American Journal of Environmental Sciences

Original Research Paper

Valuation of Biomaterial: *Phragmites australis* in the Retention of Metal-Complexed Dyes

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Article history
Received: 24-02-2016
Revised: 27-12-2016
Accepted: 11-05-2017

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Abstract: The purpose of this research was to estimate the potential of cellulosic fibers of highly available and renewable Tunisian biomass *Phragmites australis* for the biosorption of an anionic metal complexed dye: Alpacide blue. The present study shows that the *Phragmite australis* were used successfully for the adsorption of Alpcide blue from aqueous solution. Equilibrium was reached after 5 h at 20°C and at pH 2. Optimal adsorption parameters for adsorption of dye onto fibers extract of upper rods were accomplished after 5 h of biosorption using an initial dye concentration of 50 mg L^{-1}, biosorbent amount of 0.5 g of *Phragmites australis*, pH 2 and a granulometry size between 250 and 500 µm. In these conditions, the adsorbed amount of Alpacide blue is 6.11 mg g^{-1} and the biosorption percentage is 85.9%. When the temperature increases until 60°C, the retention rate increases also to reach a value of 90.5%. Regarding fibers extracted from roots, we notice improvement of the adsorbed amount which reaches 7.0 mg g^{-1} and the overall retention rate of 92.6% at 20°C. While at 60°C the amount adsorbed is 7.4 mg g^{-1} and the fixation rate reached 94%. The biosorption phenomenon seems to be endothermic. Moreover the adsorption process is fast, following the model of pseudo-second order for both parts of the plant stems and roots. Finally, mathematical modeling of adsorption isotherms showed that the Freundlich model perfectly describes the biosorption of organic dye studied by these fibers of *Phragmites australis* for both stems and roots.

Keywords: Lingo-Cellulosic Biomass, *Phragmites australis*, Biosorption, Alpacide Blue, Modeling

Introduction

The effluents from different industries like textile industries are in general very colored and can constitute a high source of water pollution (Ben Hamissa *et al*., 2013). Colorants are very stable, resistant to light, water, soaps etc. and relatively non-biodegradable. This is due to their synthetic origin and complex aromatic molecular structures (Maurya and Mittal, 2011; Won *et al*., 2006). Consequently, remove of textile colorant effluent has become a necessity both environmentally and for water reuse. There are several techniques for water treatment whatsoever biological wastewater treatment processes (Abidin and Rahmat, 2010) or different physico-chemical techniques such as: Adsorption on activated carbon (Mahmoudi *et al*., 2015), coagulation (Rodrigues *et al*., 2013), ultrafiltration (Căilean *et al*., 2009), reverse osmosis (Vijayageetha *et al*., 2014), techniques etc. Generally, these treatments have a major drawback common is the operating cost (Ncibi *et al*., 2008).

In this present study, we were interested particularly by the valorization of highly available and renewable Tunisian lignocellulosic biomass *Phragmites australis* for the depollution of industrial wastewater and retention of pollutants considered toxic (Mahmoudi *et al*., 2015) including metal complex dyes (Ben Hamissa *et al*., 2013). This process involving adsorption of organic compounds has been called biosorption. This process is defined as the accumulation and concentration of pollutants contained on aqueous solutions by the employment of biological materials (Aksu, 2002). The

evaluation of potential use of these materials is important to propose as an alternative or complement to conventional and generally expensive methods used for remove metal ions and dyes. Indeed, these materials are very abundant in nature and are low cost.

However, the resulting wastes from the transformation of raw materials generally have little or no value. Thus, the use of these by-products as biosorbent is very timely. For the biosorption of metal cations and dyes, the most sought materials are those having a large amount of cellulose, hemicellulose and lignin such as pine bark for the treatment of effluents loaded with heavy metals (Teles De Vasconcelos and Gonzalez Beca, 1994; Vazquez *et al*., 1994; Al-Asheh *et al*., 1997; 2000), palm scheme for the elimination of basic colorants (Nassar and Magdy, 1997), the fern trunk (Ho *et al*., 2005), papaya (Saeed *et al*., 2005), the nuclei of dates (Mohamed, 2006), the Eucalyptus wood (Tancredi *et al*., 2004), the peels bananas and oranges (Annadurai *et al*., 2002), corn Rafles (Nigam *et al*., 2000), cereal straw (Robinson *et al*., 2002), the fibers of *Posidonia oceanica* for the elimination of heavy metals and dyes (Ncibi *et al*., 2008) and the *Agave americana* fibers for the elimination of colorants (Ben Hamissa *et al*., 2013).

The principal objective of this research is to investigate the biosorption capability of a new, little cost and renewable biomass, *Phragmites australis* fibers, extracted from its stems and roots, for the elimination of metalic dyes (Alpacide Blue (AB)). Several parameters such as: Contact time, initial concentration of Alpacide blue, pH, temperature, granulometry and biomass amount were studied. In addition, mathematical modeling of the kinetics and adsorption isotherms was investigated.

Materials and Methods

Materials

Phragmites australis plants have a Tunisian origin. They were taken from the "Oued el Kharroub" in Sousse. First, these plants were washed several time with water to eliminate impurities and soil, then dried in air for 24 h. The stems and roots of this plant have been sorted in order to study them separately. They were finely cut and dried in an oven at 70°C for 48 h until obtaining constant weight. Then the biomass was ground using an electric grinder. Finally, the biomass was sieved into different particle size using an electric sifter

AB employed in this research is a metal complexed dye, got from textile industry (Chimitex-Tunisia). Chemical structure of AB is unknown. Stock solutions of concentration of 100 mg L^{-1} were prepared by dissolving equal quantities of AB in distilled water. Every working solution was prepared by dilution the stock solution with distilled water to achieve the needed concentrations.

Methods

So as to determine the chemical composition of stems and roots of *Phragmites australis*, a series of extractions were achieved to isolate different substances contained in the material (fats and waxes, pectin, lignin, hemicellulose and cellulose). The protocols are described in the literature (Sedan, 2007; Garcia-Jaldon, 1992). The milled fibers (10 g dry material) is extracted with 400 mL at 80% ethanol in a flask under stirring at 80°C by reflux for 20 min in order to remove fats and waxes. The degreased material is then extracted with water at 100°C (200 mL, 1 h), then with an aqueous solution of ammonium oxalate (1% by mass) heated by reflux at 85°C (300 mL, 2 h) to remove pectins. Lignins are then extracted by two extractions in a mixture (400 mL) of sodium chlorite and glacial acetic acid (80°C, 1 h) with stirring. Lignin is totally degraded by this treatment, it cannot be recovered. Hemicelluloses are solubilized by a solution of potassium hydroxide (24% by mass) at 25°C (400 mL, 24 h) followed by a solution of sodium hydroxide (4.3% by mass) at 25°C (400 mL, 24 h) with stirring.

The biosorption experiences were realized in batch reactor. Stems or roots of fibers were added in 75 mL of dye solution with the desired concentration (10-100 mg L^{-1}), pH (2-10), biomass amount (0.1-0.5 g), granulometry (1.25-5 mm) and temperature (20-60°C). All experiences were carried out at 20°C, apart from the experience realized to study the effect of temperature on biosorption. Temperature was monitored by a thermo-regulated water bath, model Memmert BME1420. The initial pH was adjusted by dilute solutions of HCl or NaOH. The residual concentrations of AB were measured by a double beam spectrophotometer analysis (FT-IR) (Camspec M550) at wavelength λ_{max} of 616 nm. The tests were carried out in triplicate. The negative test (without biomass) was conducted to ensure that the retention capacity was only due to the *Phragmites australis* fibers. The adsorption capacity at equilibrium, Q (mg/g), was calculated by Equation 1. The evaluation of dye removal was determined according to the following Equation 2:

$$Q = \frac{(C_0 - C_i) \times V}{M} \quad (1)$$

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

Where:
C_0 = The initial AB concentration (mg/L)
C_i = The residual AB concentration at any time (mg/L)
V = The volume of solution (L)
M = The mass of the biosorbent (g)

At equilibrium, C_i is equal to C_e and Q is equal to Q_e.

Error Estimation

Nonlinear chi-square (χ^2) test is a statistical tool necessary for the best fit of an biosorption process, obtained by judging the sum squares differences between the experimental and the calculated data, with each squared difference is divided by its corresponding value (calculated from the models). Small value indicates its similarities while a larger value represents the variation of the experimental data (Boulinguiez *et al*., 2008; Foo and Hameed, 2010). The nonlinear chi-square test was calculated by Equation 3 (Foo and Hameed, 2010):

$$\chi^2 = \sum_{i=1}^{n} \frac{\left(Q_{e,calc} - Q_{e,\exp}\right)^2}{Q_{e,\exp}} \quad (3)$$

Results

Chemical Composition of Phragmites australis

The *Phragmites australis* are composed of two parts: Stems and roots. As shown in Table 1, the two parts of *Phragmites australis* are composed by: Wax and grease, pectine, lignin, hemicellulose and cellulose.

Influence of Initial AB Concentration

Dye solutions with initial concentrations from 10 to 100 mg L^{-1} were investigated to examine the ability of the stems and roots of *Phragmites australis* to eliminate different quantities of AB from aqueous solutions and the corresponding times necessary to reach equilibrium. Fig. 1a and 1b show that the biosorption capacity of AB increased proportionally as a function of contact time at all initial dye concentrations. In addition, the biosorption capacity of AB function of time is composed of two parts. In the first part, biosorption capacity increases rapidly but, in the second part, the biosorption becomes very slow and attains equilibrium after 300 min for concentration of 100 mg L^{-1} with adsorption capacities for stems and roots of 12.83 and 14.03 mg g^{-1}, respectively.

Influence of pH

The effect of pH on AB biosorption onto *Phragmites australis* fibers (stems and roots), has been studied in the pH range between 2 and 10, at an initial concentration 20 mg L^{-1}. Figure 2 show that the AB biosorption by the stems and roots presents a similar variation with pH. The maximum biosorption is obtained in the vicinity of pH = 2. The maximum retention rate is around 72 and 94% respectively for the stems and roots. Then, the biosorption capacity of the two parts of the plant decreases with increasing pH, which can reach for the stems and roots 35 and 54%, respectively.

Influence of Mass of Fibers

Figure 3 represents the influence of the variation of the mass of fibers on biosorption capacity. It is noted that greater the quantity of fibers in the solution increases, greater the quantity of AB retention raises. Indeed, the augmentation of mass from 0.1 to 0.5 g is followed by an increase of retention rate from 59.48 to 85.93% for the stems and from 59.60 to 92.58% for roots.

Table 1. Chemical composition of stems and roots of *Phragmites australis*

	Stems	Roots
Wax and grease	23.70	9.25
Pectine	13.50	31.39
Lignin	13.02	9.95
Hemicellulose	28.96	29.04
Cellulose	20.96	20.37

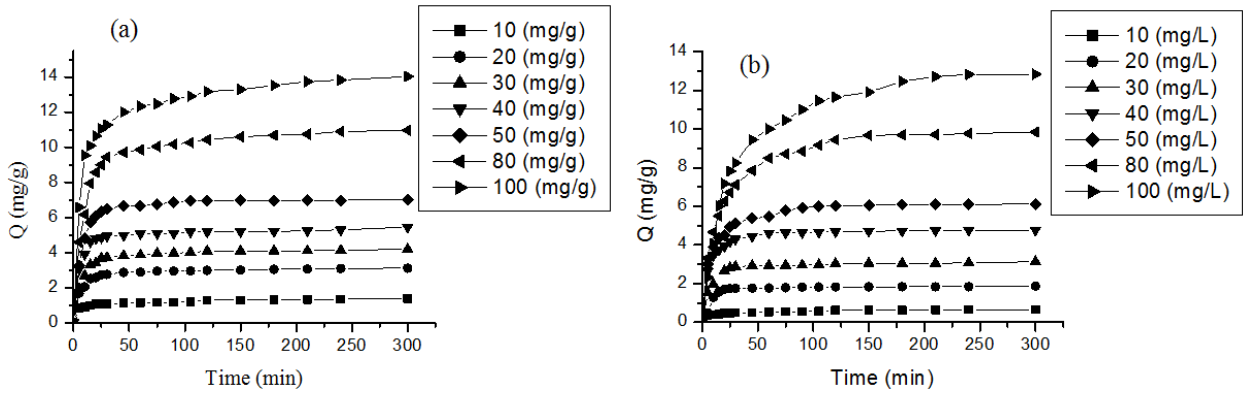

Fig. 1. Effect of initial concentration on the biosorption capacity. Temperature: 20°C, pH: 2, mass of fibers: 0.5 g, volume: 75 mL. (a) Stems and (b) roots

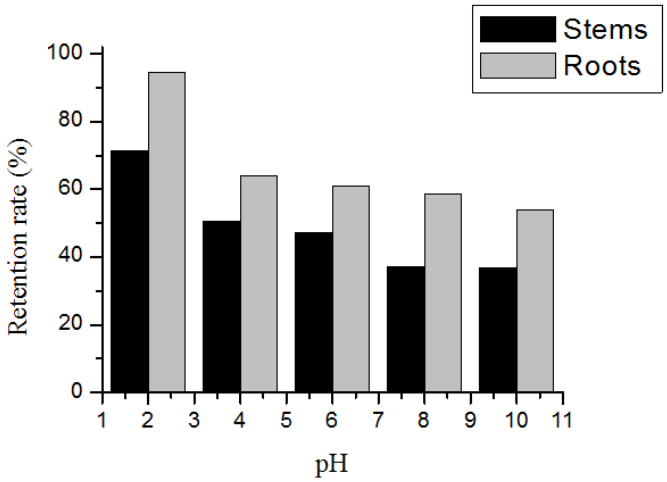

Fig. 2. Influence of pH on the biosorption capacity. Temperature: 20°C, Initial concentration: 20 mg L^{-1}, contact time: 5 h, mass of fibers: 0.5 g, volume: 75 mL

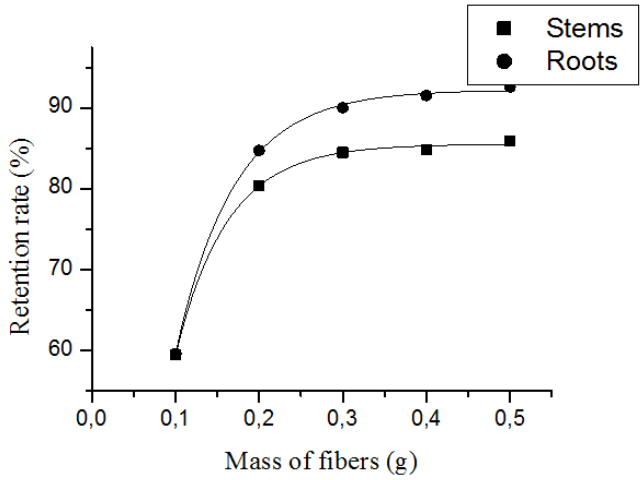

Fig. 3. Influence of mass of fibers on the biosorption capacity. pH: 2, temperature: 20°C, Initial concentration: 50 mg L^{-1}, contact time: 5 h, volume: 75 mL

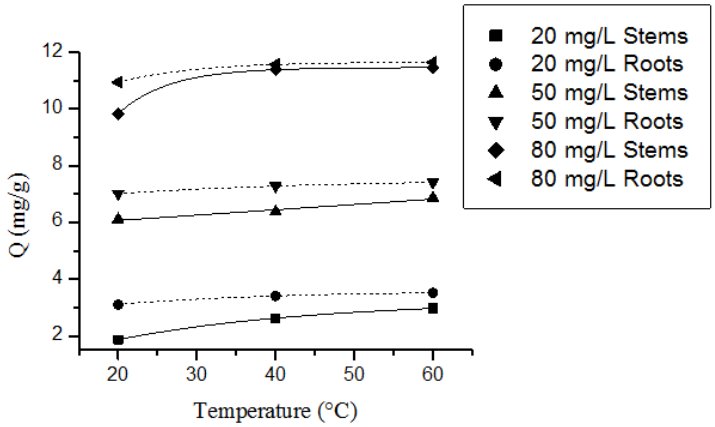

Fig. 4. Influence of temperature on the biosorption capacity. pH: 2, Initial concentration: 50 mg L^{-1}, contact time: 5 h, mass of fibers: 0.5 g, volume: 75 mL

Influence of Temperature

The biosorption capacity of the *Phragmite australis* (stems and roots) was also studied at various temperatures (20, 40 and 60°C). The investigation of the effect of temperature on the remove of AB onto *Phragmite australis* fibers was realized for initial concentrations of 20, 50 and 80 mg L^{-1} and a pH = 2 is represented in Fig. 4. When the temperature is augmented from 20 to 60°C, the biosorption capacity of AB augments for the two parts of plant. Indeed, it was found that AB biosorption onto stems increase from 1.87 to 2.97 mg g^{-1}, 6.11 to 6.86 and 9.83 to 11.45 for initial concentrations of 20, 50 and 80 mg L^{-1} respectively with rising temperature from 20 to 60°C. Similar result was found for roots. Biosorption capacity increase from 3.11 to 3.52 mg g^{-1}, 7.02 to 7.41 and 10.94 to 11.64 for initial concentrations of 20, 50 and 80 mg L^{-1} respectively with increasing temperature from 20 to 60°C.

Influence of Granulometry

The effect of biomass granulometry (stems and roots) was investigated at various granulometry (from 500 µm to 125 µm) as shown in Fig. 5. The retention rate of AB on to *Phragmites australis* fibers increased from 82,25 to 87,50% for stems and from 91,78 to 94,11% for roots with decrease granulometry of (>500 µm) to (250-125 µm) respectively. In addition, roots present a biosorption capacity higher than stems.

Thermodynamic Analysis

To investigate the influence of temperature on the AB biosorption onto *Phragmite australis* (stems and roots) at different dye concentrations, the thermodynamic was studied at temperatures of 293, 313 and 333 K. The thermodynamic parameters like Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were studied from the change of the thermodynamic equilibrium constant K_c with the variation in temperature. The apparent equilibrium constant K_c (Yurtsever *et al*., 2009) is defined by Equation 4:

$$K_C = \frac{C_{ad,eq}}{C_{r,eq}} \tag{4}$$

Where:

$C_{ad,eq}$ and $C_{r,eq}$ = Respectively the concentration of adsorbed AB at equilibrium and residual concentration AB at equilibrium respectively (mg/L)

K_c = The distribution coefficient for the biosorption employed to calculate the Gibbs free energy of biosorption in the following Equation 5:

$$\Delta G° = -RT \ln K_C \tag{5}$$

Where:

R = The gas constant (8.314 J mol^{-1} K^{-1})

T = The absolute temperature (K)

Thermodynamic parameters (ΔG°, ΔH° and ΔS°) for the biosorption of AB by *Phragmites australis* was calculated by the following Equation 6 (Ucun *et al*., 2008):

$$\Delta G° = \Delta H° - T\Delta S° \tag{6}$$

The thermodynamic was performed at 293, 313 and 333 K and the thermodynamic parameters were represented in Table 2.

Kinetic Data Analysis

To predict the mechanism of adsorption of AB during process, the pseudo-first-order and the pseudo-second-order models were analyzed.

Table 2. Thermodynamic parameters for the biosorption of AB into *Phragmite australis* (stems and roots) at initial concentrations (C_0) of 20, 50 and 80 mg L^{-1}

			Temperature (K) ΔG° (kJ mol^{-1})		
C_0 (mg/L)	ΔH° (kJ mol^{-1})	ΔS° (J $mol^{-1}K^{-1}$)	293	308	323
Stems					
20	10.72	40.32	-1.13	-1.82	-2.74
50	6.580	27.90	-1.60	-2.16	-2.71
70	4.050	21.56	-2.29	-2.67	-3.15
Roots					
20	3.897	25.29	-3.51	-4.02	-4.52
50	1.964	15.69	-2.66	-2.89	-3.29
70	0.910	11.81	-2.56	-2.79	-3.03

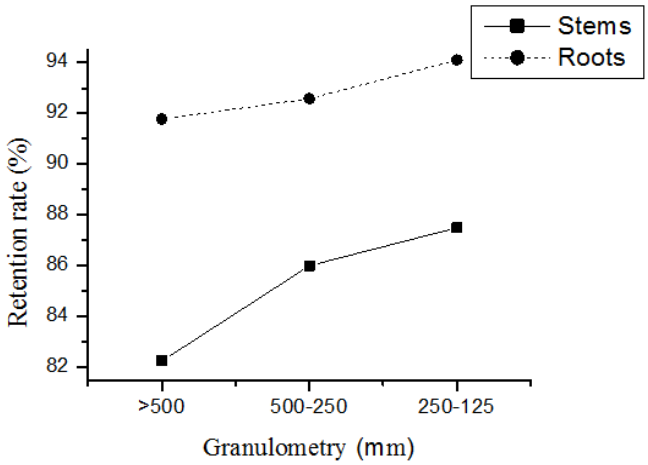

Fig. 5. Influence of granulometry on the biosorption capacity. pH: 2, Initial concentration: 50 mg L^{-1}, contact time: 5 h, mass of fibers: 0.5 g, volume: 75 mL

Table 3. Constants of biosorption kinetics of AB into *Phragmites australis* (stems and roots)

Models	Stems	Roots
Pseudo-first-order		
R^2	0.821	0.779
k_1 (min^{-1})	0.130	0.180
Qe_1 (mg/g)	2.220	1.500
χ^2	0.050	0.090
Pseudo-second-order		
R^2	0.999	0.999
k_2 (mg/g min)	0.048	0.040
Qe_2 (mg/g)	6.305	7.092
χ^2	0.018	0.010

Table 4. Mathematical equations of the used isotherm models

Isotherm model	Equation
Langmuir	$Qe = Q_{max} \times k_L \times \frac{C_e}{1 + K_L \times C_e}$
Freundlich	$Qe = k_F \times Ce^{1/n}$
Elovich	$Qe = Q_{max} K_E C_e \exp(-Q_e/Q_{max})$
Temkin	$Qe = \frac{RT}{bt} \ln (k_t \times Ce)$

The model of pseudo-first-order and the pseudo-second-order equation (Ho and McKay, 1999) were employed to fit the experimental data of the dye adsorption before reaching equilibrium. The linearized form of the pseudo-first-order model is given by expression 7:

$$\log(Q_e - Q) = \log(Q_e) - \frac{k_1 t}{2{,}303} \quad (7)$$

Where:

t = The time (min)

k_1 = The equilibrium rate constant of pseudo-first-order biosorption (min^{-1})

By against, the pseudo-second-order model is employed to a wide interval of time (Ho and McKay, 1999). This model is based on the biosorption capacity of the solid phase; it is described by the Equation 8:

$$\frac{t}{Q} = \frac{1}{k_2 . Q_e^2} + \frac{t}{Q_e} \quad (8)$$

Where, k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g/mg min).

The best-fit model was chosen according to both linear regression correlation coefficient (R^2) and the calculated Qe values and listed in Table 3.

Adsorption Isotherm Modeling

In order to optimize adsorption system for dyes removal, it is important to establish the most appropriate correlation for the equilibrium curves. The isotherms data were analyzed using Langmuir, Freundlich, Temkin and Elovich isotherm models. Further information's on the theoretical background of the mathematical expressions of those models could be found in Vargas *et al.* (2011). The mathematical expressions represented in Table 4 and 5.

Desorption Study

Desorption study was performed at three pH (7, 9 and 12) to study the reversibility of biosorption process and the type of interaction between AB and the *Phragmites australis* and also the possibility of regenerating biomass. For such studies, AB biosorption onto *Phragmites australis* (stems and roots) was carried out at 20°C and over a range of pH (5, 8, 10) values. Table 6 show that the AB desorption is better at pH 12.

Table 5. Isotherm parameters of Langmuir Freundlich, Elovich and Temkin models referred to the biosorption of AB

Isotherm model		Parameters			
Langmuir		Q_{max} (mg/g)	k_L(L/mg)	R^2	χ^2
	Stems	2.78	0.07	0.55	9.78
	Roots	13.31	0.48	0.97	0.821
Freundlich		k_F (mg/g)	n	R^2	χ^2
	Stems	0.001	1.23	0.99	0.79
	Roots	1.76	3.55	0.99	0.28
Elovich		Q_{max} (mg/g)	K_E(L/mg)	R^2	χ^2
	Stems	0.67	0.3	0.55	9.78
	Roots	2.69	0.24	0.90	2.40
Temkin		b_t (KJ/mol)	k_t (L/mg)	R^2	χ^2
	Stems	0.17	0.24	0.96	1.12
	Roots	0.41	1.75	0.87	3.26

Table 6. Investigation of the influence of pH on the amount desorbed (Q_{deq}) in equilibrium

	Q_{deq} (mg/g)		
pH	7.000	9.00	12.00
Stems	0.451	3.26	11.15
Roots	3.340	5.68	11.24

Discussion

Chemical Composition of Phragmites australis

It is noted that the two parts of the plant have the same percentage of cellulose (21%) and hemicellulose (29%). While, the percentage of all other compounds is different. In fact, the stems consist essentially of hemicellulose (29%) while the roots are formed in large part by the pectin (31%).

When compared with data for grapevine stalks (Ping *et al*., 2011) or *Posidonia oceanica* (Khiari *et al*., 2010), it appears that cellulose and hemicellulose contents are close. The lignin content of the stems is relatively low. The comparison with vine stems (Mansouri *et al*., 2012) confirms that the quantities of extractives fractions in the *Phragmites australis* are elevated. Concerning structural components, the *Phragmites australis* stems and roots are characterized by low lignin content and great quantity of hemicellulose, while the content in cellulose is relatively comparable.

Influence of Initial AB Concentration

For both part of *Phragmites australis*, the great biosorption capacity during the first period is probably due to the great number of available biosorption site during the first stage of the process and no less than 90% of AB was eliminated. However, during the second period, the amount of sites available for biosorption diminished so that the colorant molecules require longer time to attain the least accessible sites. Similar behaviors were observed in the literature for the dye adsorption by *Posidonia* fibers (Ncibi *et al*., 2007) and fiber *Agave america* (Ben Hamissa *et al*., 2008; 2013).

Influence of Initial pH

The pH of the solution presents both an important effect on the surface of dye retention sites and the chemical formula of the dye itself.

AB is a metalliferous classified among the anionic dyes. Indeed, at acidic pH, the surface of *Phragmites* fibers will be positively charged by protonation. Obtaining maximum biosorption at an acid pH is probably due to an electrostatic attraction between the charges of the anionic dye and the positive charges of the surface of the fiber (Mahmoudi *et al*., 2015). However, the interaction of the AB with all functional groups of *Phragmite australis* fibers is possible via several adsorption mechanisms such as ion exchange, Van Der Waals interaction, hydrogen bond (between cellulose-OH and the AB) and microprecipitation (Ben Douissa *et al*., 2013).

When the pH of the solution increases, the positive charges located on the surface decreasing, while the negative charges increases. In fact, these negative charges at the surface of the biosorbent don't promote the biosorption of anionic dyes. This is due to an anionic repulsion. Similar results are obtained for other biological matrices such as *Posidonia* fibers (Ncibi *et al*., 2009), *Luffa cylindrica* (Kesraoui *et al*., 2015) and Date palm leaf base (Alsenani, 2014).

Influence of Mass of Fibers

The increase of mass of fibers in the solution is accompanied by an increase number of active sites for retention of dye. Therefore, retention rate of dye increases. These results are alike to those got by Ben Hamissa *et al*. (2008).

Influence of Temperature

Increasing biosorption capacity was observed according to temperature increase. This observation may be due to the relative increase in the mobility of dyes in solution which improves their exposure to the biosorption active sites on the one step and sends them to

difficult access sites on the other. These results suggest that the biosorption of AB is an endothermic phenomenon. The same results are found by other authors (Alsenani, 2014; Ncibi *et al*., 2007).

Influence of Granulometry

Granulometry is important in the biosorption process, especially for dye biosorption. The retention rate of AB is inversely proportional to the granulometry of the fibers. This phenomenon can be explained by the fact that more particle size is low, more active area is large. As the biosorption is a surface phenomenon, the retention of the dyes will therefore greater on the fibers of smaller size. The same trend has been obtained by other researchers (Wong *et al*., 2008; Osu and Odoemelam, 2010; Seolatto *et al*., 2012).

Thermodynamic Analysis

The negative free energy values at all temperatures show that the biosorption of AB by *Phragmite australis* (stems and roots) is spontaneous. $\Delta G°$ is varying from -2.74 to -1.13 kJ mol^{-1} and from -4.52 to -3.51 kJ mol^{-1} from stems and roots, respectively. Moreover, these values are ranged from -20 to 0 kJ mol^{-1} (Ben Hamissa *et al*., 2010), this process may be considered as physisorption (Atmani *et al*., 2009). The positive value of the enthalpy change $\Delta H°$ shows that the biosorption process was endothermic. The same result has been observed for the adsorption of Direct and Reactive dyes from *Posidonia oceanic* (Ncibi *et al*., 2006). Positive values of the entropy $\Delta S°$ indicate the good affinity of the biosorbent towards AB dye (Namasivayam and Kavitha, 2002; Alsenani, 2014).

Adsorption Kinetic Modeling

The correlation coefficients obtained by the pseudo-first-order model were found close to 0.82 for stems and of 0.77 for roots, while those obtained by the second-order model were equal to 0.999 for the both parts of plant and the nonlinear chi-square test was lower (χ^2 = 0.018 for stems and 0.010 for roots). Furthermore, the calculated with the pseudo-first-order (Qe_1) did not present acceptable values when compared to the experimental ones, while, for the second order model (Qe_2) is close to the theoretical value. However, the pseudo-second-order model presents the best fit to the experimental data of the biosorption of AB by Phragmites Australis fibers. The same trend has been found by other researchers (Mahmoudi *et al*., 2015; Ben Hamissa *et al*., 2012; Ncibi *et al*., 2009).

Adsorption Isotherm Modeling

Freundlich isotherms represents very well the equilibrium biosorption data with the highest correlation coefficients of 0.99 for the both part of plant and the lowest nonlinear chi-square test test (χ^2 = 0.79 for stems and 0.28 for roots). The Freundlich isotherm can be employed for heterogeneous systems with interaction between the molecules adsorbed. Consequently, we can deduce the occurrence of multilayer coverage of AB onto *Phragmite australis* predicted by the Frendlich isotherm. The Freundlich exponent n was equal to 1.23 and 3.55 for the stems and roots, respectively. The n value between 1 and 10 indicates a beneficial biosorption of the dyes on *Phragmites australis* (Namasivayam *et al*., 1996; Ncibi *et al*., 2006).

The Freundlich isotherm supposes that the biosorption heat of all molecules diminishes linearly when the layer is covered. Also, the Freundlich isotherm assumes that the biosorption has a maximum energy distribution of uniform bond (Vargas *et al*., 2011).

Desorption Study

At pH 7, the desorbed quantity is 0.45 mg g^{-1} for the rods and 3.34 mg g^{-1} for the roots. This value is very low when compared to that of pH = 12, which is 11.15 mg g^{-1} for stems and 11.42 mg g^{-1} for the roots.

Generally desorption study of AB at basic pH can inform us that the sorption is by ion exchange (Ben Hamissa *et al*., 2013). The best biosorption was at acidic pH and the best desorption was at basic pH. This phenomenon can be assigned to electrostatic attraction/repulsion between the anionic dye and *Phragmites australis*. So the AB biosorption onto *Phragmites australis* (stems and roots) can be considered as a physico-chemical biosorption process. The same trend has been found by other researchers (Ben Hamissa *et al*., 2013; Namasivayam *et al*., 1996).

Conclusion

According the results described above, it may be concluded that *Phragmites australis* stems are composed of 20.78% of cellulose, 28.96% of hemicellulose, 13.50% of pectin, 13.02 of lignin and 23.74% of fats and waxes. While the roots are composed by 20.37% of cellulose, 29.04% of hemicellulose, 31.39% of pectin, 9.95% of lignin and 9.25 of fats and waxes.

On the other hand, the present study demonstrates that the *Phragmites australis* fibers were used successfully for removal of AB from aqueous solution. Biosorption tests of AB onto *Phragmites australis* fibers (stems and roots) were carried out in batch system and in different conditions of pH, temperature, amount of fibers, granulometry and concentration.

Equilibrium is reached after 5 h at a temperature of 20°C. The biosorption maximum is reached at an acidic pH (2). Moreover, the augmentation in the temperature and the mass of the biomaterial increases the adsorbed quantity. Whereas, granulometry does not seem to have a remarkable influence on the adsorption.

Experimental data at equilibrium was modeled and the results showed that the Freundlich model is most suitable to describe biosorption of AB by the fibers of *Phragmites australis* with correlation coefficient R^2 = 0.995 for stems and R^2 = 0.991 for roots.

Modeling of kinetics adsorption revealed that the pseudo-second-order model is most appropriate to describe the biosorption with R^2 of about 0.999 for both types of fiber (stem and root).

Acknowledgement

The authors thank the FP4BATIW project, the Higher Ministry of Education and Research and Laboratory of Energy and Materials for the financial support of this research.

Funding Information

The funders of this manuscript are the FP4BATIW project, Laboratory of Energy and Materials and Ministry of Education and Research.

Authors' Contributions

Aida Kesraoui: Designed and performed the study and drafted the manuscript.

Asma Mabrouk: Helped in the biosorption execution and study.

Mongi Seffen: Supervised the work and corrected the manuscript.

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