Available online at www.elixirpublishers.com (Elixir International Journal)

Chemical Engineering

Elixir Chem. Engg. 97 (2016) 42317-42322

ISSN: 2229-712X

Adsorption of Methylene Blue Dye onto Aleppo Pine (*Pinus Halepensis* Mill.) Fibers: A Kinetic Modeling Studies

Khalifa Riahi[1], Safa Chaabane[2] and Béchir Ben Thayer[1]

[1]Higher Institute on Rural Engineering and Equipment, Medjez El Bab City, University of Jendouba- Tunisia.

[2]National Agronomic Institute of Tunisia, Mahrajène City, University of Carthage- Tunisia.

ARTICLE INFO

Article history:

Received: 10 March 2016;

Received in revised form: 16 August 2016;

Accepted: 26 August 2016;

Keywords

Adsorption,
Methylene blue,
Kinetic modeling,
Aleppo pine fibers,
Textile wastewater.

ABSTRACT

The potential use of Aleppo pine (*Pinus halepensis* Mill.), a lignocellulosic-based fiber found in discontinuous bands along the Mediterranean basin, for the removal of a basic cationic dye: Methylene blue (MB) was investigated by adsorption in batch mode. In order to investigate the mechanism of dye sorption and potential rate controlling steps, pseudo first-order, pseudo second-order and intra-particle diffusion models equations have been used to test experimental data. Kinetic analysis of models has been carried out for initial MB dye concentration in the range of 20-100 mg/L. The rate constants models have been determined and the correlation coefficients have been calculated in order to assess which model provides the best fit predicted data with experimental results. The results showed that pseudo second-order equations model provide the best fit to experimental data for different initial MB dye concentrations implying that chemisorption mechanism may play an important role for the adsorption of dye onto Aleppo pine fibers. The results indicate also that Aleppo pine fibers adsorb Methylene blue efficiently and could be employed as a low-cost alternative in textile wastewater treatment for the removal of cationic dyes.

Introduction

Aleppo pine (*Pinus halepensis* Mill.) is a pine native coniferous species to the Mediterranean region with large geographic distribution from Morocco and Spain north to southern France, Italy, and Croatia, and east to Greece, all over Malta and northern Tunisia. In North Africa it is the most widely spread pine, and is especially well represented in Algeria, Tunisia and Morocco covering about 1.3 million hectares. Natural Aleppo pine forests grow in North Africa at elevations ranging from about 250 m above sea level (a.s.l.) in Algeria, Morocco and Tunisia to 2000 m (a.s.l.) in Morocco [1]. Aleppo pine (*Pinus halepensis* Mill.) is found in discontinuous bands along the Mediterranean Basin, usually at low elevations and in dry climates. The longitudinal variations were the most determinant geo-positional factors in Aleppo pine cone dimensions and average seed mass in natural Aleppo pine forests in Tunisia [2].

Colour is the first pollutant to be recognized in water and has to be removed from wastewater before discharging it into water bodies. Most of the textile industries in Tunisia use dyes to colour their final product. Discharge of such textile effluents imparts colour to the receiving water bodies such as rivers and lakes, impedes light penetration, retards photosynthetic activity, inhibits the growth of biota and also has a tendency to chelate metal ions which produce micro-toxicity to fish and other organisms [3,4].

The conventional methods applied for treating dye from textile effluent are anaerobic biological method, chemical oxidation [5], coagulation-flocculation coupled with membrane processes, adsorption on powdered activated carbon [6]. These techniques do not show a significant difference in their effectiveness. The high cost and regeneration is one of their major disadvantages. Still, adsorption remains the most popular method for dye-containing wastewater treatment.

Using lignocellulosic waste, as low-cost and easily available materials for the treatment of the textile wastewater is environmentally helpful and attractive.

Various techniques like coagulation, adsorption, chemical oxidation and froth floatation etc., have been used for the removal of organics as well as inorganics from wastewaters. Amongst these, adsorption is considered to be the most potential one due to its flexibility, simplicity of design, high efficiency and ability to separate wide range of chemical compounds particularly basic and acid dyes. Many authors have studied the feasibility of using ligno-cellulosic waste low cost materials, such as rosewood sawdust [7], cedar sawdust [8], meranti sawdust [9], beech sawdust [10], *Stippa Tenacissima* L. Alfa fibers [11], mansonia sawdust [12], palm kernel fiber [13], fallen *phoenix* trees leaves [14], raw date pits [15], *Luffa cylindrica* fibers [16], *Azadirachta indica* leaf powder [17] and *Posidonia oceanica* (L.) fibers [18] as adsorbents for the removal of Methylene blue dyes from wastewaters.

In the present work, adsorption kinetic studies are carried out for treatment of dyeing effluents by using Aleppo pine (*Pinus halepensis* Mill.) as natural low-cost fibers adsorbents for the removal of methylene blue (MB), the most commonly used substance for dying cotton, wood and silk. The main aim of this research was to find an appropriate model for the kinetics of methylene blue dyes removal onto Aleppo pine (*Pinus halepensis* Mill.) fibers in a batch reactor.

Tele: +21624157068

E-mail address: khalifa_riahi31@yahoo.fr

Materials and methods

Preparation of Aleppo pine fibers

Aleppo pine (*Pinus halepensis* Mill.) fibers were obtained from Ain Drahem (North-Western of Tunisia). The raw fibers was sieved through 0.63 to 1 mm sieve, washed repeatedly with distilled water to remove surface and soluble impurities, and dried at 60 °C for 48 h. The dried fibers was not subjected to further processing or chemical treatment which might enhance its adsorptive capacity in an attempt to evaluate the MB dye adsorption properties of a low-cost unprocessed materials, abundantly available in North of Tunisia.

Chemicals and analysis

Methylene blue dye with more than 98% of dye content, chemical formula = $C_{16}H_{18}ClN_3S \cdot 3H_2O$, Fw = 319.852 g/mol, fusion point at 190°C, solubility in water = 1g/25mL was used as model adsorbate (figure 1).

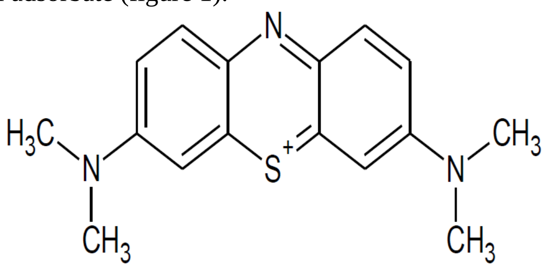

Figure 1. Molecular structure of Methylene blue dye

A stock solution of 1000 mg/L was prepared by dissolving an appropriate quantity of MB in a liter of distilled water. The working solutions were prepared by diluting the stock solution with distilled water to give the appropriate concentration of the working solutions (from 20 to 100 mg/L). The methylene blue concentration in the supernatant solution was analyzed using a UV spectrophotometer (HACH DR-4000) by monitoring the absorbance changes at a wavelength of maximum absorbance of 665 nm (figure 2).

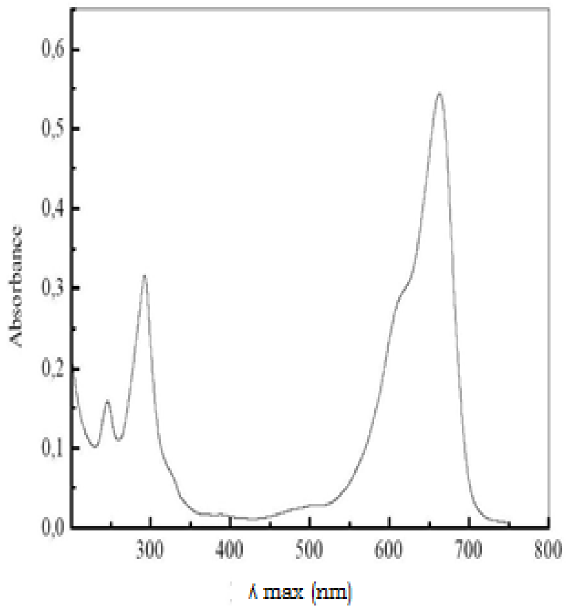

Figure 2. Absorbance spectral at variable wavelength

Textile effluent sampling

A real textile effluent was collected from discharge point of textile industry located in Menzel Jemil-Bizerte (North of Tunisia) in the Lake of Bizerte (figure 3). The lake of Bizerte covers 120 km^2 and has an average depth of seven meters up to twelve meters. The lake has a shoreline industrialized and urbanized. The industrial activities are very present particularly with textile industries.

Figure 3. Discharge of textile effluent in the Lake of Bizerte

Adsorption kinetic measurements

Methylene blue dye adsorption kinetics study was carried out with different initial concentrations of dye and a fixed dose of the adsorbent at constant temperature shaker bath (23°C ± 02). Five levels of initial dye concentrations (20, 40, 60, 80 and 100 mg P/L) were used. The flask was capped and stirred magnetically at 300 rpm, for C_i = 20-100 mg/L, for adsorbent dose = 6 g/L, for pH= 6.4 and for 120 min to ensure approximate equilibrium. At the end of the adsorption period, the solution was filtered through a 0.45µm membrane filter and then analyzed for MB dye. The triplicate experiments demonstrated the high repeatability of this adsorption method and the experimental error could be controlled within 5%. The adsorbed amount of MB at equilibrium; q_e (mg g^{-1}) was calculated by the following equation, Eq. (1):

$$q_e = \frac{C_i - C_e}{m} \times V \qquad (1)$$

where C_i and C_e are the initial and equilibrium MB concentrations (mg L^{-1}) respectively, V the volume of solution (L) and m the dry weight of the added adsorbents (g). The percentage removal of dye (R (%)) was calculated using the following relationship, Eq. (2):

$$\%R = \frac{C_i - C_e}{C_i} \times 100 \qquad (2)$$

Kinetic models

The study of adsorption kinetics is very useful for understanding the involved mechanisms and also for the design of future large scale adsorption facilities. Many models are used to fit the kinetic adsorption experiments. The most used ones are the pseudo-first order, pseudo-second order and intra-particle diffusion models. In order to examine the mechanism of dye adsorption process onto Aleppo pine (*Pinus halepensis* Mill.) fibers, three simplified kinetic models were adopted.

Pseudo first-order equation

First, the kinetics of adsorption was analyzed by the pseudo-first-order equation given by Langergren and Svenska [19] as follows:

$$\frac{dq_e}{dt} = k_I(q_e - q_t) \qquad (3)$$

After integration and applying the boundary conditions, for q_t = 0 at t = 0 and q_t = q_t at t= t, the integrated form of equation (2) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_I}{2.303} t \qquad (4)$$

Where q_e and q_t are the amounts of dye sorbed at equilibrium and at time t (mg g−1), respectively, and k_I is the rate constant of pseudo first-order sorption (l/min).

Pseudo second-order equation

If the rate of sorption is a second-order mechanism, the pseudo second-order chemisorption kinetic rate equation after integration is expressed as [20, 21]:

$$\frac{t}{q_t} = \frac{1}{k_{II} q_e^2} + \frac{1}{q_e} t \qquad (5)$$

Where k_{II} is the rate constant of pseudo second-order sorption (g/(mg.min) and qe is the amount of phosphates sorbed at equilibrium (mg/g).

Intra-particle diffusion equation

In order to investigate the mechanism of the MB adsorption onto Aleppo pine (*Pinus halepensis* Mill.) fibers, intra-particle diffusion based mechanism was studied. The possibility of intra-particle diffusion resistance affecting adsorption was explored by using the intra-particle diffusion model according to the theory proposed by Weber and Morris [22], the fractional approach to equilibrium changes according to a function of $(D/r^2)^{1/2}$, where r is the particle radius and D the diffusivity of solute within the particle. The initial rate of the intra-particle diffusion is the following:

$$q_t = k_d t^{1/2} \qquad (6)$$

Where k_d is the intra-particle diffusion rate constant (mg/g $min^{1/2}$).

All constants were calculated from the intercept and slope of the line obtained from linearized form of models. The equations corresponding to each model and their linearized forms, plots, slopes and intercepts are presented in Table 1.

Table 1. The intercept and slope from linearized form of models.

Model	Linear form	Slope	Intercept
Pseudo-first order	$\log(q_e - q_t) = \log(q_e) - \frac{k_I}{2.303} t$	$\frac{k_I}{2.303}$	$\log(q_e)$
Pseudo-Second order	$\frac{t}{q_t} = \frac{1}{k_{II} q_e^2} + \frac{1}{q_e} t$	$\frac{1}{q_e}$	$\frac{1}{k_{II} q_e^2}$
Intra-particle diffusion	$q_t = k_d t^{1/2} + C$	k_d	C

Results and discussion

Effect of contact time and initial dye concentration

Experiments were undertaken to study the effect of varying initial concentration (20-100 mg/L) on MB dye removal onto Aleppo pine (*Pinus halepensis* Mill.) fibers. The experiments were carried out at 23°C ± 02, an adsorbent dose at 6 g/L, an agitation speed at 300 rpm and for a contact period of 180 mn at pH=6.4. The results show that adsorption process is clearly time dependent. It was observed that most of the MB dye uptake occurs within a time of 30 mn at 87.8% and 99.5% respectively for initial MB dye concentration 20 and 100 mg/L of the totally dye sorbed (figure 4). For periods greater than 30 mn, the uptake is further increased but with a much slower rate. Equilibrium began establishing itself after approximately a contact period of 90 mn. This outcome is generally in line with previous similar studies such as the adsorption of MB dye onto some natural and low cost adsorbent, where the equilibrium time was evaluated to be about 1–2h [23-25].

The MB dye uptake increased with increasing initial dye concentration from 3.27 mg/g for 20 mg/L initial MB concentration to 15.10 mg/g for 100 mg/L initial MB concentration after 180 mn contact time. The sorption capacity of Aleppo pine (*Pinus halepensis* Mill.) fibers increases with increasing of initial MB dye concentration. It may be related to the initial MB concentration that provided an important driving force to overcome all mass transfer resistance.

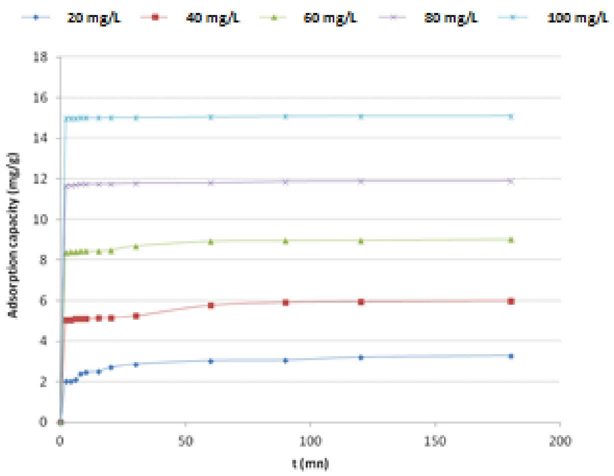

Figure 4. Effect of contact time and initial concentration on MB dye adsorption onto Aleppo pine fibers

The increases of loading capacity of Aleppo pine fibers with increasing initial MB dye concentration may also be due to higher interaction between dye and adsorbent. As Aleppo pine fibers offered a finite number of surface binding sites, MB adsorption showed a saturation trend at higher initial MB concentration [23]. Finally, the adsorption capacity did not vary significantly after 90 mn, the adsorption would be in a state of dynamic equilibrium between the dye desorption and adsorption. The reason is that during the adsorption of dye, initially the dye molecules rapidly reach the boundary layer by mass transfer, then they slowly diffuse from boundary layer film onto the adsorbent surface because many of the available external sites have been occupied, and finally, they diffuse into the porous structure of the adsorbent [24, 25].

Adsorption kinetic modeling

Adsorption kinetics modeling is very useful for better understanding of MB dye mechanisms retention onto Aleppo pine fibers such as the importance of the chemical reactions and the intra-particle diffusion processes. To fit the obtained MB dye adsorption experimental data, we used the most well-known of them, namely the pseudo first-order, the pseudo second-order and the intra-particle diffusion models. The experimental data were correlated with the linear forms of the three models, respectively (figure 5).

The derived rate constants together with the correlation coefficient R^2 for the different initial concentration of MB dye have been listed in Table 2. For the pseudo-first-order model, the correlation coefficients are relatively low lying between 0.9 and 0.97. In addition, the difference between experimental and theoretical adsorbed uptake of MB dye onto Aleppo pine fibers at equilibrium is very high (from 69 to 97%). The experimental values are three to thirty six times higher than the theoretical one. These results state a bad fit between the pseudo-first-order model and the experimental data. As a consequence, adsorption of MB dye onto Aleppo pine fibers is not an ideal pseudo-first-order reaction. For the pseudo-second-order model, the correlation coefficients for all initial MB dye concentrations are higher than 0.999. In addition, the difference between the experimental and theoretical adsorbed masses at equilibrium is very small (less than 1%). These results show a good concordance between the experimental data and the pseudo-second-order kinetic model. The analysis of the adsorption of MB dye onto Aleppo pine fibers with intra-particle diffusion model showed that the depicted two-phase plot suggests that the adsorption process proceeds by surface adsorption at the earlier stages and by intra-particle diffusion at later stages, especially, for the high aqueous concentrations

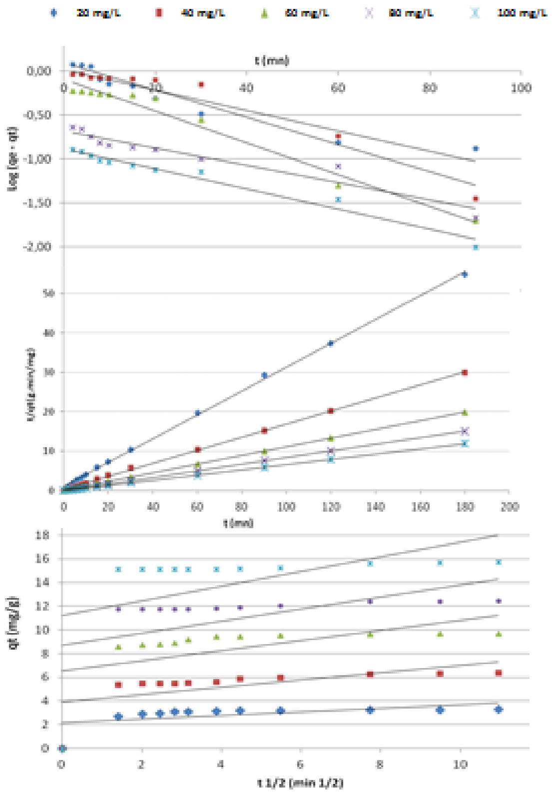

Figure 4. Plot of linearized form of the three models for MB dye adsorption onto Aleppo pine fibers.

The correlation coefficients (R^2) for the intra-particle diffusion model ranged between 0.15 and 0.59. It was observed that intra-particle rate constant values K_d increased with initial MB dye concentration. The observed increase in K_d values with increasing initial MB dye concentration can be explained by the increase in the thickness of boundary layer [26] and the decrease in the chance of external mass transfer. Hence the chance of internal mass transfer was increased [27].

Table 2. Kinetic parameters for the adsorption of MB dye onto Aleppo pine fibers.

C_i	Pseudo-first order	Pseudo-second order	intra-particle diffusion
20 mg/L	$q_{e\ Exp}$ = 3.20 $q_{e\ Cal}$ = 0.986 K_I = 0.0267 R^2 = 0.9688	$q_{e\ Exp}$ = 3.20 $q_{e\ Cal}$ = 3.29 K_{II} = 0.094 R^2 = 1	$q_{e\ Exp}$ = 3.20 K_d= 0.1625 R^2 = 0.593
40 mg/L	$q_{e\ Exp}$ = 5.95 $q_{e\ Cal}$ = 0.910 K_I = 0.0265 R^2 = 0.9192	$q_{e\ Exp}$ = 5.95 $q_{e\ Cal}$ = 6.03 K_{II} = 0.095 R^2 = 1	$q_{e\ Exp}$ = 5.95 K_d= 0.2247 R^2 = 0.3491
60 mg/L	$q_{e\ Exp}$ = 8.99 $q_{e\ Cal}$ = 0.909 K_I = 0.0415 R^2 = 0.9727	$q_{e\ Exp}$ = 8.99 $q_{e\ Cal}$ = 9.04 K_{II} = 0.177 R^2 = 1	$q_{e\ Exp}$ = 8.99 K_d= 0.2826 R^2 = 0.2255
80 mg/L	$q_{e\ Exp}$ = 11.89 $q_{e\ Cal}$ = 0.507 K_I = 0.0226 R^2 = 0.9388	$q_{e\ Exp}$ = 11.89 $q_{e\ Cal}$ = 11.90 K_{II} = 0.584 R^2 = 0.9996	$q_{e\ Exp}$ = 11.89 K_d = 0.3260 R^2 = 0.1634
100 mg/L	$q_{e\ Exp}$ = 15.10 $q_{e\ Cal}$ = 0.414 K_I = 0.0265 R^2 = 0.9082	$q_{e\ Exp}$ = 15.10 $q_{e\ Cal}$ = 15.11 K_{II}= 0.931 R^2 = 0.9990	$q_{e\ Exp}$ = 15.10 K_d= 0.4054 R^2 = 0.1551

Where $q_{e\ Exp}$ and $q_{e\ Cal}$ are expressed in (mg/g), K_I in (min^{-1}), K_{II} in ($mg.g^{-1}.min^{-1}$) and K_d in ($mg/(g.min^{0.5})$).

The pseudo first-order and intra-particle equations do not give a good fit to the experimental data for the MB dye adsorption onto Aleppo pine fibers. The pseudo second-order equation fits the experimental data well. Similar results were obtained for the adsorption of phosphate [28], heavy metal (Cadmium) [29] and textile dyes (Acid Black, Acid Green and Acid Blue) [30] onto Aleppo pine sawdust. The agreement of the pseudo second-order kinetic model with experimental data may be explained, based on the assumption that the rate limiting step, as chemisorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate. The adsorption system obeys the pseudo second-order kinetic model for the entire adsorption period and thus supports the assumption behind the model that the adsorption is due to chemisorption. These results imply that chemisorption mechanism may play an important role for the adsorption of MB dye onto Aleppo pine fibers. The adsorption of MB dye onto Aleppo pine fibers takes place probably via surface exchange reactions until the surface functional sites are fully occupied; thereafter MB dye molecules diffuse into Aleppo pine fibers pores for further interactions and/or reactions such as ion-exchange, complexation interactions [31]. This is probably due to the large amount of easily available functional groups such as alcohols, aldehydes existing in the cellulose, hemicelluloses, and lignin, which can easily make a series of chemical reactions, such as condensation, etherification, and copolymerization [29].

Textile effluent decolorization

The main objective of this section was to study a real effluent obtained from textile industry located in Menzel Jemil-Bizerte (North of Tunisia) for decolorization using an available, abundant materials such Aleppo pine fibers. The kinetic decolorization of a real textile effluent and a synthetic one using Aleppo pine fibers as an adsorbent is studied in batch system. It was found that the lowest percentage removal of MB dye is obtained with experiments performed using the real textile effluent (%R= 54) compared to a synthetic one (%R= 98). The decreases in the percentage removal of MB dye (R (%)) may be attributed to the presence of competitive inorganic anions (Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, NO_3^{-}, SO_4^{2-}, PO_4^{3-},…) in the real textile effluent. These anions are competing with MB dye on the adsorption of Aleppo pine fibers surface [25, 30]

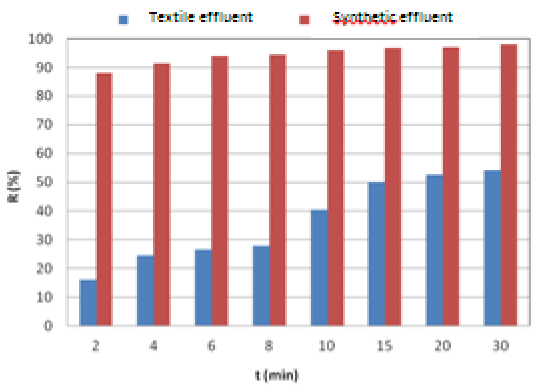

Figure 5. Kinetic of MB dye removal of textile and synthetic effluent using Aleppo pine fibers.

Comparison with other lignocellulosic adsorbents

The application of low-cost and easily available materials in textile wastewater treatment has been widely investigated during recent years. Particularly, the MB dye adsorption on different lignocellulosic materials has been widely studied during recent years. In order to situate our natural adsorbent among those used to remove MB dye from aqueous solutions, a comparison based on adsorption capacity (mg/g) was made. The results, illustrated in Table 3, had shown that the Aleppo pine fibers could be considered as a promising material to remove MB dye when compared with the common natural lignocellulosic materials. The adsorption capacity of MB dye onto Aleppo pine fibers is lower than many raw sawdust and fibers materials and higher than Indian Rose wood and raw beech sawdust, coarse and fine grinded wheat straw. Thus, raw Aleppo pine fibers could be considered among the most efficient natural material for the removal of MB dye.

Table 3. Comparison of adsorption capacities of MB onto various lignocellulosic materials.

Adsorbents	Adsorption capacity q_e (mg/g)	Reference
Indian Rose wood sawdust	11.8	[7]
Cedar sawdust	142.4	[8]
Meranti sawdust	120.5	[9]
Beech sawdust	9.8	[10]
Alfa fibers	25.9	[11]
Coarse grinded wheat straw	3.8	[12]
Fine grinded wheat straw	2.2	[12]
Palm kernel fibers	217.9	[13]
Walnut sawdust	59.2	[14]
Raw date pits	80.3	[15]
Luffa fibers	47	[16]
Aleppo pine fibers	15.1	This study

Prospect of using Aleppo pine fibers adsorbents

The results reported herein indicate that Aleppo pine fibers could be successfully used to remove MB dye from aqueous solution and textile effluent by sorption process. The regeneration of the saturated Aleppo pine fibers with MB dye does not required while the abundance of these raw materials. Thus, desorption and recovery processes could be avoided and the related costs reduced. Consequently, for environmental, economic and operational considerations, the use of Aleppo pine fibers for the removal of MB dye appears to be more interesting. Aleppo pine fibers is one of lignocellulosic wastes materials are available in abundance, renewable and low-cost. The low cost and the simplicity of the current treatment system and the abundance of these fibers in Tunisia allow the application of this technique for the removal of MB dye from industrial textile wastewater. The use of natural fibers in industrial wastewater treatment is beneficial because lignocellulosic natural fibers are usually strong, light in weight, cheap, abundant and renewable. These fibers are renewable, nonabrasive and they can be incinerated for energy recovery since they possess a good calorific value.

Conclusions

The adsorption of MB dye from aqueous solution and real textile effluent using Aleppo pine fibers was investigated. The adsorption kinetic of MB dye onto Aleppo pine fibers was studied by using pseudo first-order, pseudo second-order and intra-particle diffusion equations. The values of R^2 obtained from pseudo second-order model were higher than 0.999, indicating that the adsorption process obeyed the pseudo second-order model for entire adsorption period. This kinetic model is based on the sorption capacity on the solid-phase and is in agreement with a chemisorption mechanism being the rate controlling step. The results indicate that MB dye adsorption onto Aleppo pine fibers increased with increasing initial MB dye initial concentration. The MB dye uptake increased with increasing initial dye concentration from 3.27 mg/g for 20 mg/L initial MB dye concentration to 15.10 mg/g for 100 mg/L initial MB dye concentration. It was found that the lowest retention capacity is obtained with experiments performed using the real textile effluent (%R= 54) compared to a synthetic one (%R= 98). Finally, the low cost, availability and high adsorption capability of the Aleppo pine fibers make them promising and potentially attractive sorbents for MB dye removal and then these fibers are renewable, nonabrasive and they can be incinerated for energy recovery since they possess a good calorific value. Others studies related to the textural characterization (SEM, FT-IR) of Aleppo pine fibers should be conducted to shows fibrous and porous structure of these materials before and after adsorption in order to confirm the mechanisms of MB dye sorption.

References

[1] I. Nahal, Taxonomie et aire de géographique des pins du groupe halepensis. CIHEAM. Options Mediterranéennes, 1986, 1, 1-9.

[2] A. Ayari, D. Moya, M.N. Rejeb, A. Ben Mansoura, A. Albouchi, J. De Las Heras, T. Fezzani, B. Henchi, Geographical variation on cone and seed production of natural Pinus halepensis Mill. forest in Tunisia, Journal of Arid Environments, 2011, 75, 403-410.

[3] G. McKay, M.S. Otterburn, A.G. Sweeney, The removal of colour from effluent using various adsorbents. III. Silica: rate process, Water Res, 1980, 14, 15-20.

[4] H. Metivier-Pignon, C. Faur-Brasquet, P.L. Cloirec, Adsorption of dyes onto activated carbon cloths: approach of adsorption mechanisms and coupling of ACC with ultra filtration to treat coloured wastewaters, Sep. Purif. Technol, 2003, 31, 3-11.

[5] O. Turgay, G. Ersoz, S. Atalay, J. Forss, U. Welander, The treatment of azo dyes found in textile industry wastewater by anaerobic biological method and chemical oxidation, Separation and Purification Technology, 2011, 79, 26-33.

[6] F. Harrelkas, A. Azizi, A. Yaacoubi, A. Ben Hammou, M.N. Pons, Treatment of textile dye effluents using coagulation–flocculation coupled with membrane processes or adsorption on powdered activated carbon, Desalination, 2009, 235, 330-339.

[7] V.K. Garg, M. Amita, R. Kumar, R. Gupta, Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste, Dyes and Pigments, 2004, 63, 243-250.

[8] O. Hamdaoui, Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick, J. Hazard. Mater, 2006, B135, 264-273.

[9] A. Ahmad, M. Rafatullah, O. Sulaiman, M.H. Ibrahim, R. Hashim, Scavenging behaviour of meranti sawdust in the removal of methylene blue from aqueous solution, J. Hazard. Mater, 2009, 170, 357-365.

[10] F.A. Batzias, D.K. Sidiras, Simulation of dye adsorption by beech sawdust as affected by pH, J. Hazard. Mater, 2007, 141, 668-679.

[11] L. Hamdi, L. Boumehdi, T.· Zineb, S. Khedidja Allia, Full factorial experimental design applied to methylene blue adsorption onto Alfa stems, Desalination and water treatment, 2015. DOI:10.1080/19443994.2015.1029003

[12] F.A. Batzias, D.K. Sidiras, E. Schroeder, C. Weber, Simulation of dye adsorption on hydrolyzed wheat straw in

batch and fixed-bed systems, Chem. Eng. J, 2009, 148, 459-472.

[13] A.E. Ofomaja, Sorption dynamics and isotherm studies of methylene blue uptake on to palm kernel fibre, Chem. Eng. J, 2007, 126, 35-43.

[14] F. Ferrero, Dye removal by low cost adsorbents: hazelnut shells in comparison with wood sawdust, J. Hazard. Mater., 2007, 142, 144-152.

[15] F. Banat, S. Al-Asheh, L. Al-Makhadmeh, Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters, Process Biochem, 2003, 39, 193-202.

[16] H. Demir, A. Top, D. Balkose, S. Ulku, Dye adsorption behavior of Luffa cylindrical fibers, J. Hazard. Mater, 2008, 153, 389-394.

[17] K.G. Bhattacharyya, A. Sharma, Kinetics and thermodynamics of methylene blue adsorption on neem (Azadirachta indica) leaf powder, Dyes Pigments, 2005, 65, 51-59.

[18] M.C. Ncibi, B. Mahjoubi, M. Seffen, Investigation of the sorption mechanisms of metal-complexed dye onto Posidonia oceanica (L.) fibres through kinetic modeling analysis, Bioresour. Technol, 2008, 99, 5582-5589.

[19] B.K. Nandi, A. Goswami, M.K. Purkait, Removal of cationic dyes from aqueous solutions by kaolin: kinetic and equilibrium studies, Appl. Clay Sci, 2009, 42, 583-590.

[20] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chemical Engineering Journal, 1998, 70, 115-124.

[21] Y.S. Ho, Sorption studies of acid dye by mixed sorbents, Adsorption, 7, 2001, 139-147.

[22] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, Journal of the Sanitary Engineering Division. Proceedings of the American Society of Civil Engineers, 1963, 89, 31-59.

[23] H. Cherifi, B. Fatiha, H. Salah, Kinetic studies on the adsorption of methylene blue onto vegetal fiber activated carbons, Applied Surface Science, 2013, 282, 52-59.

[24] S. Senthilkumaar, P.R. Varadarajan, K. Porkodi, C.V. Subbhuraam, Adsorption of methylene blue onto jute fiber carbon: kinetics and equilibrium studies, J. Colloid Interface Sci., 2005, 284, 78-82.

[25] X. Han, W. Wang, X Ma, Adsorption characteristics of methylene blue onto low cost biomass material lotus leaf, Chemical Engineering Journal, 2011, 171, 1-8.

[26] L. Wang, J. Zhang, R. Zhao, C. Li, Y. Li, C.L. Zhang, Adsorption of basic dyes on activated carbon prepared from Polygonum orientale Linn: equilibrium, kinetic and thermodynamic studies, Desalination, 2010, 254, 68-74.

[27] A. Khaled, A.E. Nemr, A. El-Sikaily, O. Abdelwahab, Removal of Direct N Blue-106 from artificial textile dye effluent using activated carbon from orange peel: adsorption isotherm and kinetic studies, J. Hazard. Mater, 2009, 165, 100-110.

[28] S. Benyoucef, M. Amrani, Adsorption of phosphate ions onto low cost Aleppo pine adsorbent, Desalination, 2011, 275, 231-236.

[29] L. Semerjian, Equilibrium and kinetics of cadmium adsorption from aqueous solutions using untreated Pinus halepensis sawdust, Journal of Hazardous Materials, 2010, 173, 236-242.

[30] N.M. Mahmoodi, B. Hayati, M. Arami, C. Lan, Adsorption of textile dyes on Pine Cone from colored wastewater: Kinetic, equilibrium and thermodynamic studies, Desalination, 2011, 268, 117-125.

[31] M. Ozacar, I.A. Sengil, A kinetic study of metal complex dye sorption onto pine sawdust, Process Biochem, 2005, 40, 565-572.