

Full Length Research Paper

Extraction of dyes by succinic anhydride modified cotton

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Accepted 15 April, 2010

Chemically modified cotton has been prepared by the functionalization reaction with succinic anhydride and have been used to eliminate two dyes, basic yellow XGL 250% and the dispersed marine 5RN, by adsorption. The tests showed that the efficiency of extraction was 100% for yellow basic dye and 70% for the marine dispersed dye. The equilibrium time was found to be 60 min for 100 mg/L dye initial concentrations for an adsorbent dose of 0.01 mg/L. The models of adsorption of Langmuir and Generalized fits well the adsorption of the dyes on the support. The obtained results suggest that chemically modified cotton could be of valuable interest for the removal of different dyes from industrial textile waste water.

Key words: Adsorption, cellulose, cotton, dyes removal, isotherm, grafting, scanning electron microscopy.

INTRODUCTION

In the last decades, elimination of dyes, from industrial textile waster waters is a major challenge for scientists worldwide.

The physico-chemical and biological treatment methods used currently in the industrial textile for removal of dyes from wastewaters include flocculation and coagulation (Kacha et al., 1997), membrane filtration (Buckley, 1992), ozonation (Kunz et al., 2001; Churchley, 1994; Konsowa, 2003) and adsorption by activated carbon (Meshko et al., 2001; Pelekani et al., 2000; Walker et al., 2000). Although these processes have high efficiencies, but their relatively high price, high operating costs and problems with regeneration, hamper their large scale application. Therefore, these methods less adapted for developing countries such as Morocco.

Alternative methods such as decoloration processes are simple and cost effective. The adsorption is becoming method of high interest for the depollution of wastewaters

textile. In this way several studies have proposed natural materials locally available, renewable, and low costly such as the clays (Bagane et al., 2000), silica (Ahmed et al., 1994), wood (Baoub et al., 2000), corncob (El-Geundi, 1991), chitosan (Wong et al., 2004), fly ash (Mohan et al., 2002), recycled alum sludge (Basibuyuk et al., 2003), slag (Gupta et al., 2003), calcined alunite (Özacar et al., 2003), alumina and kaolinite (Harris et al., 2001), perlite (Dogan et al., 2003), sepiolite (Rytwo et al., 2002), Na⁺-montmorillonte (Gemeay et al., 2002), saponite (Miyamoto et al., 2000), zeolite (Meshko et al., 2001), and modified diatomite (Majeda et al., 2004).

The aim of the study is to extract the dyes by adsorption on cellulosic materials such as cotton, and raw materials from the textile industry. These natural polymers are modified by introduction of a carboxylic ester group to increase their efficiency. The process of adsorption has been tested on two types of dyes; basic yellow XGL 250% and dispersed marine 5RN. Several parameters have been studied: pH of the middle, time of contact and initial concentration of dyes. The equilibrium sorption capacity of dyes on the modified cotton was studied using various isotherm equations.

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Table 1. Effect of pH on the dispersed marine 5RN absorbance.

pH	λ_{\max}	Ab	Observation
2.3	550	0.33	Clear red
3.35	552	0.415	Purple bruise
5.75	575	0.502	Purple
6.56	572	0.608	Purple
7.4	570	0.584	Purple
8.01	570	0.597	Purple
9.88	570	0.605	Purple

MATERIALS AND METHODS

Support of adsorption

The used material is Syrian cotton fibre. For purification of the initial material, it was subjected to a mild alkaline scouring (2% NaOH and 0.2% of a wetting agent) for 5 h at 100°C, followed by washing with distilled water and drying in air at room temperature.

The chemical modification of the cellulosic support is achieved in two steps (Elbariji et al., 2005):

1. Preparation of sodium hydroxide-treated cotton (NaOH–Cotton).
2. Reaction of grafting consist a mixed NaOH–Cotton with pyridine and succinic anhydride at 90°C for 24 h was carried out.

The study of surface morphology of untreated and grafted cotton was done using JEOL-JSM-5500 Scanning electron Microscope (SEM) configured with a Noran energy dispersive X-ray analyzer (EDS system) operated a 30 KeV acceleration potential.

Dyes tested

The dyes were chosen for their extended regional use in the textile industry. The suppliers do not publish their chemical structure and their features such as the purity.

1. Basic yellow XGL 250% (B.Y), provided by a company of Moroccan textile is a cationic dye. The influence of pH on the displacement of wavelength to the maximum absorption λ_{\max} is negligible (Tahiri et al., 2003) ($\lambda_{\max} = 436$ nm).
2. Dispersed marine 5RN (D.M), is a dispersed dye. The effect of pH on the displacement of the wavelength is summarized in Table 1.

Solutions with initial concentrations (C_i) were put in contact with the support with a ratio mass/volume equal to 10 g/L. The procedure of adsorption was studied in a static system.

The quantity of fixed dye on the support (Q_a) and the output of extraction (R%) was calculated using the following equations:

$$Q_a = \frac{C_i - C_r}{m} \times V \quad R\% = \frac{C_i - C_r}{C_i} \times 100$$

Where Q_a is the amount of absorbed dyes (mg/g); C_i and C_r are the initial and residual concentration (mg/L), respectively; V is the volume of dyes aqueous solution (L); m is the dose of support (g).

The equilibrium concentrations of each solution were measured spectrophotometerally using a spectrophotometer Shimadzu UV-2101PC at the λ_{\max} value. All measurement were recorded at the wavelength corresponding to maximum absorbance, λ_{\max} which is 436 nm for Basic yellow XGL 250% and 572 nm for Dispersed marine 5RN.

RESULTS AND DISCUSSION

Preparation of support

The support was grafted by introduction of carboxylic ester functions in the structure of cellulose that allowed us to obtain a weight gain of up to 140% (Elbariji et al., 2005) as follows in the reaction (Figure 1).

Weight Percent Gain (WPG) was calculated according to the formula:

$$WPG\% = \frac{m_i - m_o}{m_o} \times 100$$

Where m_o is the initial oven dried mass of the substrate before chemical modification and m_i the oven dried mass of the substrate after chemical modification.

The grafting amount on to carboxylic ester functions in the fibers was comparable with the ungrafted fibers. This can be expected because of the chemical and morphological similarities between these two substrates.

The grafted fibers were studied by SEM. Ungrafted and grafted fibers are shown in Figure 2a. A layer of the grafted polymer can be observed on the grafted fiber shown in Figure 2b, the grafted layer nearly homogeneously covers completely the surface of the fibers. A similar result was already described in the literature by Cuiyu et al. (2007).

Adsorption experiments

The affinity study of the two dyes onto the grafted and ungrafted cotton, were performed by exploratory tests of adsorption in the aqueous phase using the batch method, for a ratio of the support mass/volume of solution equal to 10 g/L, initial concentration $C_i = 100$ mg/L of every dyes. The mixture was stirred mechanically for as 2 h at the ambient temperature. The obtained results are summarized in Table 2.

We note that, the ungraft material does not adsorb any of the two tested dyes. On the contrary, high adsorption capacities are obtained for dyes D.M 5RN and B.Y XGL 250% on grafted cotton. The presence of carboxylic acid groups at the surface of the support increases its adsorption capacity.

Also, we observed that extraction with cotton fibers and cotton powder to give the same results. The granulometry of the support doesn't have a big influence on the output of extraction. This finding can be explained by the fact that cotton doesn't constitute a compact system but rather present a porous character.

Effect of pH

Some tests were performed for different pH values in the

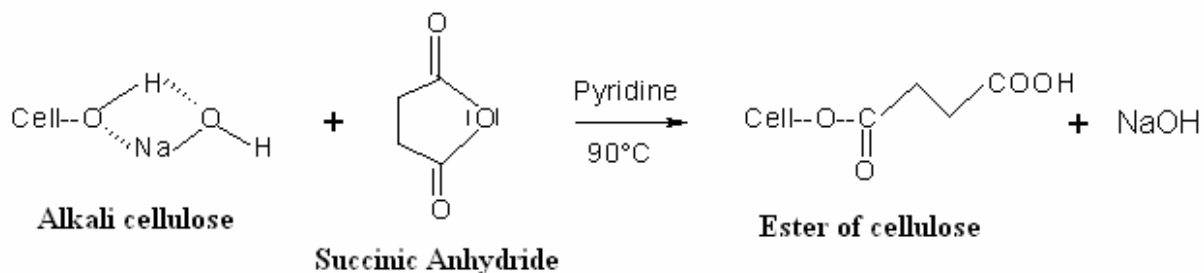


Figure 1. Reaction of grafting on the cellulose.

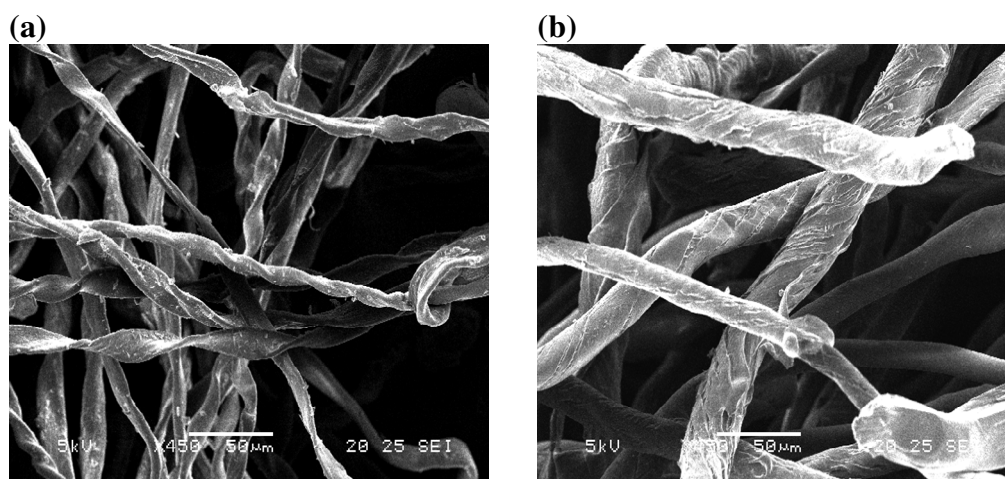


Figure 2. Scanning electron micrographs (SEM) of (a) fibre ungrafted and (b) grafted fibre.

Table 2. Adsorption of dyes onto the different supports.

Supports	D.M 5RN		B.Y XGL 250%	
	Cr (mg/L)	R (%)	Cr (mg/L)	R (%)
Grafted cotton powder	24.09	75.91	3.99	96.01
Grafted cotton fiber	27.23	72.77	1.4	98.60
Cotton fiber ungrafted	99.83	0.17	34.28	65.72

same experimental conditions ($C_i = 100$ mg/L and a ratio support mass /volume equal to 10 g/L). The pH of each solution was adjusted by adding diluted or concentrated H_2SO_4 and NaOH solutions, before mixing the support suspension. The value pH primarily affects the degree of ionization of the dyes and the surface properties of the adsorbents (Iqbal et al., 2007). Figure 3 shows that the colour removal was maximum and unaffected when the initial pH of the dye solution was in the range 2.5 - 10, and thus the pH of the system (dye solution + grafted cotton) remained 4 ± 0.5 . The percentage removal of B.Y

was 95 - 98% and 69 - 70% for D.M. Ion exchange mode of adsorption might be operative (Garg et al., 2003), the surface of the cotton modified is yet the negative charge. Therefore, the negative charge on the adsorbing surface of cellulose clearly creates a very favourable situation for the adsorption of dyes on grafted cotton. These observations are similar to the adsorption of methylene blue and azo reactive dyes by metal hydroxide sludge (Weng et al., 2006; Netpradit et al., 2004). However, cotton grafted can be easily applied in a wide range of initial pH values, without pH adjustment.

Adsorption kinetics

The kinetic survey of the adsorption permits the assessment of the necessary contact time for the establishment of the equilibrium.

The adsorption kinetics of the basic yellow XGL 250% and dispersed marine 5RN on the modified cotton was evaluated at 25°C, using initial dye concentration of 100 mg/L and support mass/volume at 10 g/L (Figure 4).

Figure 4 shows that the equilibrium of adsorption is reached after one hour with approximately 99% efficiency

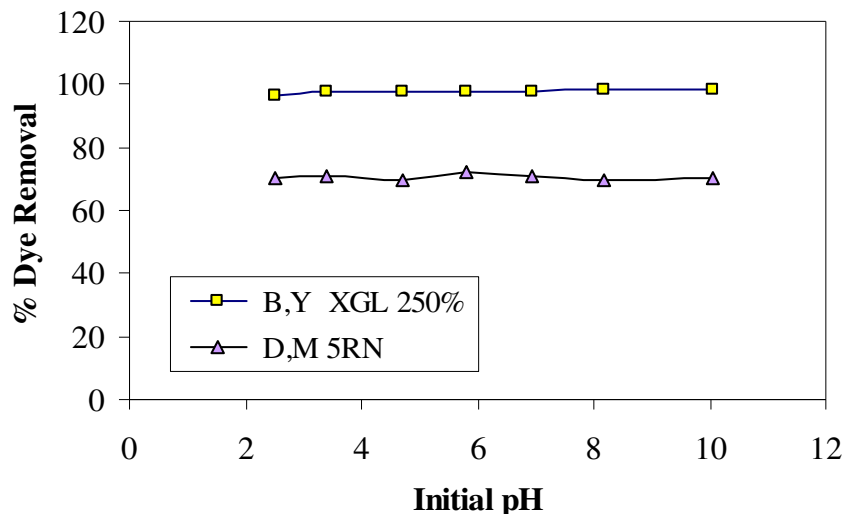


Figure 3. Effect of pH on the adsorption of the dyes, Contact time, 2 h; temperature, 25°C; initial concentration, 100 mg/L; adsorbent dose, 10 g/L.

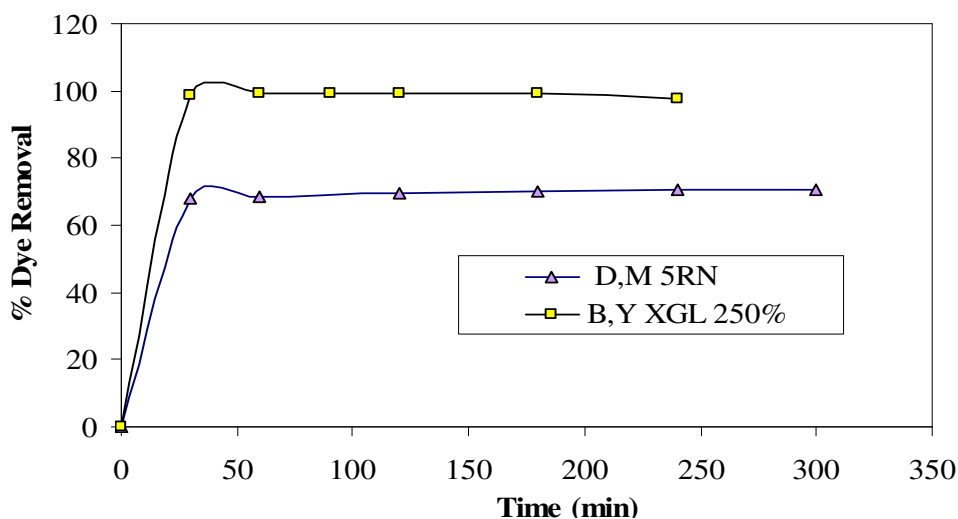


Figure 4. Kinetic of adsorption of the dyes on the grafted cotton, $C_i = 100$ mg/L.

of the basic yellow and 68.55% of the dispersed marine indicating a high affinity between the dyes and the modified cotton. Following this phase, the adsorption process slows, suggesting a gradual reaching of equilibrium, possibly due to intraparticle diffusion of dyes molecules. Finally, the saturation is reached, showing the final equilibrium, beyond which no further adsorption takes place after approximately 60 min. Similar results were reported for various dye adsorption by other adsorbents (Namasivayam et al., 2002; Thangamani et al., 2007). Equilibrium time is one of the most important considerations in the design of water and wastewater treatment systems because it influences the size of the reactor, thereby the material economics (Deepa et al., 2006).

Adsorption isotherms

The adsorption isotherms were investigated at ambient temperature (25°C), for initial concentrations (C_i) of dye varying between 50 - 5000 mg/L for B.Y and between 20 - 1000 mg/L for D.M. The mass concentration of grafted cotton used set to be fixed to 10 g/L during 1 h of stirring. The adsorption capacity at equilibrium Q_e (mg/g) versus equilibrium concentrations (C_e) plots were drawn in Figures 5 - 6, respectively for basic yellow and dispersed marine adsorption on modified cotton.

The isotherm rises sharply in the initial stages for low C_e and Q_e values, indicating that there are plenty of readily accessible sites (Crini et al., 2006). A limit value Q_e is obtained for each dye; high adsorption capacities

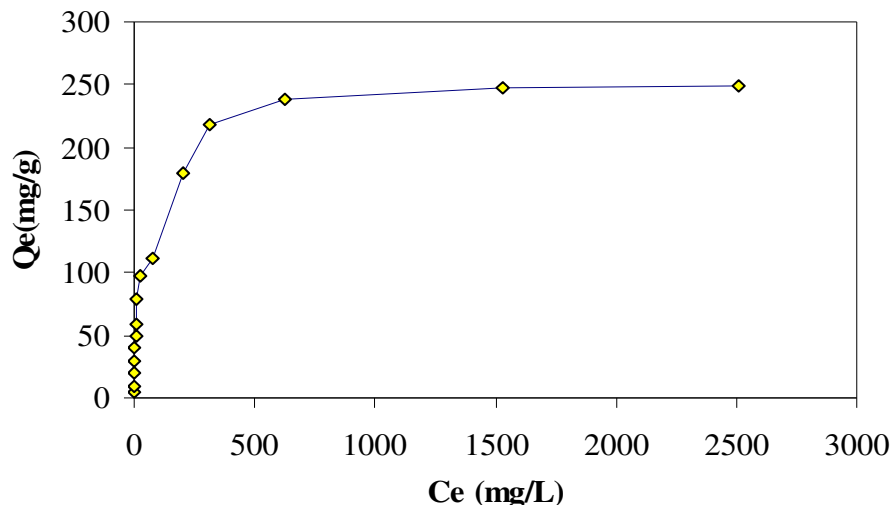


Figure 5. Adsorption isotherm for the adsorption of basic yellow dye at ambient temperature; contact time, 1 h; adsorbent dose, 10 g/L.

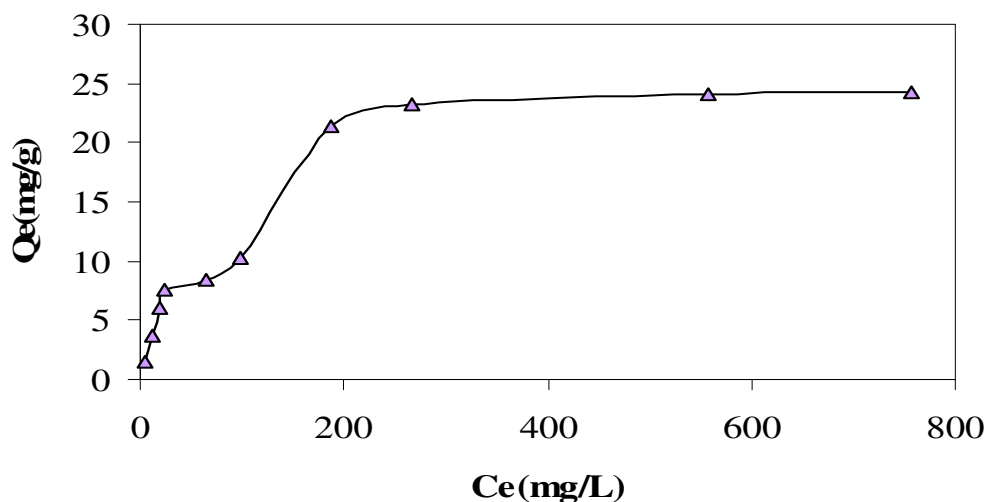


Figure 6. Adsorption isotherm for the adsorption of dispersed marine dye at ambient temperature; contact time, 1 h; adsorbent dose, 10 g/L.

are observed for B.Y (249 mg/g) and lower adsorption is exhibited by D.M (24.27 mg/g).

There are several isotherm equations available for analyzing experimental sorption equilibrium data, including the Freundlich, the Langmuir, the Temkin, and the generalized models.

The distribution of dye between the adsorbent and the solution at equilibrium, has been expressed using various equations.

The theoretical Langmuir isotherm (Langmuir, 1918) equation can be represented as:

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

Where K_L ($L \text{ mg}^{-1}$) is the Langmuir isotherm constant related to the energy of adsorption and Q_m (mg/g) the maximum adsorption capacity of the adsorbent corresponding to complete monolayer coverage on the surface. These parameters are evaluated through linearization of Equation (2):

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{1}{Q_m} C_e \quad (2)$$

The essential characteristics of Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant called the separation factor or equilibrium parameter RL (Mall et al., 2005) which describes the type of

isotherm and is defined by:

$$R_L = \frac{1}{(1 + K_L C_o)} \quad (3)$$

If,
 $R_L > 1$, unfavorable;
 $R_L = 1$, linear;
 $0 < R_L < 1$, favorable;
 $R_L = 0$, irreversible.

The Freundlich isotherm (Freundlich, 1926), can be used for non-ideal sorption that involves heterogeneous surface energy systems and is expressed by the following equation:

$$Q_e = K_f \cdot C_e^{1/n} \quad (4)$$

The capacity constant K_f (l/g) and $1/n$ is indicative of the energy or intensity of the reaction. The magnitude of the exponent n gives an indication of the favorability and capacity of the adsorbent / adsorbate systems. A linear form of the Freundlich expression can be obtained by taking logarithms of Equation (5):

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy (Kim et al., 2004; Temkin et al., 1940). The Temkin isotherm has been used in the following form:

$$Q_e = B \ln(K_T C_e) \quad (6)$$

A linear form of Equation (6) can be expressed as:

$$Q_e = B \ln K_T + B \ln C_e \quad (7)$$

Where $B = RT/b$ and K_T are the Temkin isotherm constants, T is the absolute temperature in K, R the universal gas constant, 8314 J/mol. K_T is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy and constant B is related to the heat of adsorption. A plot of Q_e versus $\ln C_e$ enables the determination of the isotherm constants K_T and B .

The generalized adsorption isotherm has been used in the following form (Kargi, 2004; Crini et al., 2006):

$$Q_e = Q_m \frac{C_e^{nb}}{K + C_e^{nb}} \quad (8)$$

A linear form of this equation is:

$$\ln \left(\frac{Q_m}{Q_e} - 1 \right) = \ln K - n_b \ln C_e \quad (9)$$

Where K is the saturation constant (mg L^{-1}); n_b is the cooperative binding constant; Q_m is the maximum adsorption capacity of the adsorbent (mg/g); Q_e (mg/g) and C_e (mg/L) are the equilibrium dye concentrations in the solid and liquid phase, respectively. A plot of the equilibrium data in form of $\ln [(Q_m/Q_e)-1]$ versus $\ln C_e$ gives K and n_b constants.

Parameters related to each isotherm were determined by using linear regression analysis and the square of the correlation coefficients (R^2) have been calculated. A list of the parameters obtained together with R^2 values is provided in Table 3.

A comparison of the experimental isotherms with the adsorption isotherm models showed that the Freundlich equation represented the poorest fit of experimental data as compared to the other isotherm equations with less correlation coefficients (R^2) of 0.8219 and 0.9088 for B.Y and D.M, respectively. It has been found that the best fitted isotherm equation was Langmuir with high correlation coefficients (R^2) 0.999 and 0.9786 for B.Y and D.M. The R_L values are found in the range of 0.009 - 0.468 and 0.085 - 0.822 for B.Y and M.D, respectively, showing favorable adsorption (Table 3). The maximum quantity (Q_m) of the experimental value (248.99; 24.27 mg/g) is in the good agreement between the calculated value (256.41; 27.77 mg/g) respectively for B.Y and D.M.

Figure 7 shows a comparison of adsorption isotherms of the experimental results with four adsorption isotherms.

As can be seen, the best isotherm model that fits the experimental data in the entire range of concentration was the Generalized and Langmuir isotherm models. The weakness of the Langmuir isotherm is highlighted in the region of monolayer coverage (Baouab et al., 2001).

The Freundlich isotherm does not appear to be able to characterize the adsorbent/adsorbate system in all the range of concentrations. But the Temkin isotherm is in good agreement with experimental data at high concentration.

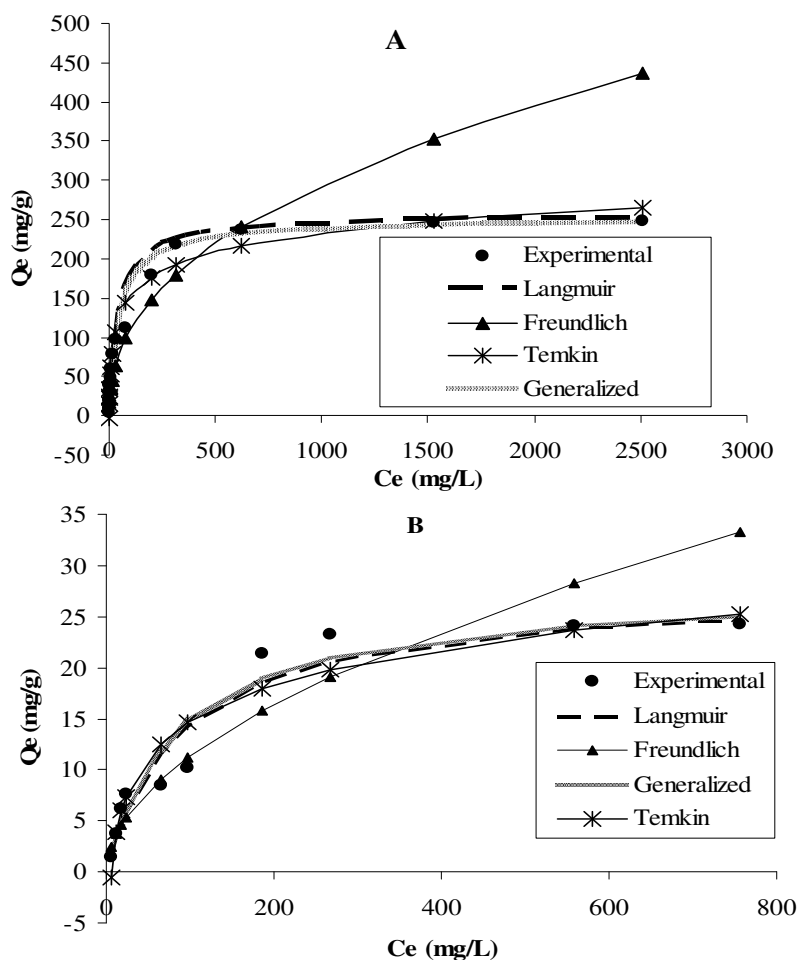
Conclusion

Nature cotton is effective after the grafting of the carboxylic acid function for the removal of the textile dye from aqueous solution. High adsorptive capacities are observed for the adsorption of dyes, namely, 249 and 24.27 mg dye g^{-1} cotton modified for basic yellow XGL 250% and the dispersed marine 5RN, respectively. Equilibrium sorption was achieved in about 60 min.

A good agreement was obtained by comparison of the Langmuir and generalized isotherms with experimental results. All isotherms were shown to be favorable and the

Table 3. Summary of the isotherm constants and the correlation coefficients for different isotherms equations.

Model equations	parameters	Basic yellow XGL 250%	Dispersed marine 5RN
Langmuir isotherm	Q _m (mg/g)	256.41	27.77
	K _L (L.mg ⁻¹)	0.023	0.011
	R ²	0.9990	0.9786
	r _L	0.009 - 0.468	0.085 - 0.822
Freundlich isotherm	K _f	15.373	0.978
	n	2.340	1.880
	R ²	0.8219	0.9088
Temkin isotherm	B	35.179	5.219
	K _T (L/mg)	0.752	0.168
	R ²	0.9773	0.9171
Generalized isotherm	K (mg/L)	28.18	85.36
	n _b	0.8769	0.9979
	R ²	0.9661	0.9481

**Figure 7.** Comparison of theoretical isotherms with experimental results for adsorption of (A) B.Y and (B) D.M.

effect of the carboxylic-cotton content was significant. It could be concluded that cellulosic material is recommended as effective and a cheap adsorbent for removal of dye from textile effluents.

REFERENCES

- Ahmed MN, Ram RN (1994). Removal of basic dye from waste-water using silica as adsorbent, *Environ. Pollut.*, 77(1): 79-86.
- Bagane M, Guiza S (2000). Removal of a dye from textile effluents by adsorption, *Ann. Chim. Sci. Mat.*, 25: 651-626.
- Baouab MHV, Gauthier R, Gauthier H, Rammah MB (2001). Cationized sawdust as ion exchanger for anionic residual dyes, *J. Appl. Polym. Sci.*, 82: 31-37.
- Baoub MHV, Gauthier R, Gauthier H, Chabert B, Rammah M (2000). Immobilization of residual dyes onto ion-exchanger cellulosic materials. *J. Appl. Polym. Sci.*, 77: 171-183.
- Basibuyuk M, Forster CF (2003). An examination of the adsorption characteristics of a basic dye (Maxilon Red BL-N) on to live activated sludge system, *Process Biochem.*, 38(9):1311-1316.
- Buckley CA (1992). Membrane technology for the treatment of dye house effluents, *Water Sci. Technol.*, 25: 203-209.
- Churchley JH (1994). Removal of dyewaste colour from sewage effluent: The use of a full scale ozone plant. *Water Sci. Technol.*, 30(3): 275-284.
- Crini G, Peindy HN (2006). Adsorption of C.I. basic blue 9 on cyclodextrin-based material containing carboxylic groups, *Dyes Pigments*, 70: 204-211.
- Cuiyu Yin, Jianbo Li, Qun Xu, Qi Peng, Yabei Liu, Xinyuan S (2007). Chemical modification of cotton cellulose in supercritical carbon dioxide: Synthesis and characterization of cellulose carbamate, *Carbohydr. Polym.*, 67(2): 147-154.
- Deepa KK, Sathishkumar M, Binupriya AR, Murugesan GS, Swaminathan K, Yun SE (2006). Sorption of Cr (VI) from dilute solutions and wastewater by live and pretreated biomass of *Aspergillus flavus*. *Chemosphere*, 62: 833-840.
- Dogan M, Alkan M (2003). Adsorption kinetics of methyl violet onto perlite, *Chemosphere*, 50(4): 517-528.
- Elbariji S, Elamine M, Eljazouli H, Kabli H, Lacherai A, Ait Addi E, Albourine A (2005). Elaboration of grafted celluloses as ion exchangers from natural materials. Application to the metallic extraction. *Phys. Chem. News*, 23: 96-102.
- El-Geundi MS (1991). Colour removal from textile effluents by adsorption techniques. *Water Res.*, 25: 271-273.
- Freundlich H (1926). *Colloid and Capillary Chemistry*, translated from the 3rd German Edn. by H.S. Hat_eld, Methuen, London, pp. 61-66
- Garg VK, Gupta R, Yadav AB, Kumar R (2003). Dye removal from aqueous solution by adsorption on treated sawdust, *Bioresour. Technol.*, 89: 121-124.
- Gemeay AH, El-Sherbiny AS, Zaki AB (2002). Adsorption and kinetic studies of the intercalation of some organic compounds onto Na-montmorillonite. *J. Colloid Interface Sci.*, 245(1): 116-125.
- Gupta VK, Suhas IA, Mohan D (2003). Equilibrium uptake and sorption dynamics for the removal of a basic dye (basic red) using low-cost adsorbents, *J. Colloid Interface. Sci.*, 265 (2): 257-264.
- Harris RG, Wells JD, Johnson BB (2001). Selective adsorption of dyes and other organic molecules to kaolinite and oxide surface, *Colloid Surface A*, 180 (1-2): 131-40.
- Iqbal MJ, Ashiq MN (2007). Adsorption of dyes from aqueous solutions on activated charcoal, *J. Hazard. Mater.*, 139: 57-66.
- Kacha S, Ouali MS, Elmeh S (1997). Elimination des colorants des eaux résiduaires de l'industrie textile par la bentonite et des sels d'aluminium, *Rev. Sci. Edu.*, 2 : 233-248.
- Kargi F, y Ozmihci S (2004). Biosorption performance of powdered activated sludge for removal of different dyestuff, *Enzyme Microb. Tech.*, 35: 267-271.
- Majeda AM, Khraisheh Y, Al-degs S, Mamin WAM (2004). Remediation of wastewater containing heavy metals using raw and modified diatomite. *Chem. Eng. J.*, 9(2): 177-184.
- Kim Y, Kim C, Choi I, Renggaraj S, Yi J (2004). Arsenic Removal Using Mesoporous Alumina Prepared via a Templating Method, *Environ. Sci. Technol.*, 38(3): 924-931.
- Konsowa AH (2003). Decolorization of wastewater containing direct dye by ozonation in a batch bubble column reactor, *Desalination and the Environment: Fresh Water All*, 158: 233-240.
- Kunz A, Reginatto V, Duran N (2001). Combined treatment of textile effluent using the sequence *Phanerochaete chrysosporium*-ozone. *Chemosphere*, 44: 281-287.
- Langmuir I (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.*, 40: 1316-1403.
- Mall ID, Srivastava VC, Agarwal NK, Mishra IM (2005). Adsorptive Removal of Malachite Green Dye from Aqueous Solution by Bagasse Fly Ash and Activated Carbon- Kinetic Study and Equilibrium Isotherm Analyses. *Colloids Surface A*. 264: 17-28.
- Meshko V, Markovska L, Mincheva M, Rodrigues AE (2001). Adsorption of basic dyes on granular activated carbon and natural zeolite, *Water Res.*, 35(14): 3357-3366.
- Miyamoto N, Kawai R, Kuroda K, Ogawa M (2000). Adsorption and aggregation of a cationic cyanine dye on layered clay minerals, *Appl. Clay Sci.*, 16 (3-4):161-170.
- Mohan D, Singh KP, Singh G, Kumar K (2002). Removal of dyes from wastewater using fly ash: a low-cost adsorbent, *Ind. Eng. Chem. Res.*, 41(15): 3688-3695.
- Namasivayam C, Kavitha D (2002). Removal of Congo Red from water by adsorption on to activated carbon prepared from coir pith, an agricultural solid waste. *Dyes Pigments*, 54: 47-58.
- Netpradit S, Thiravetyan P, Towprayoon S (2004). Adsorption of three azo reactive dyes by metal hydroxide sludge: effect of temperature, pH, and electrolytes, *J. Colloid Interface Sci.*, 270: 255-261.
- Ozacar M, Sengil IA (2003). Adsorption of reactive dyes on calcined alunite from aqueous solutions *J. Hazard. Mater.*, 98(1): 211-224.
- Pelekani C, Snoeyink VL (2000). Competitive adsorption between atrazine and methylene blue on activated carbon: the importance of pore size distribution, *Carbon*, 38 (10): 1423-1436.
- Rytwo G, Serban C, Tropp D (2002). Adsorption and interactions of diquat, paraquat and methyl green on sepiolite: experimental results and model calculations. *Appl. Clay Sci.*, 20(6): 273-282.
- Tahiri S, Messaoudi A, Albizane A, Azzi M, Bouhria M, Younssi SA, Bennazha J, Mabrou J (2003). Removal of textile dyes from aqueous solutions by adsorption on chrome tanned solid wastes generated in the leather industry, *Water Qual. Res. J. Can.*, 38(2): 393-411.
- Temkin MJ, Pyzhev V (1940). Recent modifications to Langmuir isotherms. *Acta Physiochim. URSS* 12 :217.
- Thangamani KS, Sathishkumar M, Sameena Y, Vennilamani N, Kadirvelu K, Pattabhi S, Yun SE (2007). Utilization of modified silk cotton hull waste as an adsorbent for the removal of textile dye (reactive blue MR) from aqueous solution, *Bioresour. Technol.*, 98: 1265-1269.
- Walker GM, Weatherley LR (2000). Textile Wastewater Treatment Using Granular Activated Carbon Adsorption in Fixed Beds, *Sep. Sci. Technol.*, 35 (9):1329-1341.
- Weng CH, Pan YF (2006). Adsorption characteristics of methylene blue from aqueous solution by sludge ash. *Colloids Surface A.*, 274: 154-162.
- Wong YC, Szeto YS, Cheung WH, McKay G (2004). Adsorption of acid dyes on chitosan equilibrium isotherm analyses. *Process Biochem.*, 39(6): 695-704.