmed that the adsorption of AB25 onto [Cu (II)/DET-Smar] complex is an exothermic process. The exothermic nature of adsorption is probably due to an existence of a high number of adsorption sites on the surface of [Cu (II)/DET-Smar] so that they improve dye molecules uptake [30]. The negative value of ΔS° accords with the fact that the mobility of the adsorbate was more restricted on the adsorbent surface than in solution [31].

Freundlich Model

The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface [25] and is expressed as follows:

$$\ln Y_e = \ln P + \frac{1}{n} \ln C_e \quad (11)$$

Where P ($L \cdot g^{-1}$) is a Freundlich constant related to adsorption capacity, $1/n$ is an empirical parameter related to adsorption intensity.

Values of P and n were calculated from the intercept and slope of the plot of $\ln Y_e$ versus $\ln C_e$ and are given in Table VII. It is clear that the values of P increases as the temperature decreases, indicating the suitability of the removal of AB 25 at lower temperature [32]. The exponent n greater than unity at various temperatures indicates a favorable adsorption processes. Furthermore, the highest value of n recorded at 20°C reflects the greatest stability of the adsorbent/adsorbate system formed under these studied conditions.

TABLE VII. Freundlich and Jossens Constants for the Adsorption of AB25 onto [Cu(II)/DET-Smar] complex.

T (°C)	Freundlich constants			Jossens constants			R ²
	P	n	R ²	i	j	m	
20	2.081	1.945	0.922	11.326	0.010	1.050	0.999
40	1.184	1.897	0.956	4.642	0.008	0.991	0.999
60	0.779	1.824	0.992	3.837	0.062	0.685	0.999
80	0.611	1.351	0.997	1.107	0.007	0.773	0.999

The parameter n can be also represented as $1/n$ value which is related to the degree of surface heterogeneity. A smaller $1/n$ value reveals more heterogeneous surface while a value closer to or even one indicates that the adsorbent has relatively more homogeneous binding sites [33]. The $1/n$ values obtained for AB25 adsorption ranged between 0.51

and 0.74 suggesting that the present adsorption process involved heterogeneous binding sites. This behavior is in agreement with results earlier reported in the equilibrium isotherms study.

Jossens Model

Jossens isotherm is considered as a combination of Langmuir and Freundlich isotherms, and its adsorption mechanism does not obey ideal monolayer adsorption, but an impure one [34]. The Jossens equation is given as follows:

$$Y_e = \frac{i \cdot C_e}{1 + j \cdot (C_e)^m} \quad (12)$$

Where i ($L \cdot g^{-1}$), j ($L \cdot mmol^{-1}$) and m are the jossens constants that may be obtained from the adsorption data via an iterative procedure using a computer program.

The calculated parameter values as well as the correlation coefficients are given in Table VI. As can be seen, Jossens model showed higher correlation coefficients than that of Langmuir and Freundlich models over the whole temperature range studied, indicating that the Jossens equation is the best one in simulating the adsorption isotherm of AB25 onto [Cu (II)/DET-Smar] complex. Langmuir equation provides a reasonable description of the experimental data at low temperature as can be seen in Table V. The Freundlich isotherm does not appear to be able to characterize the adsorbent/adsorbate tested systems. This is confirmed by Figure 7 which exhibits a comparison of the fitting of experimental data with the above-mentioned three adsorption isotherms. The obtained results suggest that some heterogeneous pores or surface of the [Cu (II)/DET-Smar] complex could play a role in the dye adsorption process [34].

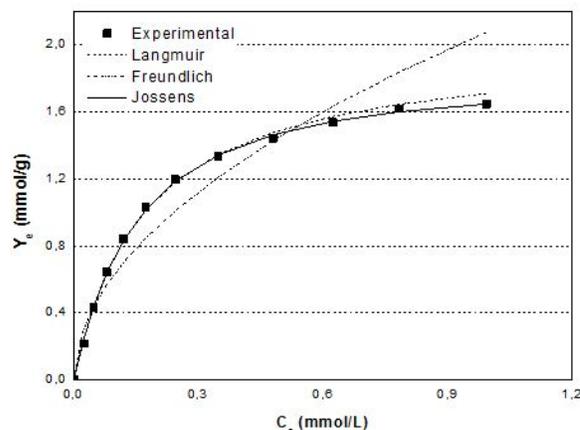


FIGURE 7. Fitting of the adsorption equilibrium data by the Langmuir, Freundlich and Jossens isotherms, T = 20°C.

CONCLUSION

Diethylenetriamine grafted cellulose fibers isolated from *Juncus acutus* L plants was valorized as a promising adsorbent for Cu (II) and AB25 sorption. The uptake of Cu (II) was studied by varying the solution pH, initial metal concentration and contact time. Kinetic studies reveal that the adsorption followed the pseudo second-order model. [Cu (II)/DET-Smar] was then used for AB25 adsorption and it was found that the loading of aminated cellulose fibers by Cu(II) ions has extensively increased the magnitude of dye removal. Jossens isotherm showed the best interpretation for the equilibrium data. Thermodynamic parameters reveal that the adsorption process is spontaneous and exothermic.

NOMENCLATURE

b Langmuir constant related to the affinity of binding sites ($L \cdot \text{mmol}^{-1}$)
 C_a number of coordinating sites per gram of support
 C_e liquid-phase concentration of the adsorbate at equilibrium ($\text{mmol} \cdot L^{-1}$)
 C_{ref} highest fluid-phase concentration ($\text{mmol} \cdot L^{-1}$)
 C_t concentration of the solute remaining in the solution at a given time ($\text{mmol} \cdot L^{-1}$)
 C_0 initial concentration of the solute ($\text{mmol} \cdot L^{-1}$)
 ΔG^0 standard free energy ($\text{kJ} \cdot \text{mol}^{-1}$)
 ΔH^0 enthalpy change ($\text{kJ} \cdot \text{mol}^{-1}$)
 i constant in Jossens isotherm ($L \cdot g^{-1}$)
 j constant in Jossens isotherm ($L \cdot \text{mmol}^{-1}$)
 k_1 Lagergren rate constant of adsorption (min^{-1})
 k_2 pseudo-second-order rate constant ($g \cdot \text{mmol}^{-1} \cdot \text{min}^{-1}$)
 K_L Langmuir equilibrium constant ($L \cdot g^{-1}$)
 m constant in Jossens isotherm
 M_N molecular weight of nitrogen
 $1/n$ empirical parameter related to adsorption intensity
 $\%N$ nitrogen content of the DET-Smar
 P Freundlich constant related to adsorption capacity ($L \cdot g^{-1}$)
 Q concentration of adsorbate in the adsorbent corresponding to complete coverage of the available site ($\text{mmol} \cdot g^{-1}$)
 q_e amount of Cu(II) adsorbed at equilibrium ($\text{mmol} \cdot g^{-1}$)
 q_{ref} maximum quantity of Cu(II) ions adsorbed at $\text{pH} = 7$ ($\text{mmol} \cdot g^{-1}$)
 q_t amount of Cu(II) adsorbed at time t ($\text{mmol} \cdot g^{-1}$)
 R gas constant ($J \cdot \text{mol}^{-1} \cdot K^{-1}$)
 R_L separation factor
 ΔS^0 entropy change ($J \cdot K^{-1} \cdot \text{mol}^{-1}$)
 T solution temperature (K)
 V volume of the solution (L)
 W weight of the adsorbent (g)

Y_e amount of adsorbate adsorbed at equilibrium ($\text{mmol} \cdot g^{-1}$)
 Y_{ref} maximum solid-phase dye concentration ($\text{mmol} \cdot g^{-1}$)

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