


Biosorption of alpacide blue from aqueous solution by lignocellulosic biomass: *Luffa cylindrica* fibers

Aida Kesraoui¹  · Asma Moussa¹ · Ghada Ben Ali¹ · Mongi Seffen¹

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Abstract The aim of the present work is to develop an effective and inexpensive pollutant-removal technology using lignocellulosic fibers: *Luffa cylindrica*, for the biosorption of an anionic dye: alpacide blue. The influence of some experimental parameters such as pH, temperature, initial concentration of the polluted solution, and mass of the sorbent *L. cylindrica* on the biosorption of alpacide blue by *L. cylindrica* fibers has been investigated. Optimal parameters for maximum quantity of biosorption dye were achieved after 2 h of treatment in a batch system using an initial dye concentration of 20 mg/L, a mass of 1 g of *L. cylindrica* fibers, and pH 2. In these conditions, the quantity of dye retained is 2 mg/g and the retention rate is 78 %. Finally, a mathematical modeling of kinetics and isotherms has been used for mathematical modeling; the model of pseudo-second order is more appropriate to describe this phenomenon of biosorption. Concerning biosorption isotherms, the Freundlich model is the most appropriate for a biosorption of alpacide blue dye by *L. cylindrica* fibers.

Keywords Lignocellulosic materials · *Luffa cylindrica* · Biosorption · Alpacide blue · Modeling · Kinetics · Isotherms

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✉ Aida Kesraoui
aida.kesraoui@gmail.com

¹ Laboratory of Energy and Materials (LABEM), High School of Sciences and Technology of Hammam Sousse, FP4BATIW Project, Sousse University-Tunisia, BP 4011, Hammam, Sousse, Tunisia

Introduction

Water pollution by different types of pollutants is a topical issue (Ben Aissa 2012). Especially in the textile industry, the wastewaters are one of the most important sources of pollution of surface water and groundwater (Ben Hamissa et al. 2013).

Indeed, the world production of dyes is estimated at 800,000 tons/year (Palmieri et al. 2005). Some of these dyes, approximately 140,000 tons/year, are released during the process of dyeing textile fibers (Ben Mansour et al. 2009). The textile sector is one of six industries producing half of pollution flows (Ben Mansour et al. 2011). The effluents from this area are very colorful and difficult to treat (Ben Mansour et al. 2011). The presence of this dye wastewater is increasingly considered a major nuisance (Ben Mansour et al. 2011). Among the dyes used in most textile industries are metallic dyes (Lajili 2010). Textile industries, especially the phase of coloration and finishing, mainly use chemicals harmful to health and generate pollution of surface water and groundwater (Lajili 2010).

When water is polluted by toxic and persistent substances, adequate treatment is necessary for the protection of the environment. Several procedures used for dye removal from industrial effluents are essentially coagulation (Rodrigues et al. 2013), ultrafiltration (Căilean et al. 2009), reverse osmosis (Vijayageetha et al. 2014), the adsorption on activated carbon (Ncibi et al. 2008a), and biological treatment (Abidin and Rahmat 2010). Indeed, the physicochemical treatments require considerable amounts of oxidants (expensive) (Ncibi et al. 2006) and sometimes lead to the formation of undesirable intermediate products (Zawlotzki Guivarch 2004). Moreover, certain products are resistant to this type of treatment which can be toxic (Zawlotzki Guivarch 2004). Although biological treatments are massively used, they remain powerless to eliminate certain toxic and persistent compounds such as dyes, hence the need to search for better alternatives (Zoughuir et al. 1998).

Other alternatives to eliminate discharges of textile dyes are today the subject of study, especially biosorption which is a very interesting method using natural materials that are often little or poor recovered (Ben Hamissa et al. 2013; Ncibi et al. 2007). Among these natural materials, we can mention rice husk (Vadivelan and Kumar 2005), beech sawdust (Batzias and Sidiras 2004), agro-industry wastes (Garg et al. 2004), *Posidonia oceanica* fibers (Ncibi et al. 2006), and *Agave americana* (Ben Hamissa et al. 2010).

Luffa cylindrica belongs to the Cucurbitaceae family (Demir et al. 2008). It is generally grown in China, Japan, Asia, Africa, and Central and South America (Demir et al. 2008). The fibers are composed of 63 % cellulose, 18 % hemicellulose, and 11.5 % lignin and can be used by industry for many purposes, such as packaging, insulating, or filling materials (Mazali and Alves 2005). *L. cylindrica* fiber has a fibrous vascular system that can enable removal of water pollutants (Adie et al. 2013). Moreover, many environmentally conscious consumers appreciate that *L. cylindrica* fibers are biodegradable and natural and are renewable resources (Demir et al. 2008).

The main objective of the present work is to evaluate the biosorption capability of a low-cost and renewable biomass (Demir et al. 2008), *L. cylindrica* fibers, for the removal of alpacide blue as a model of compound for metallic dyes. In fact, this dye is widely used in the textile industry in Tunisia. The effects of pH, contact time, initial dye concentration, temperature, and biomass amount on the biosorption capacity were investigated. Moreover, mathematical modeling of the kinetics and adsorption isotherms was also performed.

Materials and methods

Biosorbent and sorbate preparation

The adsorbent used in this study is the *L. cylindrica* fibers. This biomass was purchased at the local market Sousse. First, the fibers were cut finely, washed several times with distilled water to remove all impurities, and then dried in an oven at 70 °C for 48 h at a constant weight.

Alpacide blue used in this study is a metal dye, obtained from a textile industry (Chimitex, Tunisia). The metal dye chemical structure is unknown. Stock solutions were prepared by dissolving accurately weighed amounts of dye (100 mg) in 1 L of distilled water. All working solutions were prepared by diluting the stock solution with distilled water to achieve the needed concentrations.

Sorption tests and analytical methods

The biosorption experiments were carried out in batch reactor by adding 0.6 g dried *L. cylindrica* fibers in 75 mL of dye

solution (i.e., a solid/liquid ratio of 8 g/L) with the desired concentration, pH, and temperature. All the tests were investigated at 20 °C, except the tests carried out to investigate the influence of temperature on biosorption. Temperature was controlled by a thermoregulated water bath, model Memmert BME1420 operating at 105 oscillations/min. The initial pH was adjusted by adding dilute solutions of HCl or NaOH. All experiments were conducted in triplicate, and the negative controls (without *L. cylindrica*) were simultaneously carried out to ensure that the biosorption capacity was due solely by the biomass and did not involve the walls of the container. After biosorption of alpacide blue, the residual concentrations were determined by spectrophotometry double faisceaux analysis (FT-IR) (Camspec M550) at λ_{max} of 660 nm. Fourier transform infrared spectrometry (PerkinElmer Spectrum two) was used to analyze the functional groups in the adsorbent. The transmission spectrum was acquired with 4 cm⁻¹ resolution and the spectrum was corrected for a KBr background. For BET specific surface area estimation, a porosimeter accelerated surface area and porosimetry system (ASAP 2010) was used.

Kinetics studies

For kinetic studies, 3 mL of the alpacide blue solution was taken periodically and then analyzed to assess the dye concentration. To evaluate the alpacide blue removal, the biosorption capacity at equilibrium time (Q_e) or biosorption removal efficiency will be determined respectively according to the following equations:

$$Q = \frac{(C_0 - C_i) \times V}{M} \text{ (mg/g)} \tag{1}$$

$$\% \text{ dye removal} = \frac{(C_0 - C_i) \times 100}{C_0} \tag{2}$$

where C_0 is the initial alpacide blue concentration (mg/L), C_i is the residual alpacide blue concentration at any time (mg/L), V is the volume of solution (L), and M is the mass of the sorbent (g). At equilibrium, C_i is equal to C_e and Q is equal to Q_e .

The model of pseudo-first-order and the pseudo-second-order equation (Lagergren 1898; Ho 2004; Ho and McKay 1998) was used to fit the experimental data of the dye sorption before reaching equilibrium. The linearized form of the model of pseudo-first order is determined by expression 3:

$$\log(Q_e - Q) = \log(Q_e) - \frac{k_1 \cdot t}{2.303} \tag{3}$$

where t is the time (min) and k_1 is the equilibrium rate constant of pseudo-first-order sorption (min⁻¹).

Unlike the pseudo-first-order model, the pseudo-second-order model is applicable to a larger interval of time (McKay and Ho 1999; Ncibi et al. 2006). The pseudo-second order is based on the sorption capacity of the solid phase and is described by Eq. 4:

$$\frac{t}{Q} = \frac{1}{k_2 \cdot Q_e^2} + \frac{t}{Q_e} \quad (4)$$

where k_2 is the equilibrium rate constant of pseudo-second-order sorption (g/mg.min).

Evaluation of thermodynamic parameters

Thermodynamic parameters such as free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) for the sorption of alpacide blue on *L. cylindrica* were calculated according to the following equations (Ucun et al. 2008):

$$\Delta G^\circ = -RT \ln K_C \quad (5)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (6)$$

where R is the gas constant (8.314 J/mol/K), T is the absolute temperature (K), and K_C is the apparent equilibrium constant K_d , defined according Eq. 7 (Yurtsever and Sengil 2009):

$$K_C = \frac{C_{ad,eq}}{C_{r,eq}} \quad (7)$$

where $C_{ad,eq}$ and $C_{r,eq}$ being the concentration of adsorbed dye at equilibrium and remaining concentration dye at equilibrium, respectively (mg/L).

Evaluation of equilibrium isotherms

The Langmuir, Freundlich, and Temkin adsorption isotherms were used to describe the sorption of a dye solution. Linear form of the Langmuir equation can be expressed by

expression 8 (Langmuir 1916):

$$\frac{C_e}{Q_e} = \frac{1}{Q_m \cdot K_L} + \frac{C_e}{Q_m} \quad (8)$$

where Q_m is the maximum sorption capacity (mg/g) and K_L the Langmuir equilibrium constant (L/mg).

After, other fittings were done by the linearized form of the isotherm of Freundlich (Freundlich 1906):

$$\ln Q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (9)$$

where K_F [(mg/g) × (L/mg)^{1/n}] is Freundlich constant indicating the adsorption capacity and n (dimensionless) is Freundlich constant indicating the adsorption intensity.

The Temkin equation, based on the heterogeneous surface of the adsorbent, has the form (Temkin 1941)

$$Q_e = B \cdot \ln A + B \cdot \ln C_e \quad (10)$$

where A (L/g) and B (J/mol) are Temkin constants, and $B = RT/b$. b is variation of adsorption energy. R is universal gas constant (8.314 J/mol/K) and T is temperature at 298 K (Dada et al. 2012).

Results and discussion

Characterization of *L. cylindrica*

Determining the fiber humidity rate allows to calculate the dry matter rate. This gives an idea on the fiber yield of plants. Humidity rate and dry matter rate of *L. cylindrica* fibers are 9.6 and 90.4 %, respectively. In general, these results are comparable to those of some lignocellulosic materials such as the *A. americana* (L.) fibers having a dry matter rate of order of 84 % (Ben Hamissa 2005).

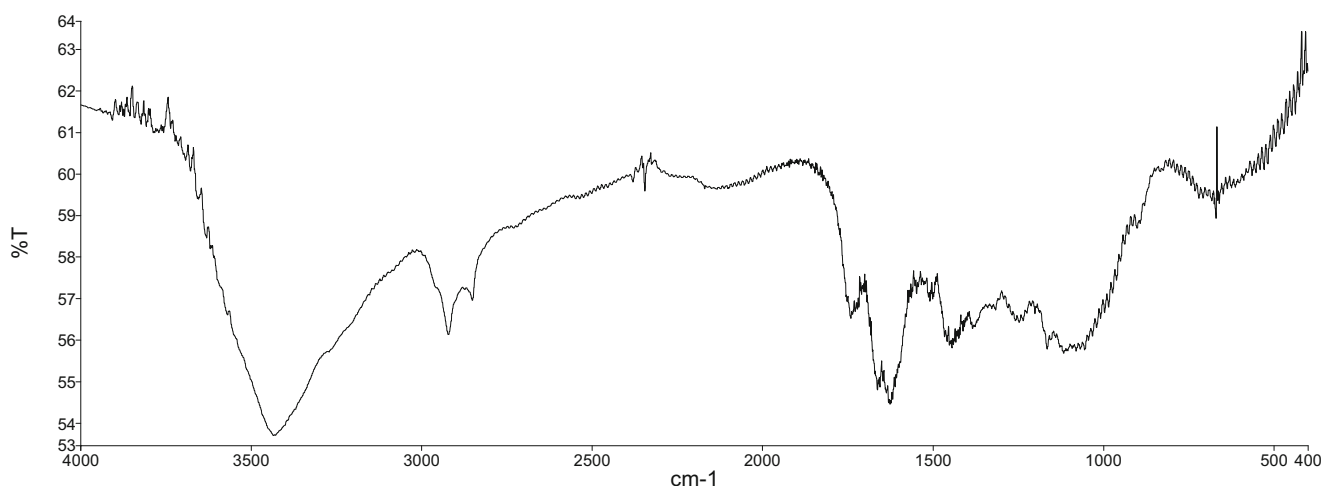


Fig. 1 Fourier transform infrared (FT-IR) absorption spectrum of *Luffa cylindrica* fibers

To have an idea on the rate of minerals of *L. cylindrica*, we determined the rate of ash (1 %). The rate of ash of *L. cylindrica* fibers is comparable to that reported in the literature (0.4 %) (Satyanarayana et al. 2007). These results are comparable with those on the *Posidonia* with a rate of 1.8 % (Satyanarayana et al. 2007).

For determining the size of the surface of the studied fibers, we measured their specific surface. This measure is interesting when it is a surface phenomenon such as the biosorption. Specific surface area of the *L. cylindrica* is 0.49 m²/g. This result is low compared to those of commercially activated carbons whose specific surface varies from 500 to 1500 m²/g (Aznar 2011).

However, this value is comparable to certain lignocellulosic biomasses studied for biosorption dye textiles such as sugar cane bagasse dyes with a surface of 0.67 m²/g (Aznar 2011).

FT-IR characterization of *L. cylindrica* fibers

Figure 1 shows the FT-IR spectrum of *L. cylindrica* fibers. IR spectra of *L. cylindrica* present absorption peaks which demonstrate the complex nature of the *L. cylindrica*. Several intense bands can be attributed to functional groups present in cellulose and lignin which are the major chemical composition of *L. cylindrica*.

The spectrum obtained is comparable to other spectra of cellulose and lignin described in the literature (El Hage 2010). The absorptions at 3435 cm⁻¹ are attributed to -OH and -NH groups (Ncibi et al. 2006). Two peaks present at 2922 and 2850 cm⁻¹ correspond to symmetric -CH₂ valence vibration and -CH stretching vibration, respectively, corresponding to the aliphatic fragments of the cellulose (Schwanninger et al. 2004). While bands at 2378 and 2344 cm⁻¹ are indicative of amine and amide groups (Williams and Fleming 1995). Peaks at 1705 and 1639 cm⁻¹ are an indication of the presence of unconjugated ester groups (Mahmoudi et al. 2015). In addition, the peak at 1444 cm⁻¹ may be associated with phenolic -OH and C-O stretching. The peaks present at 1116 and 896 cm⁻¹ originate from the elongation of the C-O-C (Liu et al. 2006).

Effect of contact time and initial alpacide blue concentration

The influence of contact time on the biosorption of alpacide blue dye using *L. cylindrica* fibers is presented in Fig. 2. The amounts of dye adsorbed at equilibrium under operating conditions (pH 2, T 20 °C, and particle size 250–500 μm) were 9.258 mg/g for the alpacide blue.

Dye solutions with initial concentrations of 20, 30, 40, 60, and 80 mg/L were studied. The sorbed amount of dye progressively increased with their respective initial concentrations, either before or after the achievement of equilibrium (Fig. 2). Furthermore, raising the dye concentration from 20 to 80 mg/

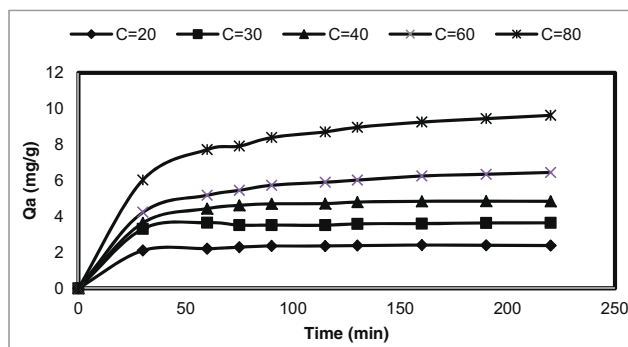


Fig. 2 Influence contact time and of initial alpacide blue concentration on the biosorption capacity of alpacide blue by *Luffa cylindrica* fibers (solid/liquid ratio=8 g/L, pH=2, T=20 °C)

L allows the fibers to increase their biosorption capacities from 2.20 to 9.63 mg/g, respectively, at pH 2 and 20 °C. In every case, it was observed that dye uptake was rapid for the first 60 min and thereafter proceeded at a slower rate to finally attain saturation after 150 min. The higher biosorption rate during the initial period may be due to the high number of sites available for the biosorption, and no less than 80 % of total dye was removed. The higher biosorption rate during the initial period may be due to the high number of sites available for the sorption, and no less than 80 % of total dye was removed. After this period, the number of sites available for biosorption decreased so that the dye molecules required longer time periods in order to reach the least accessible sites (Ben Hamissa et al. 2010).

Effect of pH

Textile dyes are complex organic compounds which possess various aromatic rings and functional groups. As shown by the FT-IR spectrum (Fig. 1), the *L. cylindrica* fibers contain different functional groups such as carboxyl, hydroxyl, amine, and other groups. Firstly, the point of zero charge of *L. cylindrica* was determined (Fig. 3). The point of zero charge is a concept relating to the phenomenon of adsorption, expressing the pH at which the electrical charge density on a biomass surface is zero. The point of zero charge of

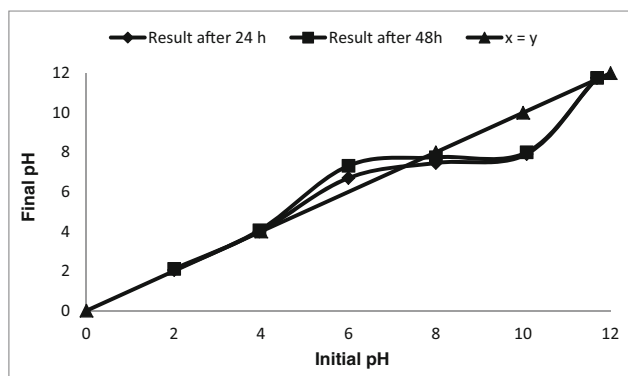


Fig. 3 Influence point of zero charge of *Luffa cylindrica* fibers

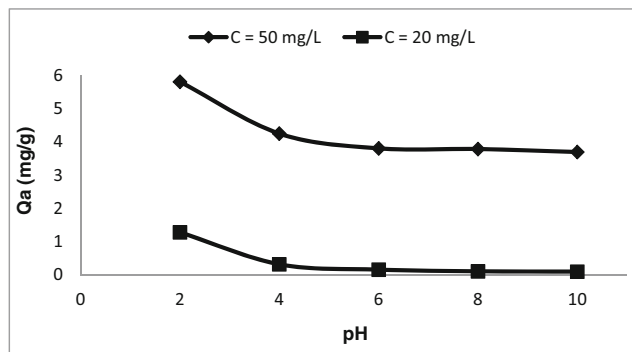


Fig. 4 Influence of initial pH on the biosorption capacity of alpacide blue by *Luffa cylindrica* fibers ($C=20$ and 50 mg/L, solid/liquid ratio= 8 g/L, temperature= 20 °C)

L. cylindrica was found to be 7.85. This result demonstrates that the *L. cylindrica* surface has a positive charge at pH values less than the point of zero charge and thus should be able to absorb anions. The initial pH of the solution is an important parameter that must be taken into account in any biosorption study. The effect of this factor on the change of the biosorption capacity was analyzed on a range of pH from 2 to 10. The results presented in Fig. 4, show that the equilibrium biosorption capacity is maximum at pH 2 (5.80 mg/g) and decreased up to 6, and then remained nearly constant (3.65 mg/g) over the initial pH ranges of 6–10. At higher pH, the surface charge may get negatively charged, thus making (OH^-) ions compete effectively with dye anions causing a decrease in the amount of dye adsorbed (Ben Hamissa et al. 2008; Ncibi et al. 2008b). At lower pH, the fiber biomass, mainly lignin and cellulose chains, may get positively charged, which enhances the negatively charged dye anions through electrostatic forces of attraction (Tunc et al. 2009; Wong et al. 2009; Ncibi et al. 2006; Mahmoudi et al. 2015). This may be attributed to hydrogen bonding between the anionic dye and the functional groups (mainly hydroxy and carboxy) on the surface of the biosorbent (Ncibi et al. 2006). In addition, the hydrogen ion can act as a bridging ligand between the *L. cylindrica* fibers and the alpacide blue (Ben Hamissa et al. 2010; Ncibi et al. 2006). However, the interaction of the alpacide blue with all functional groups is possible

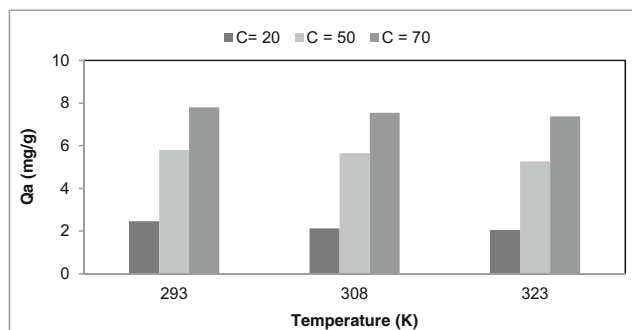


Fig. 5 Influence of temperature on the biosorption capacity of alpacide blue by *Luffa cylindrica* fibers (solid/liquid ratio= 8 g/L, pH= 2)

Table 1 Thermodynamic parameters estimated for alpacide blue biosorption by *Luffa cylindrica* at initial concentrations (C_0) of 20, 50, and 70 mg/L

C_0 (mg/L)	ΔH° (kJ/mol)	ΔS° (J/mol/K)	Temperature (°K)		
			293	308	323
			ΔG° (kJ/mol)		
20	-6.601	-12.640	-2.895	-4.938	-5.114
50	-9.019	-14.020	-2.711	-4.648	-4.741
70	-9.854	-16.320	-2.516	-4.517	-4.624

via many sorption mechanisms including ion exchange, van der Waals interaction, hydrogen bond (between cellulose-OH and the alpacide blue), and microprecipitation (Ben Douissa et al. 2013).

Effect of temperature

The dye removal ability of the *L. cylindrica* was also investigated at different temperatures (293, 308, and 323 K). The study of the influence of temperature on the biosorption of the alpacide blue by *L. cylindrica* fibers, for initial concentrations of 20, 50, and 70 mg/L and a pH=2, is shown in Fig. 5. It was found that alpacide blue biosorption decreases from 2.46 to 2.05 mg/g, 5.80 to 5.26 mg/g, and 7.8 to 7.38 mg/g for initial concentrations of 20, 50, and 70 mg/L, respectively, with increasing temperature from 293 to 323 K. This phenomenon may be due to weakening of the bonds between the dye molecules and active sites of adsorbents for high temperature (Ben Hamissa et al. 2013; Fakhry 2013). This result suggests that the process can be considered as an exothermic process (Atmani et al. 2009). Similar results were obtained in other studies for the biosorption of methylene blue onto sawdust (Ben Hamissa et al. 2013).

Thermodynamic analysis

To estimate the effect of temperature on the alpacide blue biosorption by *L. cylindrica* fibers at different dye

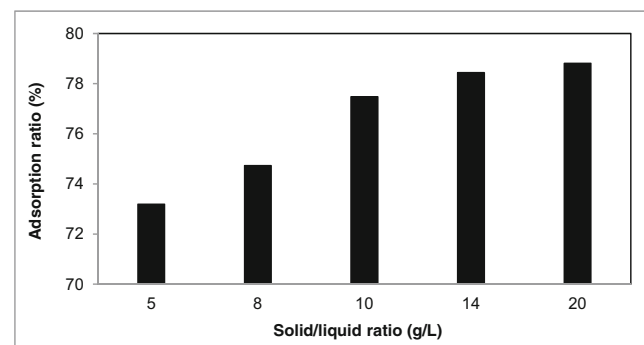


Fig. 6 Influence of biomass amount on the biosorption capacity of alpacide blue by *Luffa cylindrica* fibers ($C_0=20$ g/L, pH= 2 , $T=20$ °C)

Table 2 Kinetic rate constants related to the biosorption of alpacide blue onto *Luffa cylindrica* fibers

	Initial alpacide blue concentration (mg/L)				
	20	30	40	60	80
Pseudo-first order					
k_1 (min ⁻¹)	0.043	0.029	0.034	0.013	0.018
Calculated Q_{e1} (mg/g)	2,210	1,502	1,771	1,640	2,398
R^2	0.950	0.862	0.966	0.567	0.985
Second-first order					
k_2 (mg/g.min)	0.08	0.079	0.022	0.007	0.004
Calculated Q_{e2} (mg/g)	2,457	3,690	5,102	7,092	10,752
R^2	0.999	0.999	0.999	0.999	0.999
Q_{exp} (mg/g)	2,405	3,643	4,716	6,350	9,632

concentrations (20, 50, and 70 mg/L), the thermodynamic was studied at 293, 308, and 323 K, and the thermodynamic parameters such as Gibbs free energy ΔG° (kJ/mol), enthalpy ΔH° (kJ/mol), and entropy ΔS° (J/mol/K) were estimated as described in “Effect of pH” section and listed in Table 1. The negative value of ΔG° indicates the spontaneous nature of biosorption of alpacide blue by *L. cylindrica* for all studied concentrations and temperatures (Ben Hamissa et al. 2013; Bouhamed et al. 2012). The negative value of ΔH° confirms the exothermic process, while the negative value of ΔS° suggested that this biosorption would lead to decreasing randomness (Atmani et al. 2009; Ncibi et al. 2007).

Effect of the biomass amount

Solid/liquid ratio of 5, 8, 10, 14, and 20 g/L of biomass were separately tested in a dye solution of 20 mg/L at pH=2. Figure 6 shows that the amount of dye adsorbed to the equilibrium has increased significantly in the weight range examined. Furthermore, it is observed that the maximum retention is obtained with a mass of 20 g/L. For this quantity, the capacity

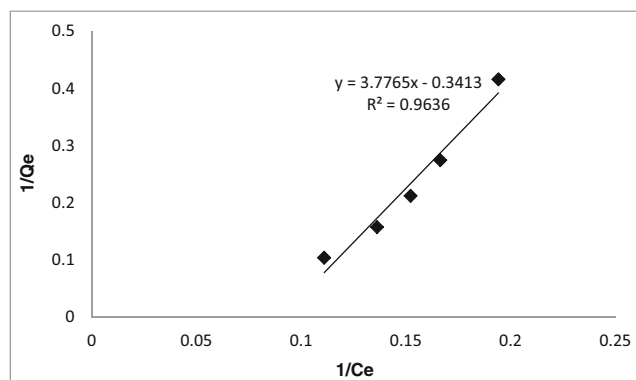


Fig. 7 Linear plot of Langmuir isotherm on the biosorption capacity of alpacide blue by *Luffa cylindrica* fibers (solid/liquid ratio=8 g/L, pH=2, T=20 °C)

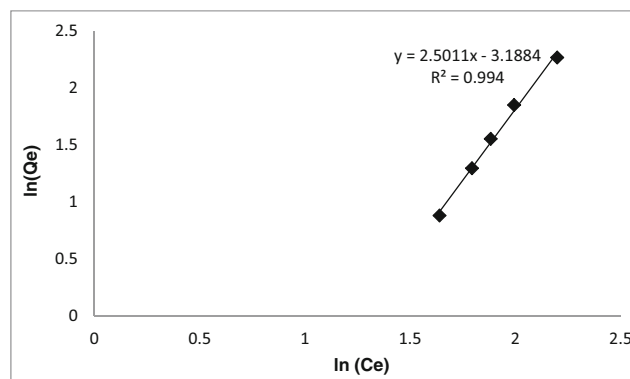


Fig. 8 Linear plot of Freundlich isotherm on the biosorption capacity of alpacide blue by *Luffa cylindrica* fibers (solid/liquid ratio=8 g/L, pH=2, T=20 °C)

of biosorption registers its highest value (2.03 mg/g, i.e., 79 % retention rate). The increase of the rate of dye retention in function of the increase of the fiber mass is due mainly to the high number of sites available for biosorption on the surface of the biomass sites. A similar trend has been observed for the biosorption of Cr(VI) onto *P. oceanica* (L.) biomass (Ncibi et al. 2008b).

Adsorption kinetic modeling

To predict the mechanism during the alpacide blue biosorption process, two kinetic models were used to fit the experimental data, namely the pseudo-first-order and the pseudo-second-order models. The best-fit model was selected based on both linear regression correlation coefficient (R^2) and the calculated Q_e values as described in “Effect of contact time and initial alpacide blue concentration” section and listed in Table 2. The correlation coefficients obtained by the pseudo-first-order model at all initial alpacide blue concentrations explored were found to be less than 0.985, whereas those of the second-order model were equal to 0.999. In addition, the calculated Q_e with the pseudo-first-order (Q_{e1}) did not give acceptable values

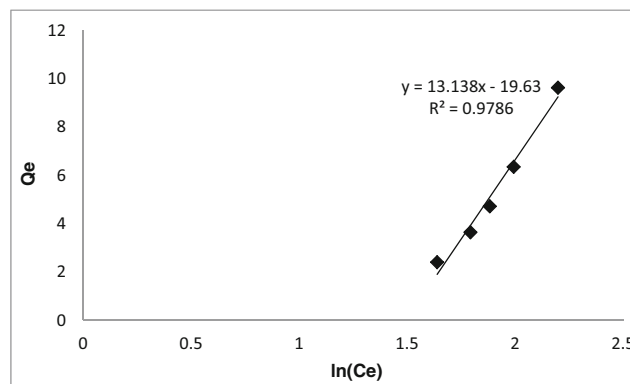


Fig. 9 Linear plot of Temkin isotherm on the biosorption capacity of alpacide blue by *Luffa cylindrica* fibers (solid/liquid ratio=8 g/L, pH=2, T=20 °C)

Table 3 Langmuir, Freundlich, and Temkin model constants and correlation coefficients for the biosorption of alpacide blue by *Luffa cylindrica* fibers (pH=2, $T=20$ °C)

Langmuir	Freundlich	Temkin
$Q_m=2.932$	$K_F=0.250$	$b=188.831$
$K_L=0.090$	$n=0.399$	$A=0.224$
$R^2=0.963$	$R^2=0.994$	$R^2=0.978$

when compared to the experimental ones, whereas the second-order model (Q_{e2}) gives acceptable values. However, the pseudo-second-order model shows the best fit to the experimental data related to the biosorption of alpacide blue by *L. cylindrica* fibers. The value of rate constant (k_2) were found to decrease with increasing concentration. A similar result has been observed by other authors (Ben Hamissa et al. 2008; Ncibi et al. 2009).

Adsorption isotherm modeling

To optimize biosorption system to remove dyes, it is important to establish the most appropriate correlation for the equilibrium curves. The isotherm data were analyzed using three equilibrium models, Langmuir (Fig. 7), Freundlich (Fig. 8), and Temkin (Fig. 9) isotherm models. The mathematical expressions are given in “Effect of temperature” section and listed in Table 3. The best-fit equilibrium model was determined based on the linear-squared regression correlation coefficient R^2 . The equilibrium biosorption data were very well represented by both Freundlich and Temkin isotherms with high correlation coefficients of 0.994 and 0.978, respectively. The fit to experimental data ($R^2=0.963$) in Table 3 shows that the Langmuir isotherm is less adequate to explain the biosorption of alpacide blue into *L. cylindrica*, as compared to the Freundlich and Temkin isotherms, thus confirming the poor applicability

of Langmuir isotherm for this type of biosorption process. The Freundlich isotherm may be used for heterogeneous systems with interaction between the molecules adsorbed. On the basis of these results, one should infer the occurrence of multilayer coverage of alpacide blue on *L. cylindrica* predicted by the Freundlich isotherm.

As the Freundlich isotherm, the Temkin isotherm considers the interactions between adsorbates assuming that the biosorption heat of all molecules decreases linearly when the layer is covered and that the adsorption has a maximum energy distribution of uniform bond (Vargas et al. 2011). The constant b is related to the heat of biosorption. The positive value of b found ($b=185.507$) confirms an exothermic process. The n values ranging between 1 and 10 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to 10. The calculated n values were less than 1 (0.399), which represent a very low heterogeneity of the surface. A similar trend has been observed for the biosorption of reactive dyes onto apple pomace (Robinson et al. 2002).

Comparison of dye biosorption by *L. cylindrica* fibers and other low-cost adsorbents

To establish the relative efficiency of *L. cylindrica* relative to others used to remove textile dye from aqueous solutions, a comparison was made on the basis of the biosorption capacity (Q_m). Dealing with the comparative study, the related results (Table 4) revealed that the *L. cylindrica* fibers could be considered as a promising biomaterial to remove textile dyes when compared to orange peel (Namasivayam et al. 1996), apple pomace (Robinson et al. 2002), alunite (Ozacar and Sengi 2003), *P. oceanica* (Ncibi et al. 2006), and coir pith (Namasivayam and Kavitha 2002). Despite its low biosorption capacity, the *L. cylindrica* had a better potential of biosorption relative to other cheap biological materials.

Table 4 Comparison of biosorption capacities between *Luffa cylindrica* fibers and other studied sorbents for textile dye

Sorbents	Textile dyes	pH	T (°C)	Q_m (mg/g)	T (h)	References
<i>Luffa cylindrica</i>	Alpacide blue	2	20	9.63	4	This study
Natural skin almonds	Methyl orange	NA	23	20.24	1.66	Atmani et al. 2009
<i>Agave americana</i>	Methylene blue	6	20	63.77	1	Ben Hamissa et al. 2013
Raw date pits	Methyl orange	2	25	46	24	Mahmoudi et al. 2015
Langsat peel	Methylene blue	8	30	39.46	5	Mohd Salleh et al. 2012
Orange peel	Procion orange	5.2	29	1.33	1	Namasivayam et al. 1996
Coir pith	Direct red 28	7.6	35	6.72	0.5	Namasivayam and Kavitha 2002
<i>Posidonia oceanica</i>	Direct Solophenyl brown	2	30	5.74	24	Ncibi et al. 2006
<i>Posidonia oceanica</i>	Reactive Cibacron red	2	30	9.62	24	Ncibi et al. 2006
Apple pomace	Mixture of 5 reactive dyes	7.2	20	1.10	24	Robinson et al. 2002
Alunite	Reactive red 124	10	25	2.85	3	Ozacar and Sengi (2003)

Conclusion

The present work shows that the *L. cylindrica* fibers were applied successfully for the biosorption of alpacide blue textile dye. The pH value of the aqueous solution played a significant role in affecting the biosorption capacity of alpacide blue. The highest amount adsorbed for dye removal was attained at pH 2. In addition, the increase in the temperature of solution decreases the adsorbed quantity. While the increase of the biomass amount, increases the retention rate of dye by the *L. cylindrica*. The calculated thermodynamic parameters showed that the biosorption of alpacide blue onto *L. cylindrica* is an exothermic and spontaneous process. The biosorption isotherm studies showed that the Freundlich model presents a good fit to the experimental data ($R^2=0.994$). The mechanism follows a pseudo-second-order reaction model ($R^2=0.999$).

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References

- Abidin FCZA, Rahmat NR (2010) Multi-stage ozonation and biological treatment for removal of azo dye industrial effluent. *Int J Environ Sci Dev* 1(2):2010
- Adie DB, Igboro SB, Daouda N (2013) Determination of the filter potential of *Luffa* sponge (*Luffa aegyptiaca*) in water quality analysis. *Am Int J Contemp Res* 3(3):117–123
- Atmani F, Bensmaili A, Mezener NY (2009) Synthetic textile effluent removal by skin almonds waste. *J Environ Sci Technol* 2:153–169
- Aznar JS (2011) Characterization of activated carbon produced from coffee residues by chemical and physical activation, PhD Thesis, KTH Chemical Science and Engineering Sweden
- Batzias FA, Sidiras DK (2004) Dye adsorption by calcium chloride treated beech sawdust batch and fixed-bed systems. *J Hazard Mater* 18:167–174
- Ben Aissa A (2012) Etude de la faisabilité d'élimination de certains colorants textiles par certains matériaux déchets d'origine naturelle. Université Abou Bakr Balkaid, Tlemcen - Algérie
- Ben Douissa N, Bergaoui L, Mansouri S, Khiaria R, Mhenni MF (2013) Macroscopic and microscopic studies of methylene blue sorption onto extracted celluloses from *Posidonia oceanica*. *Ind Crop Prod* 45:106–113
- Ben Hamissa AM (2005) Biosorption des colorants textiles par des végétaux lignocellulosiques: cas de la *Stypha Tenacissima*. ISAC Chott Meriem. Sousse University
- Ben Hamissa AM, Ncibi MC, Mahjoub B, Seffen M (2008) Biosorption of metal dye from aqueous solution onto *Agave americana* (L.) fibres. *Int J Environ Sci Technol* 5(4):501–508
- Ben Hamissa AM, Lodi A, Seffen M, Finocchio E, Botter R, Converti A (2010) Sorption of Cd(II) and Pb(II) from aqueous solutions onto *Agave americana* fibers. *Chem Eng J* 159:67–74
- Ben Hamissa AM, Brouers F, Ncibi MC, Seffen M (2013) Kinetic modeling study on methylene blue sorption onto *Agave americana* fibers: fractal kinetics and regeneration studies. *Sep Sci Technol* 48:1–9
- Ben Mansour H, Mosrati R, Corroler D, Bariller D, Ghedira K, Bariller D, Chekir-Ghedira L (2009) In vitro study of DNA damage induced by acid orange 52 and its biodegradation derivatives. *Environ Toxicol Chem* 28:489–495
- Ben Mansour H, Boughzala O, Dridi D, Barillier D, Chekir-Ghedira L, Mosrati R (2011) Les colorants textiles sources de contamination de l'eau : CRIBLAGE de la toxicité et des méthodes de traitement. *J Water Sci* 24(3):209–238
- Bouhamed F, Elouear Z, Bouzid J (2012) Adsorptive removal of copper(II) from aqueous solutions on activated carbon prepared from Tunisian date stones: equilibrium, kinetics and thermodynamics. *J Taiwan Inst Chem Eng* 43:741–749
- Căilean D, Barjoveanu G, Musteret CP, Sulitanu N, Manea LR, Teodosiu C (2009) Reactive dyes removal from wastewater by combined advanced treatment. *8(3):503–511*
- Dada AO, Olalekan AP, Olatunya AM, Dada O (2012) Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ onto phosphoric acid modified rice husk. *OSR J Appl Chem (IOSR-JAC)* 3(1):38–45
- Demir H, Top A, Balkose D, Ulk S (2008) Dye adsorption behavior of *Luffa cylindrica* fibers. *J Hazard Mater* 153:389–394
- El Hage R (2010) Prétraitement du *Miscanthus x giganteus*. Vers une valorisation optimale de la biomasse Lignocellulosique, PhD thesis, Nancy University
- Fakhry EM (2013) *Padina pavonica* for the removal of dye from polluted water. *Am J Plant Sci* 4:1983–1989
- Freundlich H (1906) Über die adsorption in Lösungen. *Z Phys Chem* 57:385–470
- Garg VK, Kumar R, Gupta (2004) Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of *Prosopis cineraria*. *Dyes Pigments* 62:1–10
- Ho YS (2004) Citation review of Lagergren kinetic rate equation on adsorption reactions. *Scientometrics* 59(1):171–177
- Ho YS, McKay G (1998) Sorption of dye from aqueous solution by peat. *Chem Eng J* 70(2):115–124
- Lagergren S (1898) Zur theorie der sogenannten adsorption gelöster stoffe. *Bihang till Kongliga Svenska Vetenskaps-Akademiens Handlingar*, Band 24, Afd. II, No. 4, 1–39
- Lajili F (2010) Agriculture durable. Institut Supérieur Agronomique Chott- Mériem
- Langmuir I (1916) The constitution and fundamental properties of solids and liquids. *J Am Chem Soc* 2221:38
- Liu XF, Sun J, Ren J, Curling S, Sun R (2006) Physicochemical characterization of cellulose from perennial leaves (*Lolium perenne*). *Carbohydr Res* 341(16):2677–2687
- Mahmoudi K, Hosni K, Hamdi N, Srasra E (2015) Kinetics and equilibrium studies on removal of methylene blue and methyl orange by adsorption onto activated carbon prepared from date pits—a comparative study. *Korean J Chem Eng* 32(2):274–283
- Mazali IO, Alves OL (2005) Morphosynthesis: high fidelity inorganic replica of the fibrous network of loofa sponge (*Luffa cylindrica*). *An Acad Bras Cienc* 77(1):25–31
- McKay G, Ho YS (1999) Pseudo-second-order model for sorption processes. *Process Biochem* 34:451–465
- Mohd Salleh MA, Mahmoud DK, Abu NABA, Abdul Karim WAW, Idris AB (2012) Methylene blue adsorption from aqueous solution by langsat (*Lansium domesticum*) peel. *J Purity Util React Environ* 1(10):472–495
- Namasivayam C, Kavitha D (2002) Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. *Dyes Pigments* 54:47–58
- Namasivayam C, Muniasamy N, Gayatri K, Rani M, Ranganathan K (1996) Removal of dyes from aqueous solutions by cellulosic waste orange peel. *Bioresour Technol* 57:37–43
- Ncibi MC, Mahjoub B, Seffen M (2006) Studies on the biosorption of textile dyes from aqueous solutions using *Posidonia oceanica* (L.) leaf sheath fibres. *Adsorpt Sci Technol* 24:461–473

- Ncibi MC, Mahjoub B, Seffen M (2007) Adsorptive removal of textile reactive dye using *Posidonia oceanica* (L.) fibrous biomass. *Int J Environ Sci Technol* 4(4):433–440
- Ncibi MC, Altenorç S, Seffen M, Brouerse F, Gaspard S (2008a) Modelling single compound adsorption onto porous and non-porous sorbents using a deformed Weibull exponential isotherm. *Chem Eng J* 145:196–202
- Ncibi MC, Mahjoub B, Seffen M (2008b) Étude de la biosorption du chrome (VI) par une biomasse méditerranéenne : *Posidonia oceanica* (L.) delile. *Rev Sci Eau J Water Sci* 21(4):441–449
- Ncibi MC, Jeanne-Rose V, Mahjoub B, Jean-Marius C, Lambert J, Ehrhardt JJ, Bercion Y, Seffen M, Gaspard S (2009) Preparation and characterisation of raw chars and physically activated carbons derived from marine *Posidonia oceanica* (L.) fibres. *J Hazard Mater* 165(1):240–249
- Ozacar M, Sengi IA (2003) Adsorption of reactive dyes on calcined alunite from aqueous solutions. *J Hazard Mater B98*:211–224
- Palmieri G, Cennamo G, Sannia G (2005) Remazol Brilliant Blue R decolourisation by the fungus *Pleurotus ostreatus* and its oxidative enzymatic system. *Enzym Microb Technol* 36:17–24
- Robinson T, Chandran B, Nigam P (2002) Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. *Water Res* 36:2824–2830
- Rodrigues CS, Madeira LM, Boaventura RA (2013) Treatment of textile dye wastewaters using ferrous sulphate in a chemical coagulation/flocculation process. *Environ Technol* 34(5–8):719–729
- Satyanarayana KG, Guilmaraes JL, Wypych F (2007) Studies on ligno-cellulosic fibers of Brazil. Part I: source, production. Morphology, properties and applications. *Compos Part A* 38(7):1694–1709
- Schwanninger M, Rodrigues JC, Pereira H, Hinterstoisser B (2004) Effects of short time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose. *Vib Spectrosc* 36:23–40
- Temkin MI (1941) Adsorption equilibrium and kinetics of process on non homogeneous surfaces and in the interaction between adsorbed molecules. *J Phys Chem (USSR)* 15:296–332
- Tunc O, Tanacı H, Aksu Z (2009) Potential use of cotton plant wastes for the removal of Remazol Black B reactive dye. *J Hazard Mater* 163:187–198
- Ucun H, Bayhan YK, Kaya Y (2008) Kinetic and thermodynamic studies of the biosorption of Cr(VI) by *Pinus sylvestris* Linn. *J Hazard Mater* 153:52
- Vadivelan V, Kumar K (2005) Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. *J Colloid Interface Sci* 286:90–100
- Vargas AMM, Cazetta AL, Kunita MH, Silva TL, Almeida VC (2011) Adsorption of methylene blue on activated carbon produced from flamboyant pods (*Delonix regia*): study of adsorption isotherms and kinetic models. *Chem Eng J* 168:722–730
- Vijayageetha VA, Pandia Rajan A, Arockiaraj SP, Annamalai V, Janakarajan VN, Saravana Balaji MD, Dheenadhayalan MS (2014) Treatment study of dyeing industry effluents using reverse osmosis technology. *Research Journal of Recent Sciences* ISSN 2277–2502 (3)(ISC-2013):58–61
- Williams DH, Fleming I (1995) *Spectroscopic methods in organic chemistry*, 5th edn. McGraw-Hill Publisher Company Limited, UK
- Wong SY, Tan YP, Abdullah AH, Ong ST (2009) Removal of basic blue 3 and reactive orange 16 by adsorption onto quarterized sugar cane bagasse. *Malays J Anal Sci* 13(2):185–193
- Yurtsever M, Sengil IA (2009) Biosorption of Pb(II) ions by modified quebracho tannin resin. *J Hazard Mater* 163:58–64
- Zawlotzki Guivarch L (2004) Organic pollutant treatment in aqueous medium by electrochemical advanced oxidation process “Electro-Fenton”. Application to the mineralization of synthetic dyes. Marne La Vallée University
- Zoughuir H, Khalef, Bouras O, Chenouf N, Belkaiss D (1998) Traitement des eaux résiduaires colorées de l’unité de SOITEX de Boufarik par adsorption sur argiles modifiées. *Proceeding de la 3ème conférence Maghrébine de Génie des Procédés*, Tome 3, 296–299