

KINETIC AND ISOTHERM MODELING OF METHYLENE BLUE SORPTION ONTO KRAFT PULP MODIFIED BY ACYLATION

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ABSTRACT

Nicotinoyl chloride hydrochloride (NCHC), which possesses a pyridine ring able to adsorb cationic pollutants, was grafted on “Kraft cellulose” under mild conditions. The grafting efficiency was checked by infrared spectroscopy, thermogravimetric analysis (TGA) and elemental analysis. Afterwards Methylene Blue (MB) was used to compare adsorption capacity of unmodified and grafted cellulose. It appeared that retention capacity of modified cellulose is largely enhanced and a pseudo order model can be applied to describe the adsorption kinetics for this dye. Besides, a Langmuir-type isotherm gives a good representation of the adsorption phenomenon indicating the formation of a monolayer. Moreover, we have observed that the reaction is spontaneous and exothermic which could be interesting from a recycling point of view since the dye could be desorbed at elevated temperature.

KEYWORDS: Cellulose, dye adsorption, isotherms, kinetics, modeling.

INTRODUCTION

Dyes and heavy metals contained in textile industry effluents generally have a high stability and a low biodeterioration (Guivarch et al. 2003, Kadirvelu et al. 2003, Jain et al. 2003). Eliminating these substances is consequently necessary and for this purpose, many different methods can be used such as: precipitation, ions exchange, extraction, physico-chemical or biological

treatments. Nevertheless most of these methods are inefficient, because of their weak selectivity and/or their expensive cost (Bagane and Guiza 2000, Benguella and Yacouta-Nour 2009). 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, research focused on the use of cheap and renewable materials and merely cellulose for waste treatment. As a matter of fact, cellulose which is the most abundant polymer on earth (Satge et al. 2002, Chauvelon et al. 1998, Gourson et al. 1999) and its 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 (Li and Bai 2005, Navarro et al. 1999) pollutants. Chemical modification of cellulose (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 NCHC. After characterization of the resulting material, we investigated its adsorption capability towards a current dye i.e. diméthylamino-3.7 phenazthionium, more commonly called MB, by varying experimental conditions (residence time, concentration and temperature). The kinetic and thermodynamic parameters of the reaction have been established.

MATERIAL AND METHODS

The used cellulose is "Kraft cellulose", 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 dried at 80°C in an oven and then chemically modified according to the following protocol:

First cellulose (0.22 g) was put in 10 ml of dimethyl acetamide DMA. The mixture was heated at 120°C for 2 hours and then cooled at 100°C. At this temperature, anhydrous lithium chloride LiCl (0.9 g) was added to the mixture and the reaction proceeded for 4 hours at this temperature. NCHC (C₆H₄ClNO.HCl, 0.9 g) and triethylamine (2mL) 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 K₂CO₃ 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.

Raw and modified celluloses were characterized with:

- 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 spectro-photometer 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 %.

- Thermogravimetric analyzes (TGA): Sample (about 10 mg) was introduced into the combustion boat of a thermobalance SETARAM Setsys TG 12 and heated from 20 to 600°C at 5° C.min⁻¹ under a nitrogen flow (80 mL.min⁻¹).

Adsorption isotherms of MB (biological analyzes grade provided by JANSEN CHIMICA)

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.

After adsorption and once the equilibrium reached, concentrations in residual MB were determined by UV-visible spectrophotometry (SHIMADZU UV-2550) via the BEER-LAMBERT's law and plotted versus the quantity of adsorbed dye.

The quantity of adsorbed dye at time t , Q_t (mg.g⁻¹), is given by the equation 1:

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

where: C_0 is initial concentration of dye (mg.L⁻¹), C_r is residual concentration at time t (mg.L⁻¹), m is mass of adsorbent media (g) and V is volume of solution (L).

To determine 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 was determined in a temperature range from 25 to 60°C.

RESULTS AND DISCUSSION

Grafting evidence

To give evidence of the grafting reaction between cellulose and NCHC, analyses with IR spectroscopy, elemental analysis and thermogravimetry were performed.

Fig. 1 shows the infrared spectra of raw and functionalized cellulose. The large band corresponding to valence vibrations of hydroxyl groups is slightly narrowed and shifted from $3350.\text{cm}^{-1}$ for raw cellulose to $3460.\text{cm}^{-1}$ for treated one. The other bands characteristic for OH groups (1455 and $1205.\text{cm}^{-1}$) are also slightly affected. These modifications are explained by the disappearance of the alcoholic functions and thus of the hydrogen bonds in the starting material. Besides we notice the appearance of a band around $1740.\text{cm}^{-1}$ allotted to the vibration of the carbonyl bond C=O and another one around $1300.\text{cm}^{-1}$ corresponding to C-O stretching vibration in ester functions. A band around $1410.\text{cm}^{-1}$, related to the elongation of a C=N bond, proves the presence of the pyridinic cycle on cellulose after reaction. All these experimental observations show that cellulose was modified and an ester bond was created.

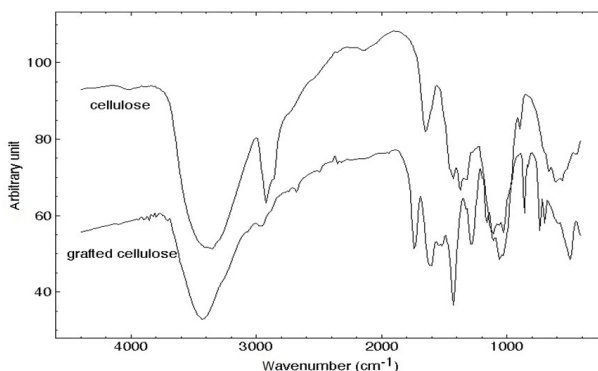


Fig. 1: IR Spectra of unmodified and grafted cellulose.

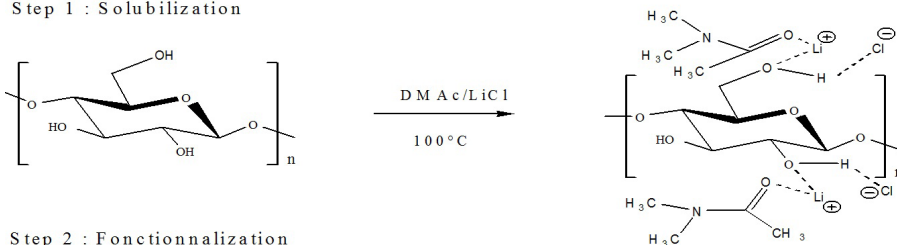
Tab. 1 shows the results of the centesimal analyze carried out on the various substrates. The analysis of raw cellulose leads to percentages of carbon and hydrogen in strong correlation with the empirical formula $C_6H_{10}O_5$.

Tab. 1: Elemental analysis of cellulose before and after reaction.

Samples	C (%)	H (%)	N (%)
Cellulose	44.21	6.26	-
Grafted cellulose	50.00	4.98	3.51

After grafting reaction, we notice that the H/C mass ratio decreases from 0.142 to 0.100 in agreement with expected results. Indeed the modification of cellulose from $C_5H_{10}O_5$ to $C_{11}H_{16}O_6N$ induces a reduction of mass ratio H/C from 0.167 to 0.121. Moreover, the analyses show the presence of nitrogen element that highlights the presence of the pyridinic cycle grafted on cellulose. These results enable us to state that the grafting took place and that the grafting rate can be evaluated close to 1. The reactivity of cellulose towards acyl chlorides being well-known (Krouit et al. 2009), one can suppose the reaction pathway as shown on Fig. 2:

Step 1 : Solubilization



Step 2 : Fonctionnalization

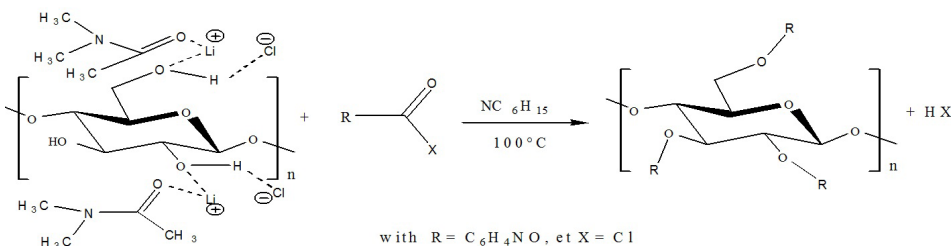


Fig. 2: Reaction pathway proposed for the grafting of cellulose.

Figs. 3 and 4 give the results obtained with TGA and DTG respectively. As indicated on these curves, the cellulose partly loses its adsorbed water around $100^\circ C$ and is degraded between 240 and $360^\circ C$. Fig. 4 highlights a maximum rate of mass loss around $300^\circ C$. These results are in agreement with those reported elsewhere (Kifani-Sahban et al. 1996, Shen and Gu 2009, Rousset et al. 2006) a very similar DTG layout and a residual mass after decomposition, very close to that obtained from our experiments.

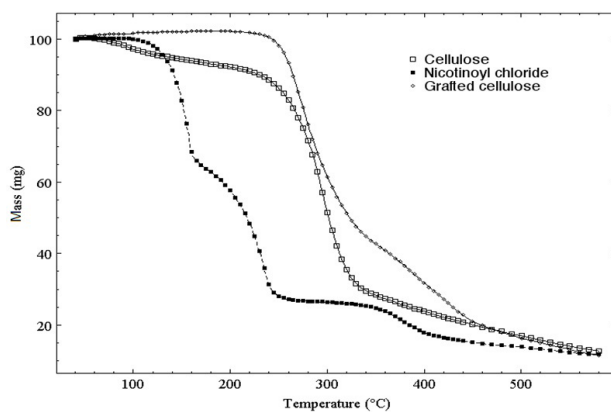


Fig. 3: TGA results for cellulose, NCHC and grafted cellulose.

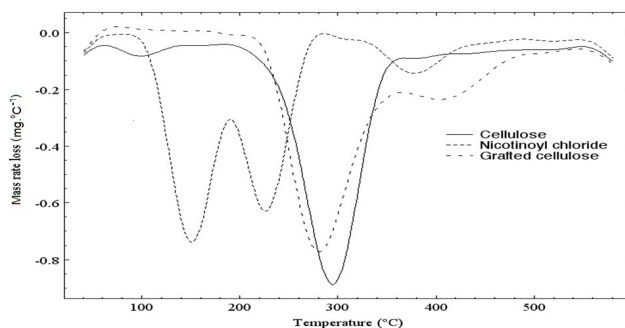


Fig. 4: Derivative TGA curves for cellulose, NCHC and grafted cellulose.

In the case of NCHC, the TGA and DTG curves can be divided into three zones. The first one between 100 and 180°C shows a fast decomposition, DTG peak being centered with 150°C. The second zone ranges from 180 to 250°C with a maximum rate of mass loss to 225°C. The third zone between 340 and 460°C corresponds to slower processes of decomposition, with the DTG peak being centered at 380°C. On our knowledge, literature does not give any result on the decomposition of this compound and the interpretation of its spectrum is not easy.

The TGA and DTG layouts of treated cellulose basically differ from the spectra of the separate components. DTG peaks observed at low temperature for NCHC (150°C and 225°C) and cellulose (100°C) disappeared. The DTG spectrum of the final compound presents only two main peaks: the first one is observed at 280°C i.e. at a lower temperature than the decomposition temperature of raw cellulose (300°C), the second one around 400°C, at a higher temperature than the final decomposition temperature of NCHC (380°C). Even if interpretation remains difficult, we observe an important chemical modification of the initial substrates and especially the formation of a chemical bond between these molecules, confirming that the grafting effectively took place.

Methylene blue adsorption

Fig. 5 shows the adsorption kinetics of methylene blue on both substrates studied: Cellulose and grafted Cellulose.

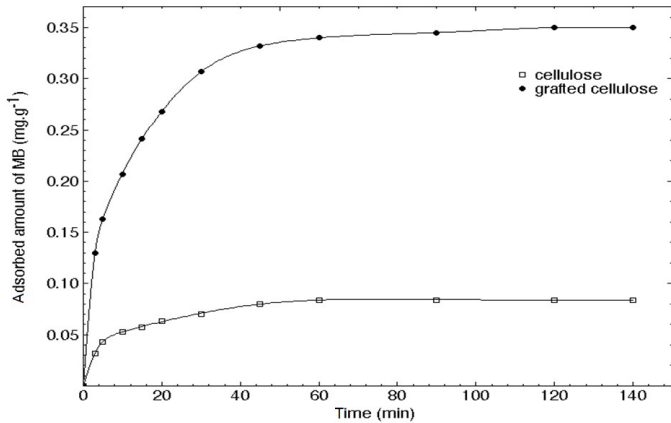


Fig. 5: Variation of the amount of MB adsorbed versus time.

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 0.35 mg.g⁻¹ for the grafted substrate against 0.11 mg.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. Different mathematical kinetic models were applied to propose a reaction mechanism. For first order reaction, the model of Lagergreen (Lagergreen 1898) gives :

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

While carrying log (Q_e-Q_t) versus t (Fig. 6), a straight line should be obtained whose slope gives K₁, the rate constant of adsorption (min⁻¹).

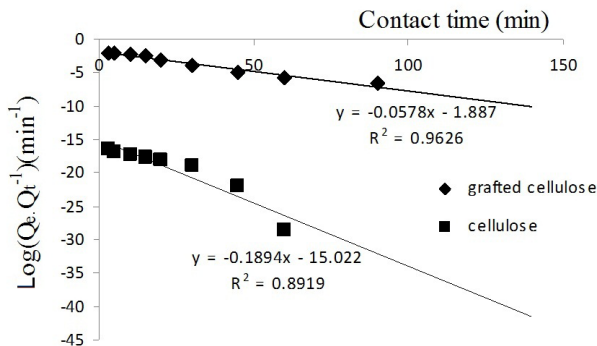


Fig. 6: Determination of the rate constant K₁ by applying the first order kinetic model.

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

$$\frac{t}{Q_e} = \frac{1}{2K_2Q_e^2} + \frac{t}{Q_e} \tag{3}$$

By plotting $t.Q_t^{-1}$ versus t (Fig. 7), K_2 ($g.min.mg^{-1}$) can be derived. For a second order reaction, the rate constant K_3 results from the following relation (Ho and McKay 1999, 2000):

$$\frac{1}{Q_e - Q_t} = \frac{1}{Q_e} + K_3 \times t \tag{4}$$

Thus K_3 ($min^{-1}.g.mg^{-1}$) is determined from the chart of $1/(Q_e - Q_t)^{-1}$ versus t (Fig. 8).

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

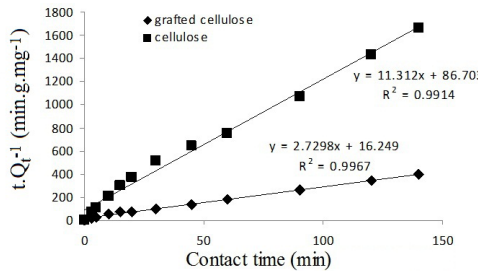


Fig. 7: Determination of the rate constant K_2 by applying the pseudo second order kinetic model.

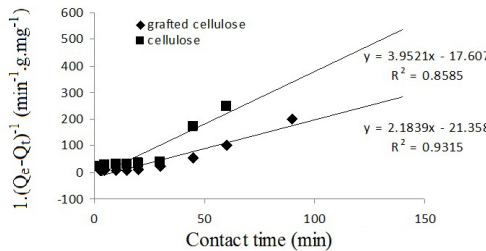


Fig. 8: Determination of the rate constant K_3 by applying the second order kinetic model.

Even if we obtained straight lines with the three models (Figs. 6,7,8), the best suitable model to describe the adsorption of MB on both substrates is the pseudo second order. The correlation coefficient in this case is close to unity ($R^2 = 0.99$). Tab. 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).

Tab. 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

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 (It was observed that 80 minutes only were necessary with a MB solution at $6 \cdot 10^{-5}$ mol.L⁻¹).

Fig. 9 shows the isotherms obtained. 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.

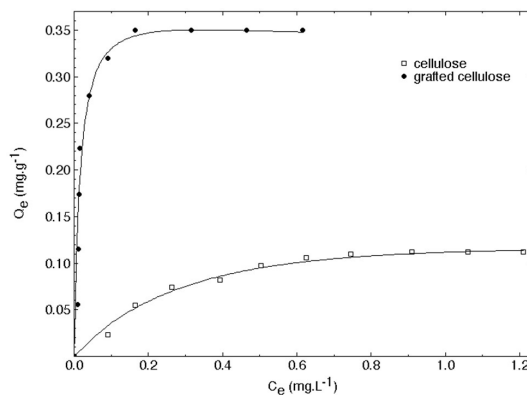


Fig. 9: Quantity of adsorbed MB (mg.g⁻¹) on unmodified and grafted cellulose versus dye concentration.

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

Adsorption isotherms modeling and thermodynamic parameters

Modeling of adsorption isotherms is very important and mandatory, as it allows better understanding the mechanisms involved in adsorption. The three most commonly used models

are: Langmuir, Freundlich and Jossens derived from Redlich and Peterson. (Kumar and Porkodi 2006).

According to Langmuir's model, adsorption occurs through the formation of a monolayer of adsorbate and leads to the following equation 5:

$$Q_e = Q_m \times \frac{K_L \times C_e}{1 + K_L \times C_e} \quad (5)$$

where: Q_m is maximum adsorption capacity (mg.g^{-1}), K_L is equilibrium constant, characteristic of the adsorbent (L.mg^{-1}), depending on temperature and operating conditions and C_e is concentration of the adsorbate at equilibrium (mg.L^{-1}).

The Freundlich's model which application is limited to diluted media does not provide an upper limit to the adsorption and admits the existence of interactions between adsorbed molecules (Yang 1998). It is based on an empirical equation (6) as follows:

$$Q_e = K_F \times (C_e)^{1/n} \quad (6)$$

where: C_e is concentration of adsorbate at equilibrium (mg.L^{-1}), K_F is constant related to the adsorption capacity and n is heterogeneity factor. 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 Langmuir's model 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. The equation (7) of the Jossens's isotherm is written as:

$$Q_e = \left(\frac{K_I \times C_e}{1 + K_J \times (C_e)^n} \right) \quad (7)$$

where: n , K_I and K_J , three constants characteristic of the material which are determined from an iterative calculation.

Our calculated values according to these three models are summarized in Tab. 3 while the theoretical curves corresponding to the three modeling systems are represented and compared with experimental results for cellulose (Fig. 10) and modified cellulose (Fig. 11).

Tab. 3: Maximum amounts adsorbed and different constants calculated for both materials according to studied models.

	Langmuir		Freundlich			Jossens	
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

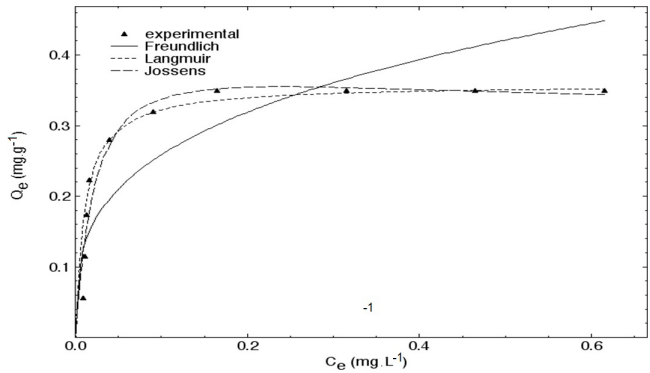


Fig. 10: Fittings of different models to the adsorption results obtained for grafted cellulose.

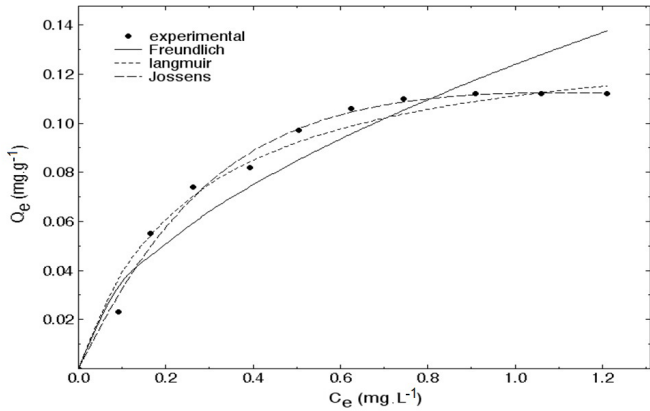


Fig. 11: Fittings of different models to the adsorption results obtained for unmodified cellulose.

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 ($0.140 \text{ mg}\cdot\text{g}^{-1}$) which is 25 % greater than the experimental value ($0.112 \text{ mg}\cdot\text{g}^{-1}$).

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

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 is initial concentration (mg.L^{-1}) and C_e is 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 Tab. 4.

Tab. 4: Thermodynamics associated with adsorption.

Substrate	ΔH° (kJ.mol^{-1})	ΔS° ($\text{J.mol}^{-1}\text{K}^{-1}$)	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 adsorbent 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 BM are weak. The value of the entropy change suggests that structural variations take place in the adsorbing material and the adsorbent during the adsorption.

CONCLUSIONS

By using infrared spectroscopy, TGA and elemental analysis, we confirmed that cellulose can be grafted by NCHC. This support is about three times more efficient in the removal of MB 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 showed that kinetics is in good agreement with a pseudo second order model. The results showed 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. 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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