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CHEMICAL MODIFICATION OF CELLULOSE BY ACYLATION: APPLICATION TO ADSORPTION OF METHYLENE BLUE♣

R. Bouhdadi¹, S. Benhadi², S. Molina², B. George², M. El Moussaouiti¹, A. Merlin².

ABSTRACT

Cellulose was modified under mild conditions in order to increase its capability to trap pollutants. Nicotinoyl chloride hydrochloride (NCHC), with its pyridine ring able to adsorb cations, was grafted on the substrate. This grafting has been monitored by infrared spectroscopy and elemental analysis. We have studied the adsorption of Methylene Blue (MB) onto grafted and unmodified cellulose. It was observed that grafting increases three times the retention capacity of cellulose and the kinetics of adsorption is perfectly represented by a pseudo second order model. The adsorption is well described by a Langmuir-type isotherm showing a homogeneous adsorption phenomenon through the formation of a monolayer. Besides the reaction is spontaneous and exothermic, suggesting the possibility of recycling the substrate by desorbing the dye at elevated temperature.

Keywords: Cellulose, dye adsorption, isotherms, kinetics, modeling

INTRODUCTION

The effluents of textile industry contain dyes and heavy metals which are poisonous for fauna and flora, because of their stability and their low biodegradability (Guivarch *et al.* 2003, Kadirvelu *et al.* 2003, Jain *et al.* 2003). Many different methods of elimination have been used such as: precipitation, ions exchange, extraction, physico-chemical or biological treatments. Most of these methods are inefficient, because of their weak selectivity and/or their high cost (Bagane and Guiza 2000, Benguella and Yacouta-Nour 2009, Mazet *et al.* 1990). For example, adsorption process using activated carbon is one of the mostly used techniques for water purification (Benturki *et al.* 2008), but its cost limits its use in the developing countries. During the last years, many research teams have had an interest in cellulose compounds for waste treatment, because they are quite easily available and renewable. Cellulose is the most abundant polymer on earth (Satge *et al.* 2002, Chauvelon *et al.* 1998, Gourson *et al.* 1999) and derived substrates are suitable for trapping dyes (Marchetti *et al.* 2000), organic (Maurin *et al.* 1999, Aloulou *et al.* 2006, Alila and Boufi, 2009) and inorganic (Randall *et al.* 1976, Li and Bai 2005, Navarro *et al.* 1999) pollutants. Chemical modification of cellulose (e.g. surface fixation or grafting of groups able to interact with pollutants) allows to improve its adsorption capacity and to enhance its reactivity. In this work, we are modifying cellulose under mild conditions by Nicotinoyl chloride hydrochloride (NCHC). Nicotinoyl chloride hydrochloride (NCHC) was chosen because the reaction of an acyl halogenide on an alcohol function is the most frequently quantitative (formation of the ester favored) and quite fast. Moreover, the grafting of nitrogenous functions is well documented due to the fact that these functions both confer properties for ions exchange and greatly modify the affinity of cellulose towards organic or inorganic pollutants (Alila and Boufi 2009, Zghida *et al.* 2002).

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After characterization of the resulting material, we investigated its adsorption capability towards a current dye i.e. 3,7-bis (Dimethylamino)-phenothiazin-5-ium chloride (methylene blue MB), by varying experimental conditions (residence time, concentration and temperature). The kinetic and thermodynamic parameters of the reaction have been established.

MATERIALS AND METHODS

Products

Preparation of modified cellulose

The cellulose used is “Kraft pulp”, provided by “Morocco Cellulose” company. It was crushed using a crusher SIEBTECHNIK and sieved to keep only particles size 0,5-1 mm. Cellulose was then activated by dipping, during one minute, in a 3 % aqueous solution of sulphuric acid, filtered, washed with distilled water and dried at 40°C in an oven. It was finally washed with methanol in a soxhlet for 6 hours in order to eliminate any residual water and contamination (Krouit *et al.* 2009). The material obtained was then dried in an oven at 80°C.

Its chemical modification took place in two steps:

- The first consisted in dissolving cellulose in Dimethyl Acetamide/ lithium chloride (DMA/LiCl). Cellulose (0.22 g) was put in 10 mL of DMA. The mixture was heated at 120°C for 2 hours and then cooled at 100°C. At this temperature, anhydrous LiCl (0.9 g) was added to the mixture and the reaction proceeded for 4 hours at this temperature.

- The second step consisted in functionalizing cellulose. Nicotinoyl chloride hydrochloride NCHC ($C_6H_4ClNO.HCl$, 0.9 g) and triethylamine (2 mL) were added to the above mixture. The temperature was then raised up to 120°C, where the mixture was maintained under agitation for 12 hours. The solvent was evaporated to yield a gray solid. This solid was first washed with an aqueous solution saturated with K_2CO_3 then with distilled water until obtaining neutral rinsing water. To remove any residual NCHC, modified cellulose was washed in a soxhlet with ethanol for 6 hours, vacuum filtered and dried overnight in an oven at 80°C.

2.1.2. Characterization of media

Grafting efficiency was checked by characterization of raw and modified celluloses with the following methods:

- Infrared spectroscopy : Substrate (1 mg) was crushed then mixed with potassium bromide KBr (99 %) provided by ALDRICH TM (50 mg). The powder obtained was then pelletized under 6 bars pressure. The analysis was carried out using a spectrophotometer PERKIN ELMER Spectrum 2000.

- Ultimate analyzes were carried out on an elementary analyzer THERMOFINNIGAN EA 1112 fitted with an automatic sampler and a chromatographic column PORAPAK. The results were given at +/- 0.2 %.

Dye used

Preparation of Solutions

Methylene blue MB (biological analyzes grade) was provided by JANSEN CHIMICA. Adsorption isotherms of this dye were established from a set of aqueous solutions with concentrations varying in a range from 4.10^{-6} to 6.10^{-5} mol.L⁻¹ (i.e. 1.28 mg.L⁻¹ to 19.19 mg.L⁻¹).

Residual dye concentration

After adsorption, concentrations in residual MB were determined by UV-visible spectrophotometry (SHIMADZU UV-2550) via the BEER-LAMBERT's law.

Determination of adsorption parameters.

Equilibrium time

Raw or functionalized cellulose (0.1 g) was put in 40 mL of a 6.10^{-5} mol.L⁻¹ (19.19 mg.L⁻¹) MB solution. This system was maintained under agitation in a regulated bath at temperature 25°C. The residual concentration of MB was determined for different contact times (from 3 to 140 min) so that the equilibrium time can be evaluated.

The quantity of dye fixed at the time t is given by the following relation:

$$Q_t = \frac{(C_0 - C_r) \times V}{m} \quad (1)$$

With Q_t : the amount of dye adsorbed in mg.g⁻¹ at t ; C_0 : the initial concentration of dye in mg.L⁻¹; C_r : the residual concentration at time t in mg.L⁻¹; m : the mass of adsorbent media in g and v : the volume of solution in L.

Isotherms of adsorption

To establish adsorption isotherms, aqueous solutions of MB were prepared, in a concentration range from 4.10^{-6} to 6.10^{-5} mol.L⁻¹. Once the equilibrium has been reached, the quantity of adsorbed dye, as well as the residual concentration of dye in solution, was evaluated. This set of values gives one point of the isotherm.

Thermodynamic parameters

We have studied the influence of the temperature in the adsorption of MB on both cellulosic materials. For this series of experiments, the maximum quantity adsorbed by 100 mg of substrate in contact with an aqueous solution of MB at 6.10^{-5} mol.L⁻¹ (19.19 mg.L⁻¹) was determined in a temperature range from 25 to 60°C.

RESULTS AND DISCUSSION

Grafting Evidence

Infrared spectroscopy

Figure 1 shows the infra-red spectra of raw and functionalized cellulose.

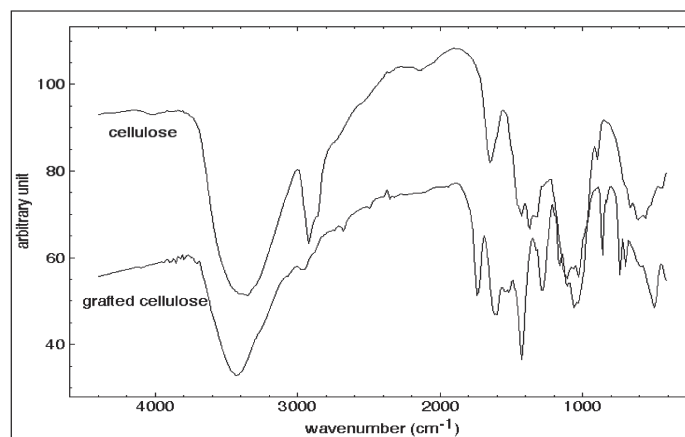


Figure 1. IR Spectra of unmodified and grafted cellulose

A broad absorption band which corresponds to valence vibrations of hydroxyl groups can be observed around 3350 cm^{-1} . In the case of treated cellulose, this band is slightly narrowed and shifted to 3460 cm^{-1} . The other characteristic bands of OH groups (1455 and 1205 cm^{-1}) are also slightly affected. These modifications are explained by the disappearance of the alcoholic functions and thus of the hydrogen bonds in the starting cellulose. We can notice that the intensity decrease is correlated with the appearance of a band around 1740 cm^{-1} allotted to the vibration of the carbonyl bond $\text{C}=\text{O}$ and characteristic of ester functions. The reaction of esterification is also confirmed by the appearance of new bands around 1300 cm^{-1} . Another band, around 1410 cm^{-1} is related to the elongation of a $\text{C}=\text{N}$ bond and proves the presence of the pyridinic cycle on cellulose after reaction. All these experimental observations show that cellulose was modified and that an ester bond was created.

Elemental analysis

Table 1 shows the results of the centesimal analyzes carried out on the various substrates. We were only interested in the elements C, H and N.

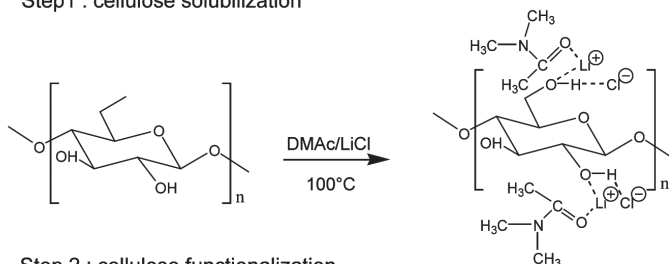
Table 1. Elemental analysis of cellulose before and after reaction.

Samples	%C	%H	%N
1-Cellulose	44.21	6.26	-
2- Dissolved cellulose	44.25	5.95	0.09
3- Grafted Cellulose	50.00	4.98	3.51

The analysis of cellulose leads to percentages of carbon and hydrogen in strong correlation with the empirical formula $\text{C}_6\text{H}_{10}\text{O}_5$. The carbon rate of cellulose in solution seems identical whereas the hydrogen one is slightly reduced due to the rupture of intermolecular hydrogen bonds (Joly *et al.* 2004) in cellulose. Raw cellulose is able to trap water molecules between its polymer chains and during dissolution this adsorbed water is released. A decreasing in the hydrogen content confirmed by the elementary analysis, is then observed. In the case of dissolved cellulose, the presence of nitrogen traces corresponds to the remaining solvent (dimethyl acetamide).

The results for modified cellulose enable us to state that the grafting took place. During the reaction, we notice that the H/C ratio decreases significantly from 1.67 to roughly 1.08. Moreover, the analyses show the presence of nitrogen element which previously appeared only in the form of traces. This highlights the presence of the pyridinic cycle grafted on cellulose. From these results, we evaluate that the grafting rate is close to 0.7. This could indicate that only 70% of cellulose ($\text{C}_6\text{H}_{10}\text{O}_5$) is monosubstituted to $\text{C}_{12}\text{H}_{13}\text{O}_6\text{N}$. The results obtained by ultimate analysis thus confirm the previous observations from infrared spectroscopy. The reactivity of cellulose towards acyl chlorides being well-known (Krouit *et al.* 2009), one can suppose the following reaction pathway as shown on figure 2:

Step1 : cellulose solubilization



Step 2 : cellulose functionalization

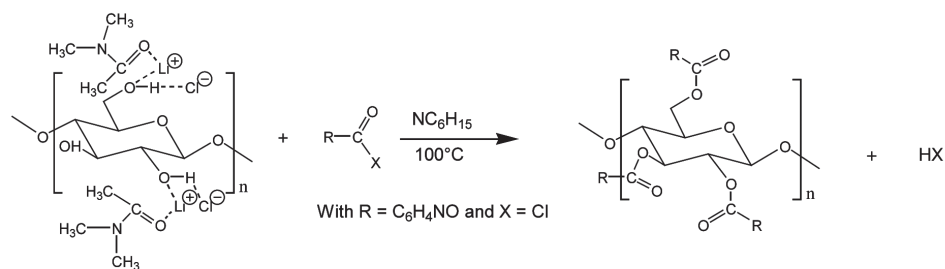


Figure 2. Reaction pathway proposed for the grafting of cellulose

Methylene Blue Adsorption

Kinetic study

Figure 3 shows the adsorption kinetics of methylene blue on both substrates studied:

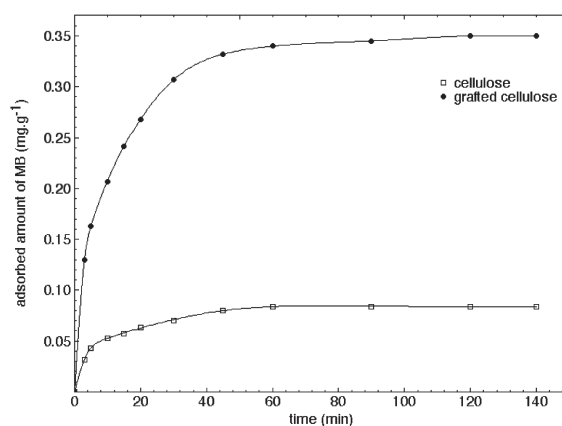


Figure 3. Variation of the amount of MB adsorbed versus time

It appears that the adsorption of MB is faster on modified cellulose than on cellulose. The adsorption equilibrium is reached in 80 minutes. After 140 minutes, the adsorption rate is about 0.35mg.g⁻¹ for the grafted substrate against 0.11mg.g⁻¹ for pure cellulose. This can be related to the presence of an electron rich pyridinic cycle which is able to interact with cationic MB.

From these experimental results we applied different kinetic models to derive a reaction mechanism. These mathematical models have been chosen because they are quite simple and thus commonly used when dealing with the adsorption of organic compounds on various adsorbents.

The kinetic model of adsorption of Lagergreen (Lagergreen 1898) gives, for first order reaction:

$$\log \frac{(Q_e - Q_t)}{Q_e} = -\frac{K_1 \times t}{2.3} \quad (2)$$

While carrying $\log (Q_e - Q_t)$ versus t , a straight line should be obtained whose slope gives K_1 , the rate constant of adsorption (min^{-1}).

For a pseudo second order reaction, the rate constant K_2 is given by the following relation (Ho and Mckay 1999, Ho and Mckay 2000):

$$\frac{t}{Q_t} = \frac{1}{2K_2Q_e^2} + \frac{t}{Q_e} \quad (3)$$

By plotting t/Q_t versus t , K_2 ($\text{g} \cdot \text{min} \cdot \text{mg}^{-1}$) can be derived.

For a second order reaction, the rate constant K_3 results from the following relation (Ho and Mckay, 1999, Ho and Mckay 2000):

$$\frac{1}{Q_e - Q_t} = \frac{1}{Q_e} + K_3 \times t \quad (4)$$

Thus K_3 ($\text{min}^{-1} \cdot \text{g} \cdot \text{mg}^{-1}$) is determined from the chart of $1/(Q_e - Q_t)$ versus t .

With, in all the cases: Q_e : quantity adsorbed at equilibrium ($\text{mg} \cdot \text{g}^{-1}$), Q_t : quantity adsorbed at time t ($\text{mg} \cdot \text{g}^{-1}$), t : time of contact (min).

Even if, we obtain straight lines with the three models, the best suitable model to describe the adsorption of MB on both substrates is the pseudo second order (Fig. 4).

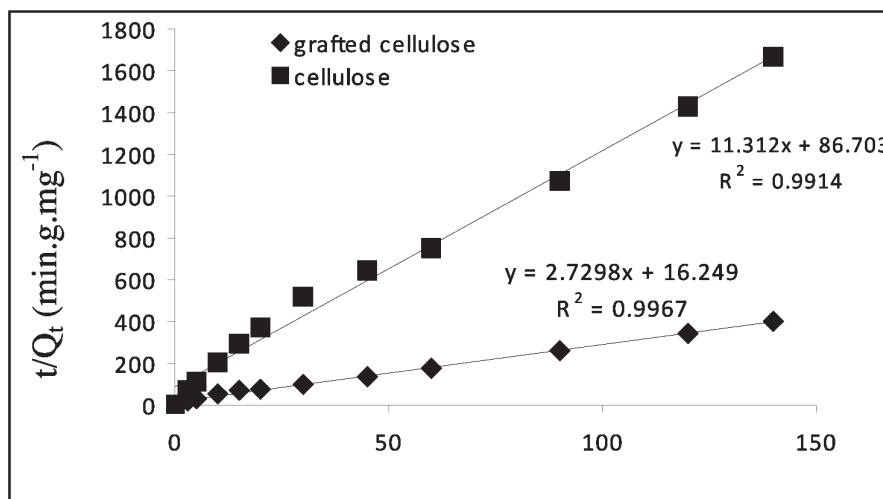


Figure 4. Determination of the rate constant K_2 by applying the pseudo second order kinetic model

The correlation coefficient in this case is close to unity ($R^2 = 0.99$). Table 2 summarizes all these results which are in good agreement with those of the literature. Indeed Uddin *et al.* (2009) showed that the adsorption of MB on cellulose substrates followed a pseudo second order law. Moreover, MB is a cationic dye and the adsorption of cations on such substrates also obeys this law (Shin *et al.* 2007).

Table 2. Kinetic constants and adsorption capacities calculated for different models studied

	First order		Pseudo Second order			Second order		
	K_1	R^2	K_2	Q_e calc.	R^2	K_3	Q_e calc.	R^2
Cellulose	2,052	0,891	0,73	0,088	0,991	3,952	0,0568	0,858
Modified cellulose	0,115	0,962	0,229	0,36	0,996	2,183	0,049	0,931

Adsorption isotherms

The adsorption isotherms of MB on both cellulosic materials were obtained by plotting the amount of dye adsorbed by the substrate (Q_e) as a function of the residual dye concentration in solution at equilibrium (C_e) at 25°C. The contact time between dye and adsorbent was fixed at 6 hours, assuming that equilibrium is reached and that there is no significant variation in the concentration of dye (80 minutes only were necessary with MB solution at $6 \cdot 10^{-5}$ mol.L⁻¹ (19.19 mg.L⁻¹) as previously mentioned). Figure 5 shows the isotherms obtained.

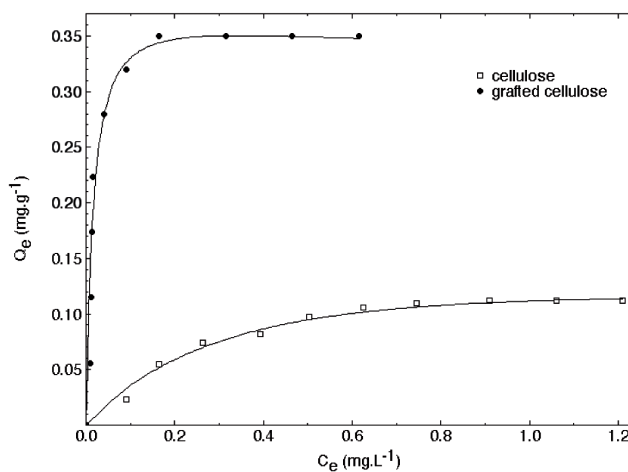


Figure 5. Quantity of adsorbed MB (mg.g⁻¹) on unmodified and grafted cellulose versus dye concentration

Whatever the medium, the same trend is observed: the amount of adsorbed dye increases rapidly and then levels off to reach a plateau. The increase observed at low concentration is significantly faster for grafted cellulose. Saturation is reached at a concentration of only 0.15 mg.L⁻¹ versus 0.9 mg.L⁻¹ for unmodified cellulose giving evidence of the efficiency of grafted substrate for discoloring low concentrated aqueous solutions. The adsorption capacity of the new substrate is about 0.35 mg.g⁻¹ versus 0.112 mg.g⁻¹ for cellulose. Grafting improves therefore the adsorption capacity by a factor of 3.

The plateau observed can only be explained by the saturation of adsorption sites. The isothermal curves obtained are similar to Langmuir-type isotherms, as generally observed for colored effluents from textile industry (Khalfaoui *et al.* 2002).

Thermodynamic Analysis

Adsorption Isotherms Modeling

Modeling of adsorption isotherms is very important and mandatory, as it allows to better understand the mechanisms involved in adsorption. The three most commonly used models are: Langmuir, Freundlich and Jossens derived from Redlich and Perterson (Kumar and Porkodi 2006).

The Langmuir's model is based on the following assumptions: the surface is uniform with no interactions between adsorbed molecules (Langmuir 1916). It presents specific sites for adsorption and the adsorption occurs through the formation of a monolayer of adsorbate. **The Freundlich's model** is based on an empirical equation which expresses a change in adsorption energy with the amount adsorbed (Freundlich 1906). This distribution is explained by the heterogeneity of adsorption sites and this model admits the existence of interactions between adsorbed molecules (Yang 1998). In most cases, the adsorption of dye does not follow a simple law and both previous models are not always convenient. In the case of grafted cellulose, Khalfaoui *et al.* (2002) showed that the adsorption results from the superposition of two mechanisms: on one hand, adsorption and saturation on homogeneous sites according to a curve of Langmuir type and on the other hand, adsorption on sites with heterogeneous energy according to a Freundlich-type isotherm. The model which better describes such a mechanism is that of Jossens (Redlich and Peterson 1959). Our calculated values are summarized in table 3.

Table 3. Maximum amounts adsorbed and different constants calculated for both materials according to studied models with Q_m : maximum adsorption capacity (mg.g^{-1}), C_e : concentration of adsorbate at equilibrium (mg.L^{-1}), K_L : equilibrium constant, characteristic of the adsorbent (L.mg^{-1}), K_F : constant related to the adsorption capacity, K_I and K_J , two constants characteristic of the material, n : heterogeneity factor.

	Langmuir		Freundlich		Jossens		
	$Q_e = Q_m \times \frac{K_L \times C_e}{1 + K_L \times C_e}$		$Q_e = K_F \times (C_e)^{1/n}$		$Q_e = \frac{K_I \times C_e}{(1 + K_J \times (C_e)^n)}$		
	(5)		(6)		(7)		
Samples	Q_m	K_L	n	K_F	K_I	K_J	n
Cellulose	0,141	3,85	1,82	0,124	0,353	2,142	1,40
Grafted Cellulose	0,358	89,9	3,30	0,520	16,606	48,96	1,09

The theoretical curves corresponding to the three modeling systems are represented and compared with experimental results for cellulose (Fig. 6a) and modified cellulose (Fig. 6b).

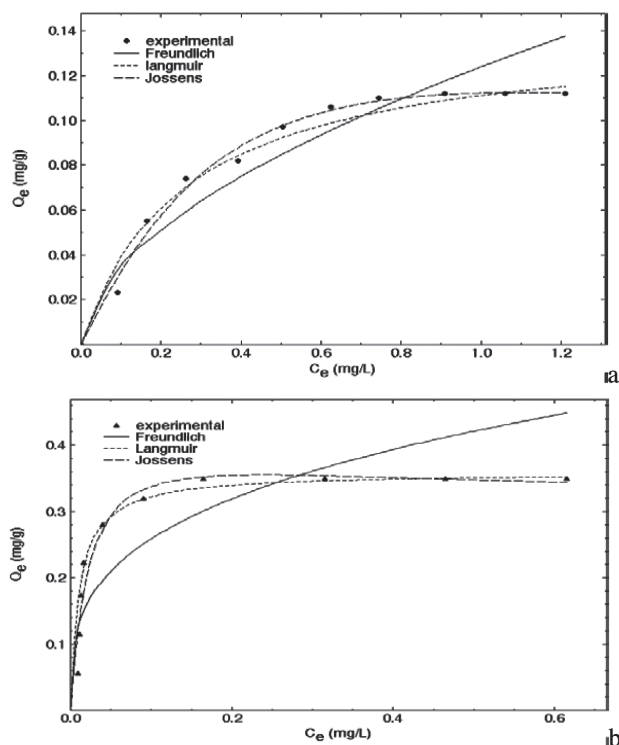


Figure 6. Fittings of different models to the adsorption results obtained for a) unmodified and b) grafted cellulose

It appears that the Freundlich's model is not suitable for modeling the adsorption of MB on both studied substrates. The Langmuir's model fits correctly with the experimental results obtained for grafted cellulose over the whole concentration range. Jossens's model does not give clear improvements since the heterogeneity factor n is close to 1.

Regarding cellulose, Jossens's model seems to be the most representative for the adsorption mechanism even if the factor of heterogeneity remains close to 1. Besides, the Langmuir's model leads to satisfactory results and the slight discrepancy between experimental and theoretical values can be explained by the calculated value of Q_m (0.140 mg.g^{-1}) which is 25 % greater than the experimental value (0.112 mg.g^{-1}).

Generally speaking, it seems that dye adsorption occurs through a monolayer on sites with the same energy. These results seem to be in good agreement with those of the literature (Uddin *et al.* 2009).

The thermodynamic parameters.

The equilibrium constant for MB adsorption onto a substrate is given by the relationship:

$$K_c = \frac{(C_0 - C_e)}{C_e} \quad (8)$$

where C_0 : initial concentration (mg.L^{-1}) and C_e : equilibrium concentration (mg.L^{-1}).

K_c is related to the Gibbs energy of reaction (ΔG°) by $\Delta G^\circ = -R.T.Ln(K_c)$ and therefore: $Ln(K_c) = -\Delta H^\circ/RT + \Delta S^\circ/R$ where ΔH° and ΔS° are respectively the enthalpy and standard entropy of adsorption which can be assessed by plotting $Ln(K_c)$ versus $1/T$. The results are reported in table 4.

Table 4. Thermodynamics associated with adsorption.

Substrate	ΔH° (kJ.mol ⁻¹)	ΔS° (J.mol ⁻¹ K ⁻¹)	ΔG° (kJ.mol ⁻¹) at 25°C
Cellulose	2,500	-1,41	2,921
Grafted Cellulose	-43,091	-109,5	-10,471

On the modified cellulose, the negative value of Gibbs free energy ΔG° indicates that the adsorption process is spontaneous and favored at low temperature (Benturki *et al.* 2008). For this substrate, the standard enthalpy is negative indicating that the process is exothermic. Consequently increasing temperature reduces the adsorption phenomenon and lowers the maximum adsorbed amount Q_m by decreasing ionic interactions between the electron-rich pyridinic ring and cationic dye. If this temperature effect is unfavorable for the adsorption, it can be interesting, regarding the adsorbent media. Saturated substrate could be recycled by desorbing dye at high temperature (by hot washing for example).

The ΔH° value close to -40 kJ.mol⁻¹ shows that the interactions between adsorbate and adsorbing material are strong and that the adsorption is not limited by the diffusional step. The negative sign of ΔS° is in good agreement with the adsorption mechanism i.e. from a random state (dye in solution) to a more ordered one (dye interacting with the substrate).

For cellulose, the adsorption process is endothermic, which is consistent with an increase in the amount adsorbed with temperature. The value of enthalpy shows that the interactions between the substrate and MB are weak. The value of the entropy change suggests that structural variations take place in the adsorbing material and the adsorbate during the adsorption.

CONCLUSION

By using infrared spectroscopy, TGA and elemental analysis, we confirmed that cellulose can be grafted by Nicotinoyl chloride hydrochloride (NCHC) with a degree of substitution DS lower than 1 (0.7). This support is about three times more efficient in the removal of methylene blue from aqueous solution than raw cellulose (adsorption capacity = 0.35 mg against 0.11 mg per gram of solid). The adsorption process depends on the contact time and equilibrium is reached in 80 minutes. A comprehensive study has shown that kinetics is in good agreement with a pseudo second order model. The results show that the adsorbed amount depends on the initial concentration of dye and that the adsorption obeys a Langmuir-type law. Thermodynamics analysis showed that adsorption occurs spontaneously on this modified cellulose but is disadvantaged at elevated temperature since the process is exothermic. Note that this result shows interesting prospects for recycling. Indeed desorption of MB from saturated substrate is made possible by hot washing as we have observed from preliminary experiment. Regarding this aspect, further experiments are scheduled to approach the kinetics of MB liberation as a function of temperature. Besides it would be interesting to investigate the influence of DS on its adsorption capacity, on the kinetics and thermodynamics of this phenomenon. In addition, the synthesized media will now be tested in its ability to trap cations from heavy metals like cadmium Cd and lead Pb

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