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Application of aqai stalks as biosorbent for the removal of Evans Blue and Vilmafix Red RR-2B dyes from aqueous solutions

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ABSTRACT

The aqai palm stalk (*Euterpe oleracea)* is food residue used in its natural form (AS) as biosorbent for the removal of Evans Blue (EB) and Vilmafix Red RR-2B (VR) textile dyes from aqueous solutions. The effects of pH, biosorbent dosage, and shaking time on biosorption capacities were studied. The maximum adsorption of both dyes occurred at pH 2.0. The Avrami fractional-order kinetic model provided the best fit to experimental data compared with pseudo-first-order and pseudo-second-order kinetic adsorption models. The equilibrium data were fitted to Langmuir, Freundlich, and Sips isotherm models. For both dyes, the equilibrium data were best fitted to the Sips isotherm model. Simulated dyehouse effluents were used to check the applicability of the proposed AS biosorbent for effluent treatment.

Keywords: Adsorption kinetics; Aqai stalk; Biosorption; Nonlinear isotherm fitting

1. Introduction

Many industries use dyes to color their final products. It has been estimated that about 10,000 different synthetic dyes and pigments exist and that over 7×10^5 tonnes are produced annually in worldwide [1]. Approximately, 10–60% of the reactive dyes are lost during the manufacturing process, producing large quantities of colored wastewater [2]. The dye-containing wastewater discharged from industry can adversely affect the aquatic environment by impeding light penetration and, as a consequence, precluding photosynthesis of aquatic flora [3]. Moreover, most of the dyes can cause allergy, dermatitis, and skin irritation [4] and can also provoke cancer [5] and cell mutation in humans [5,6]. Therefore, effluents containing dyes require treatment before being released into the environment [7,8].

One of the most methods often employed for the removal of synthetic dyes from aqueous effluents is the adsorption procedure [9,10], due to its simplicity and high efficiency, as well as the availability of a wide range of adsorbents [10,11]. This process transfers the dyes from the aqueous effluent to a solid phase, decreasing remarkably the dye bioavailability

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to living organisms [11]. The decontaminated effluent could then be released to the environment or the water could be reutilized in the industrial process. Subsequently, the adsorbent can be regenerated or stored in a dry place without direct contact with the environment [11–13].

Activated carbon is one of the most employed adsorbents for dye removal from aqueous solution because of its excellent adsorption properties [10–13]. However, the extensive use of activated carbon for dye removal from industrial effluents is expensive, due to its high initial and regeneration costs [13,14], thus limiting more extensive application in wastewater treatment. There is therefore a growing interest in finding alternative low-cost adsorbents for the removal of dyes from aqueous solution. Among these alternative adsorbents, it can be cited: wheat bran [15], microalgae [16], aqai stalk (AS) [17,18], babassu coconut [19], cupuassu shell [20], chitosan [9], pineapple leaves [21], pine tree leaves [22], rice husk [23], mango seeds [24], etc.

Aqai palm (*Euterpe oleracea*) is native from the Brazilian Amazon; however, it has already been cultivated in the USA [16]. The palms of *E. oleracea* are multistemmed and monoecious, and may reach heights of >25 m. The fruit, a small, round and black purple drupe about 25 mm in circumference, is produced in branched panicles of 500–900 fruits [16,17]. Aqai pulp is utilized in the manufacture of a foods' variety and beverages [16,17].The Brazilian annual production of aqai is about 160,000 tons. About 20% of the weight of the aqai is the stalk (AS) that held its fruits, which is a waste material that presents no aggregate economic value [16,17]. The disposal of large amounts of AS directly in the soil and/or in natural waters may contaminate the environment in an uncontrolled way because the putrefaction of this waste material leads to the generation of various chemical compounds and microorganisms. In this context, the combining of the need to reduce costs with commercial adsorbents and the using of AS as biosorbent for the dyes removal from industrial effluents would be a good economic and environmental advantage in developing countries such as Brazil.

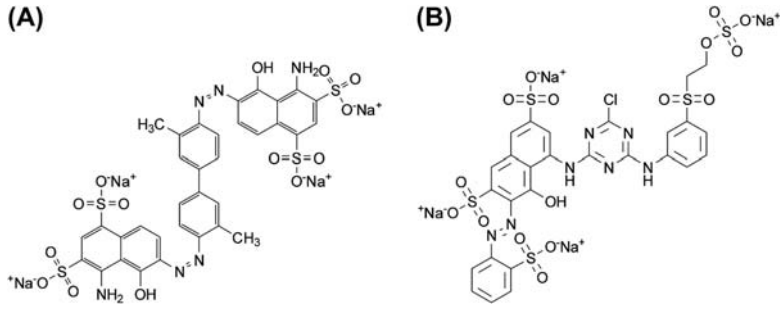
In recent works, ASs in natural form and also in protonated form were successfully used as adsorbent for removal of Reactive Black 5 and Reactive Orange 16 [16] and Procion Blue MX-R [17] from aqueous solutions. The excellent properties of this biomass could be extended for other dye applications. Therefore, the present work aimed to use only the AS in natural form as biosorbent for the successful removal of Evans Blue (EB) (EB; direct dye class) and Vilmafix Red RR-2B (VR) (VR; reactive dye class) dyes from aqueous solutions. These dyes are largely used for textile dyeing in the Brazilian cloth industries.

2. Materials and methods

2.1. Solutions, reagents and biosorbent

De-ionized water was used throughout the experiments for solution preparations.

The textile dye EB (EB; direct dye; C.I. 23860; CAS 314-13-6; $C_{34}H_{24}N_6O_{14}S_4Na_4$; 960.81 g mol^{-1}; λ_{max} 607 nm) was furnished by Sigma-Aldrich (Switzerland) at 85% of purity and the textile dye VR (VR; reactive dye; C.I. 18214; CAS 23354-52-1; $C_{27}H_{18}N_7O_{16}S_5ClNa_4$; 984.21 g mol^{-1}; λ_{max} 508 nm) was furnished by Zhou Fang Pharm Chemical (China) at 80% of purity (see Scheme 1). These dyes were used without further purification. The EB dye has four sulfonate groups and the VR dye has three sulfonate groups and one sulfato-ethyl-sulfone group. These groups present negative charges even in highly acidic solutions due to their pK_a values lower than zero [3]. The stock solution was prepared by dissolving the dyes in de-ionized water to the concentration of 5.00 g L^{-1}. Working solutions were obtained by diluting the dye stock solutions to the required concentrations. To adjust the pH solutions, 0.50 mol L^{-1} sodium hydroxide or hydrochloric acid solutions were used. The pH of the solutions was measured using a Schott Lab 850 set pHmeter.



Scheme 1. Structural formulae of: (A) EB and (B) VR.

AS was furnished by an ice cream industry in Belém-PA, Brazil, as a residual material and it was prepared as already reported [16].

2.2. Adsorption and desorption studies

The biosorption studies for evaluation of the AS biosorbent for the EB and VR dyes removal from aqueous solutions were carried out in triplicate using the batch contact biosorption procedure. For these experiments, fixed amounts of biosorbent (20.0–200.0 mg) were placed in 50 ml cylindrical high-density polystyrene flasks (117 mm height and 30 mm diameter) containing 20.0 ml of dye solutions (20.00–300.0 mg L^{-1}), which were agitated for a suitable time (0.5–48 h) at an acclimatized shaker at 298 K. Blanks without biosorbent were carried out in order to verify the possibility of the dye to be adsorbed by the flask. No dye adsorption by the high-density polypropylene flask was observed after 48 h of contact. The pH of the dye solutions ranged from 2.0 to 9.0. Subsequently, in order to separate the adsorbent from the aqueous solutions, the flasks were centrifuged at 14,000 rpm for 10 min using a Unicen M Herolab centrifuge (Stuttgart, Germany), and aliquots of 1–10 mL of the supernatant were properly diluted with an aqueous solution fixed at pH 2.0.

The final concentrations of the dyes remained in the solution were determined by visible spectrophotometry using a T90 + UV–VIS spectrophotometer furnished by PG Instruments (London–England) provided with quartz optical cells. Absorbance measurements were made at the maximum wavelength of EB and VR which were 607 and 508 nm, respectively.

The amount of dyes uptaken and the percentage of dyes removal by the biosorbent were calculated by applying the Eqs. (1) and (2), respectively:

$$q = \frac{(C_o - C_f)}{X} \tag{1}$$

$$\%\ \text{Removal} = 100 \cdot \frac{(C_o - C_f)}{C_o} \tag{2}$$

where q is the amount of dyes taken up by the biosorbent (mg g^{-1}); C_o is the initial dye concentration put in contact with the adsorbent (mg L^{-1}); C_f is the dye concentration (mg L^{-1}) after the batch adsorption procedure; and X is biosorbent dosage (g L^{-1}).

The experiments of desorption were carried out according to the procedure: about 100.0 mg L^{-1} of EB and VR dyes were shaken with 50.0 mg of AS biosorbent for 1 h; afterwards, the loaded biosorbent was filtered in 0.2 μm cellulose acetate and was washed with water for removing nonadsorbed dyes. Then, the dye adsorbed on the adsorbent was agitated with 20.0 mL of NaCl aqueous solutions (0.05–0.5 mol L^{-1}), 0.05 mol L^{-1} HCl + NaCl (0.05–0.5 mol L^{-1}), and HCl (0.05–0.1 mol L^{-1}) for 15–60 min. The desorbed dyes were separated and estimated as described above.

2.3. Quality assurance and statistical evaluation of the kinetic and isotherm parameters

To establish the accuracy, reliability, and reproducibility of the collected data, all the batch adsorption measurements were performed in triplicate. Blanks were run in parallel and they were corrected when necessary [25].

All dye solutions were stored in glass flasks, which were cleaned by soaking in 1.4 mol L^{-1} HNO_3 for 24 h [26] and rinsed five times with de-ionized water, dried, and stored in a suitable place.

For analytical calibration, standard solutions with concentrations ranging from 10.00 to 100.0 mg L^{-1} of the dyes were employed, running against a blank solution of water adjusted to pH 2.0. The linear analytical calibration curve was furnished by the UV-Win software of the PG Instruments spectrophotometer (model T90+). The detection limits of the method, obtained with signal/noise ratio of 3 [27], were 0.16 and 0.12 mg L^{-1}, for EB and VR, respectively. All the analytical measurements were performed in triplicate, and the precision of the standards was better than 3% ($n = 3$). For checking the accuracy of the EB and VR dye sample solutions during the spectrophotometric measurements, standards containing dyes at 20.00 mg L^{-1} were employed as quality control at each 10 determinations [28].

The kinetic and equilibrium models were fitted by employing a nonlinear method, with successive interactions calculated by the method of Levenberg–Marquardt and also interactions calculated by the Simplex method, using the nonlinear fitting facilities of the software Microcal Origin 7.0. In addition, the models were also evaluated by adjusted determination factor (R^2_{adj}), as well as by an error function (F_{error})[29], which measures the differences in the amount of dye taken up by the adsorbent predicted by the models and the actual q measured experimentally. (R^2_{adj}) and F_{error} are given below, respectively:

$$R^2_{\text{adj}}\left\{1 - \left[1 - \left(\frac{\sum_i^n (q_{i,\text{exp}} - \overline{q}_{i,\text{exp}})^2 - \sum_i^n (q_{i,\text{exp}} - q_{i,\text{model}})^2}{\sum_i^n (q_{i,\text{exp}} - \overline{q}_{i,\text{exp}})^2}\right) \cdot \left(\frac{n-1}{n-p}\right)\right]\right\} \tag{3}$$

$$F_{\text{error}} = \sqrt{\left(\frac{1}{n-p}\right) \cdot \sum_{i}^{n} \left(q_{i,\text{exp}} - q_{i,\text{model}}\right)^2} \quad (4)$$

where $q_{i,\text{model}}$ is each value of q predicted by the fitted model; $q_{i,\text{exp.}}$ is each value of q measured experimentally, $\overline{q}_{\text{exp}}$ is the average of q experimentally measured; n is the number of experiments performed; and p is the number of parameter of the fitted model [29].

2.4. Simulated dyehouse effluent

Two synthetic dyehouse effluents containing four representative reactive dyes and one direct dye used for coloring fibers and their corresponding auxiliary chemicals were prepared at pH 2.0, using a mixture of different dyes most often applied to textile fibers industries. According to the practical information obtained from a dyehouse, typically 20% of the reactive dyes and 100% of the dyebath auxiliaries remain in the spent dyebath, and its composition suffers a 5–30-fold dilution during subsequent washing and rinsing stages [2,3,13]. The concentrations of the dyes and auxiliary chemicals selected to imitate the exhausted dyebath are given in Table 1.

3. Results and discussion

3.1. Effects of acidity on adsorption

One of the most important factors in adsorption studies is the acidity effect of medium [20,24,29]. Different adsorbates may present divergent ranges of suitable pH, according to used adsorbent. Effects of initial pH on removal percentage of EB and VR dyes using AS biosorbent were evaluated within the pH range between 2 and 9 (Fig. 1). For both dyes, the percentage of dye removal was remarkably decreased from pH 2.0, attaining practically less than 0.2 and 5.0% of dye removal at pH 7.5 for EB and VR dye respectively. Similar behavior for dye removal utilizing lignocellulosic adsorbents was also observed [20,24,29].

Table 1
Chemical composition of simulated dyehouse effluents

Dye	λ (nm)	Concentration (mg L^{-1})	
		Effluent A	Effluent B
EB	607	20	40
VR	508	20	40
Cibacron Brilliant Yellow 3G-P	400	5	10
Reactive Orange 16	493	5	10
Reactive Black 5	598	5	10
Auxiliary chemical			
Na_2SO_4		80	160
NaCl		80	160
Na_2CO_3		50	120
CH_3COONa		50	120
CH_3COOH		1,300	1,300
pH		2.0	2.0

pH of the solution adjusted with 0.10 mol L^{-1}HCl and/or NaOH

The pH_{PZC} value of AS reported in our previous work is 5.84 [16]. For pH values lower than pH_{PZC}, the adsorbent presents a positive surface charge [3,13]. The dissolved EB and VR dyes are negatively charged in water solutions, because they present sulfonate and sulfato-ethyl-sulfone groups [3]. The adsorption of these dyes takes place when the biosorbent presents a positive surface charge [3]. For AS, the electrostatic interaction occurs for pH < 5.84. However, the lower the pH value from the pH_{PZC}, the more positive the surface of the biosorbent [16]. This behavior explains the high sorption capacity of AS for both EB and VR at pH 2. In order to continue the biosorption studies, the initial pH was fixed at 2.0. It is recommended to use pH of the adsorbate solution (dye solution) with a difference of at least 1 pH unit of the pH_{pzc}, in order to not alter significantly the pH of final solution, after the adsorption. When it is necessary to work with an initial pH solution closer to the pH_{pzc} of the adsorbent, a diluted appropriate buffer solution (0.05 mol L^{-1}) is required. If this requirement is not taken into account, the sorption capacity of the adsorbent could decrease remarkably. It should be highlighted that when the initial pH of both dyes were fixed at 2.0, after the adsorption experiments, the final pH did not alter significantly (<5%), because the pH_{pzc} of the AS biomass is 5.84, presenting a difference of more than 3.8 units of the initial pH [3,20,24] utilized throughout this work.

3.2. Kinetic studies

Adsorption kinetic studies are important in the treatment of aqueous effluents because they provide valuable information on the mechanism of the adsorption process [24,30,31].

Many kinetic models were developed in order to find intrinsic kinetic adsorption constants. Traditionally, the kinetics of metal ions adsorption is described following the expressions originally given by Lagergren [7,8]. A simple kinetic analysis of adsorption is the pseudo-first-order equation in the form:

$$\frac{dq}{dt} = k_f \cdot (q_e - q_t) \quad (5)$$

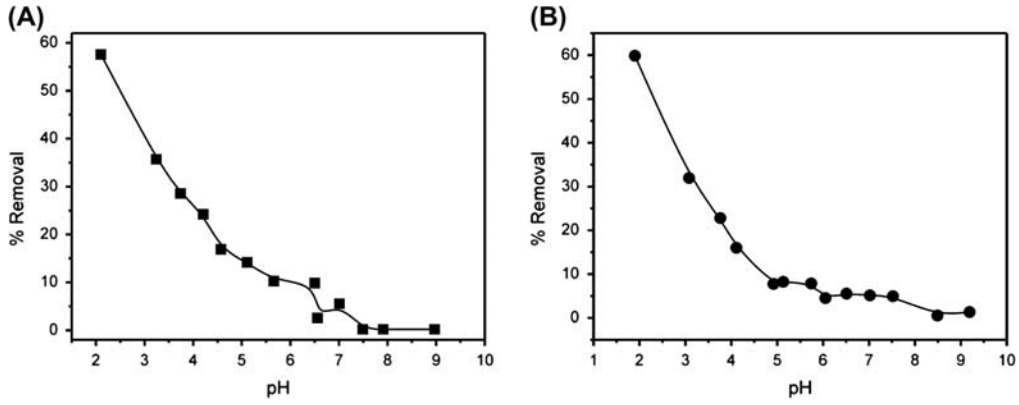


Fig. 1. Effect of pH on the biosorption of: (A) EB and (B) VR dye. Conditions: $C_o = 50.0\,\mathrm{mg\,L^{-1}}$ of dye solution; the temperature was fixed at 298 K.

Where q_t is the amount of adsorbate adsorbed at time t ($\mathrm{mg\,g^{-1}}$); q_e is the adsorption capacity in the equilibrium ($\mathrm{mg\,g^{-1}}$); k_f is the pseudo-first-order rate constant ($\mathrm{h^{-1}}$); and t is the contact time (h). The integration of Eq. (5) with initial conditions,$q_t = 0$ at $t = 0$, and $q_t = q_t$ at $t = t$ leads to:

$$Ln(q_e - q_t) = Ln(q_e) - k_f \cdot t \tag{6}$$

After rearranging this equation in a nonlinear form the pseudo-first-order kinetic equation is:

$$q_t = q_e[1 - \exp(-k_1 \cdot t)] \tag{7}$$

In addition, a pseudo-second-order equation [7,8] based on adsorption equilibrium capacity may be expressed in the form:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_s \cdot (q_e - q_t)^2 \tag{8}$$

Where k_s is the pseudo-second-order rate constant ($\mathrm{g\,mg^{-1}\,h^{-1}}$). The integration of Eq. (8) with initial conditions, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, leads to:

$$q_t = \frac{k_s \cdot q_e^2 \cdot t}{1 + q_e \cdot k_s \cdot t} \tag{9}$$

Despite the pseudo-first-order and pseudo-second-order kinetic models being used for most adsorption kinetic works, determination of some kinetic parameters, as possible changes of the adsorption rates in function of the initial concentration and the adsorption time, as well as the determination of fractionary kinetic orders, still lacks in the kinetic adsorption models [7,8]. For this purpose, an alternative Avrami kinetic equation, in order to find a good experimental and calculated data correlation, was early proposed [7,8]. The adsorption should be visualized now using Avrami's exponential function, which is an adaptation of kinetic thermal decomposition modeling [7,8].

$$\alpha = 1 - exp[-(k_{\mathrm{AV}} \cdot t)]^{n_{\mathrm{AV}}} \tag{10}$$

Where α is the adsorption fraction (q_t/q_e) at time t; k_{AV} is the Avrami kinetic constant ($\mathrm{h^{-1}}$); and n_{AV} is a fractionary reaction order which can be related to the adsorption mechanism [7,8].

By inputting the α in Eq. (10), the Avrami kinetic equation could be written as:

$$q_t = q_e \cdot \{1 - exp[-(k_{\mathrm{AV}} \cdot t)]^{n_{\mathrm{AV}}}\} \tag{11}$$

In attempting to describe the biosorption kinetics of EB and VR dyes by using AS biosorbent, three kinetic models were tested, as shown in Fig. 2 for EB and VR. The kinetic parameters for the kinetic models are listed in Table 2. As can be seen in Fig. 2, practically all the kinetic models were suitably fitted to the experimental kinetic data. However, the Avrami fractional kinetic model presented slightly better performance (with the lowest error function values and also the highest R^2 values) for the two initial concentrations of both dyes. The lower the error function, the lower the difference of the q calculated by the model from the experimentally measured q [11,13]. It should be pointed out that the F_{error} utilized in this work took into account the number of the fitted parameters (p term of Eq. (4)), since it has been reported in the literature [31] that depending on the number of parameters a nonlinear equation presents, it has the best fitting with the results. For this reason, the number of fitted parameters should be considered in the calculation of F_{error}. Also, it was verified that the q_e values found in the fractionary-order were closer to the experimental q_e values, when compared with all other kinetic models.

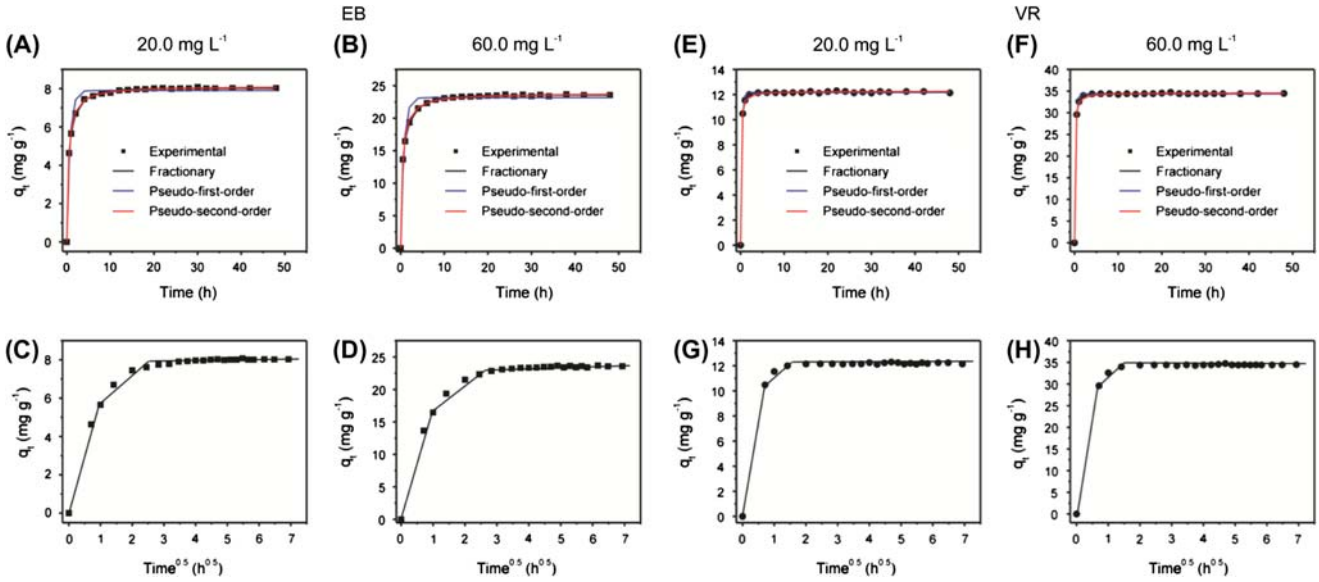


Fig. 2. Kinetic biosorption curves of: (A) C_o 20.0 mg L^{-1} EB; (B) C_o 60.0 mg L^{-1} EB; (C) C_o 20.0 mg L^{-1} EB; (D) C_o 60.0 mg L^{-1} EB; (E) C_o 20.0 mg L^{-1} VR; (F) C_o 60.0 mg L^{-1} VR; (G) C_o 20.0 mg L^{-1} VR; and (H) C_o 60.0 mg L^{-1} VR. Conditions: pH was fixed at 2.0; the AS biosorbent dosage was fixed at 2.5 g L^{-1}; and the temperature was fixed at 298 K.

Table 2
Kinetic parameters for EB and VR removal using AS biosorbent. Conditions: temperature of 298 K; pH 2.0; and biosorbent dosage 2.5 g L^{-1}

	EB		VR	
	20.0 mg L^{-1}	60.0 mg L^{-1}	20.0 mg L^{-1}	60.0 mg L^{-1}
Fractionary order				
k_{AV} (h^{-1})	1.51	1.48	6.70	6.46
q_e (mg g^{-1})	8.02	23.6	12.2	34.4
n_{AV}	0.513	0.498	0.561	0.577
h_o (mg g^{-1} h^{-1})	12.1	34.8	81.7	222.5
(R^2_{adj})	0.9995	0.9998	0.9996	0.9998
F_{error}	0.0399	0.0834	0.0534	0.0919
Pseudo-first order				
k_f (h^{-1})	1.40	1.37	3.83	3.83
q_e (mg g^{-1})	7.90	23.2	12.2	34.4
h_o (mg g^{-1} h^{-1})	11.0	31.8	46.6	131.7
(R^2_{adj})	0.9779	0.9734	0.9983	0.9986
F_{error}	0.268	0.863	0.105	0.266
Pseudo-second order				
k_s (g mg^{-1} h^{-1})	0.305	0.102	1.07	0.383
q_e (mg g^{-1})	8.14	23.9	12.3	34.6
h_o (mg g^{-1} h^{-1})	20.2	57.9	161.2	459.1
(R^2_{adj})	0.9991	0.9983	0.9989	0.9989
F_{error}	0.0540	0.214	0.0860	0.241
Intra-particle diffusion				
k_{id} (mg g^{-1} $h^{-0.5}$)[a]	1.33	3.98	2.08	6.00

[a]Second stage.

These results indicate that the Avrami fractionary-order kinetic model should explain the adsorption process of EB and VR dyes using AS biosorbent.

Since kinetic results fit very well to the Avrami-fractionary kinetic model for the EB and VR dyes using AS biosorbent (Table 2 and Fig. 2), the intra-particle diffusion model [18,20] was used to verify the influence of mass transfer resistance on the binding of EB and VR dyes to the AS biosorbent (Table 2 and Fig. 2(C), (D), (G), (H). The intra-particle diffusion constant, k_{id} ($mg\,g^{-1}\,h^{-0.5}$), can be obtained from the slope of the plot of q_t (uptaken at any time, $mg\,g^{-1}$) vs. the square root of time. These figures show the plots of q_t vs. $t^{1/2}$, with multi-linearity for the EB and VR dyes using AS biosorbent. These results imply that the adsorption processes involve more than one single kinetic stage (or adsorption rate) [18,20]. The adsorption process exhibits three stages, which can be attributed to each linear portion of the Fig. 2(C),(D),(G),(H). The first linear portion was attributed to the diffusion dye process to the AS biosorbent surface [18,20]; hence, it was the fastest sorption stage. The second portion, ascribed to intra-particle diffusion, was a delayed process. The third stage may be regarded as the diffusion through smaller pores, which is followed by the establishment of equilibrium [18,20].

It was observed in Fig. 2 that the minimum contact time of EB and VR dyes with the AS biosorbent to reach equilibrium was about 14 and 4 h, respectively (the minimum time for EB to attain the equilibrium is 3.5 times of VR dye to attain the equilibrium). This great difference in the minimum contact time to reach the equilibrium is associated with the difference in the mechanism of adsorption. The Avrami constant rate (k_{AV}) for VR was at least 4.36 times higher than the k_{AV} for EB dye, which implies that the film diffusion could explain the remarkable differences on the kinetics of adsorption of VR dye in relation to EB. In addition, the intra-particle diffusion constant (k_{id}) for VR was more than 1.5 times higher than the k_{id} for EB, indicating that the resistance to the mass transfer is much lower for VR dye. This could explain the difference of 10 h to reach the equilibrium for VR in relation to EB. Probably, EB molecules should be more aggregated, forming dimers in aqueous solution, which would increase the resistance to the mass transfer inside the porous of AS biosorbent, as already reported in the literature [16]. In order to continue this work, the contact times between the AS biosorbent and EB and VR biosorbates were fixed at 16 and 6 h, respectively. This increase in the contact time utilized in this work was to guarantee that for both dyes, the equilibrium would be attained even in higher biosorbate concentrations.

3.3. Equilibrium studies

An adsorption isotherm describes the relationship between the amount of adsorbate taken up by the adsorbent (q_e) and the adsorbate concentration remaining in the solution after the system attained the equilibrium (C_e). There are several equations to analyze experimental adsorption equilibrium data. The equation parameters of these equilibrium models often provide some insight into the adsorption mechanism, the surface properties, and affinity of the adsorbent.

In this work, the Langmuir, Freundlich, and Sips [7,8] isotherm models were tested.

The Langmuir isotherm equation is:

$$q_e = \frac{Q\max \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \tag{12}$$

where C_e is the supernatant concentration after the equilibrium of the system ($mg\,L^{-1}$); K_L is the Langmuir equilibrium constant ($L\,mg^{-1}$); and Q_{max} is the maximum adsorption capacity of the material ($mg\,g^{-1}$) assuming a monolayer of adsorbate uptaken by the adsorbent.

The Freundlich isotherm model is:

$$q = K_F \cdot C_e^{1/n} \tag{13}$$

Where K_F is the Freundlich equilibrium constant [$mg\,g^{-1}(mg\,L^{-1})^{-1/n}$]; and n is the Freundlich exponent (dimensionless).

The Sips model is an empirical model and consists of the combination of the Langmuir and Freundlich isotherm type models. The Sips [7,8] model takes the following form:

$$q = \frac{Q\max \cdot K_S \cdot C_e^{1/n}}{1 + K_S \cdot Ce^{1/n}} \tag{14}$$

Where K_S is the Sips equilibrium constant $(mg\,L^{-1})^{-1/n}$; and Q_{max} is the Sips maximum adsorption capacity ($mg\,g^{-1}$).

At low adsorbate concentrations, it effectively reduces to a Freundlich isotherm, and while at high adsorbate concentrations, it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm.

The isotherms of adsorption of EB and VR were carried out at 298 K on the AS biosorbent, using the best experimental conditions described previously (see Table 3 and Fig. 3). Based on the F_{error}, the Sips model is the best isotherm model for both dyes. The Sips model showed in Table 3 presents the lowest F_{error} values, which means that the q fit by this isotherm model was

Table 3
Isotherm parameters for EB and VR biosorption, using AS biosorbent. Conditions: temperature at 298 K; contact time 16 and 6 h for EB and VR, respectively; and pH 2.0; biosorbent dosage 2.5 g L^{-1}

Langmuir	EB	VR
Q_{max} (mg g^{-1})	45.1	62.9
K_L (L mg^{-1})	1.09	0.177
(R^2_{adj})	0.9832	0.9785
F_{error}	1.02	2.03
Freundlich		
K_F (mg g^{-1}(mg $L^{-1})^{-1/n_F}$)	28.6	19.4
n_F	14.0	3.57
(R^2_{adj})	0.8236	0.9753
F_{error}	3.31	2.17
Sips		
Q_{max} (mg g^{-1})	46.5	79.3
K_S ((mg $L^{-1})^{-1/n_S}$)	1.10	0.0912
n_S	1.31	1.58
(R^2_{adj})	0.9998	0.9999
F_{error}	0.110	0.166

close to the q measured experimentally when compared with other isotherm models. For EB, the Langmuir and the Freundlich isotherm models were not suitably fitted, presenting F_{error} values ranging from 9.30 to 30.2-fold higher than the F_{error} values obtained by the Sips isotherm model. For VR dye, the Langmuir and the Freundlich presented F_{error} values ranging from 12.2 to 13.1-fold higher than the F_{error} values obtained by the Sips isotherm model. Therefore, all these models mentioned above for EB and VR dyes, using AS as biosorbent, have no physical value. Taking into account that the Sips isotherm model presented the lowest F_{error} value for both dyes, this isotherm model was chosen as the best for describing the equilibrium of adsorption of EB and VR using AS as biosorbent. Therefore, based on the Sips isotherm model, the maximum amounts of EB and VR uptaken were 46.5 and 79.3 mg g^{-1} for both dyes, respectively. These values indicate that AS is a fair good biosorbent for the removal of these dyes from aqueous solutions. In Table 4, the maximum sorption capacity of AS utilized as biosorbent is presented. By seeing this Table, it is noted that the sorption capacity of AS obtained for removing EB and VR dye is good, when compared with other dyes.

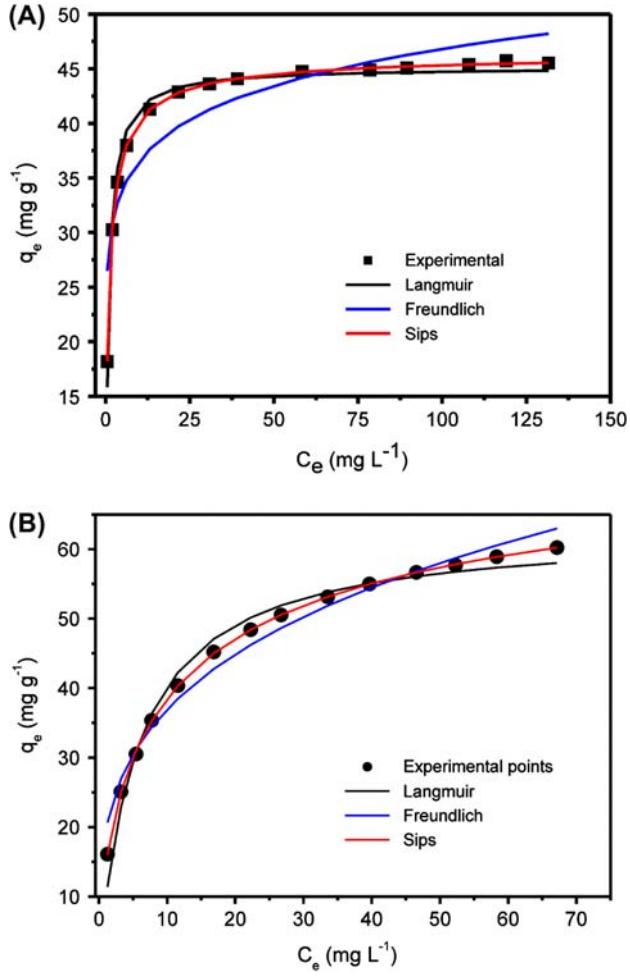


Fig. 3. Isotherm curves of (A) EB and (B) VR dye on AS biosorbent. Conditions: pH was fixed at 2.0; the biosorbent dosage was fixed at 2.5 g L^{-1}; and the temperature was fixed at 298 K. The contact time were fixed at 16 and 6 h for EB and VR dye, respectively.

Table 4
Comparison of maxima adsorption capacities for AS biosorbent. The values were obtained at the best experimental conditions of each work

Dyes	Q_{max} (mg g^{-1})	Ref.
Reactive Black 5	52.3	[16]
Reactive Orange 16	62.3	[16]
Procion Blue MX-R	43.7	[17]
EB	46.5	This work
VR	79.3	This work

3.4. Desorption experiments

In order to check the reuse of the AS biosorbent for the adsorption of EB and VR dyes, desorption experiments were carried out. The eluents such as, NaCl aqueous solutions (0.05–0.5 mol L^{-1}), 0.05 mol L^{-1} HCl + NaCl (0.05–0.5 mol L^{-1}), and HCl (0.05–0.1 mol L^{-1}) were tested for regeneration of the loaded adsorbent (see Table 5). For both dyes 0.05 mol L^{-1} HCl

Table 5
Desorption of EB and VR dyes loaded on AS biosorbent. Conditions for adsorption: initial dye concentration 100 mg L^{-1}; mass of biosorbent 50.0 mg, and pH 2.0; time of contact 1 h

C/mol L^{-1}	% Recovery	
Eluent	EB	VR
0.05 NaCl	71.62	73.56
0.1 NaCl	72.44	75.65
0.2 NaCl	74.66	77.36
0.3 NaCl	78.62	79.65
0.4 NaCl	82.94	81.56
0.5 NaCl	84.11	86.69
0.05 HCl + 0.05 NaCl	94.53	95.36
0.05 HCl + 0.1 NaCl	95.65	96.37
0.05 HCl + 0.2 NaCl	96.55	97.56
0.05 HCl + 0.3 NaCl	98.21	98.65
0.05 HCl + 0.4 NaCl	98.65	99.12
0.05 HCl + 0.5 NaCl	98.55	99.05
0.05 HCl	90.06	94.12
0.1 HCl	92.86	94.25

+ 0.4 mol L^{-1} NaCl desorbed the dyes uptaken by the AS biosorbent immediately (at least 98.65%); on the other hand, the recoveries of the adsorbent using aqueous NaCl of different concentrations as regenerating solutions occurred with lower efficiency even after 1 h of agitation (recoveries < 87%).The time of desorption was set only at 1 h, to verify the economic viability of regenerating the biosorbent material. Cycles of adsorption/desorption were carried out, and after 4 cycles, the efficiency for dyes removal was decreased by about 5%. Therefore, the use of AS biosorbent for EB and VR dye adsorption could be economically viable since it allows its regeneration.

3.5. Treatment of a simulated dyehouse effluent

In order to verify the efficiency of the AS as biosorbent for the removal of dyes from textile effluents, two simulated dyehouse effluents were prepared (see Table 1). The UV–VIS spectra of the untreated effluent (pH 2.0) and treated with AS were recorded from 350 to 800 nm (Fig. 4). The area under the absorption bands from 350 to 800 nm was utilized to monitor the percentage of dyes mixture removed from the simulated dye effluents. The AS biosorbent removed respectively 66.8 and 69.2% of the dye effluents A and B. Taking into account that the total concentration of dyes in the effluent A and B is 55 and 110 mg L^{-1} respectively (sum of concentration of five dyes), these results indicate that in the effluents A and B, the concentration of 36.7 and 76.1 mg L^{-1}, respectively, of the mixture of these five dyes was removed from aqueous effluents and was retained in the biosorbent. It should be highlighted that the effluents A and B present total saline concentration of 1560 and 1860 mg L^{-1}, respectively. Therefore, AS when used as biosorbent presents very good potentialities to be used in real wastewater treatment.

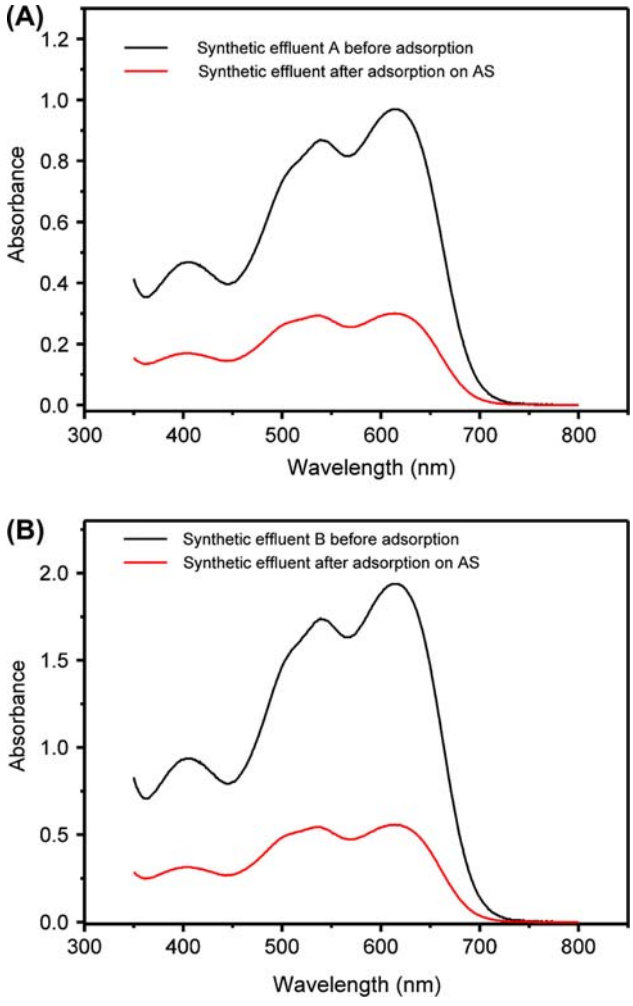


Fig. 4. UV–VIS spectra of simulated dye effluents before and after adsorption treatment with AS biosorbent. Conditions: pH 2.0 and temperature 298 K.

4. Conclusion

The aqai palm stalk (*E. oleracea)* in natural form (AS) is a good alternative biosorbent to remove EB and VR textile dyes from aqueous solutions. Both dyes interact with the AS biosorbent at the solid/liquid interface when suspended in water. The best conditions were established with respect to pH and contact time to saturate the available sites located on the adsorbent surface.

Four kinetic models were used to adjust the adsorption and the best fit was the Avrami (fractionary-order) kinetic model. However, the intra-particle diffusion model gave many linear regions, which suggested that the biosorption may also be followed by multiple adsorption rates. The equilibration time of EB and VR dyes was obtained after 14 and 4 h, of contact between the EB and VR dyes, respectively with the AS biosorbent. The equilibrium isotherm of these dyes was obtained, being these data better fitted to the Sips isotherm model. The maximum amounts of EB and VR uptaken were 46.5 and 79.3 mg g^{-1} for both dyes, respectively, using the AS biosorbent. Regeneration > 98% of both dyes on AS biosorbent was obtained using a mixture of 0.05 mol L^{-1} HCl + 0.4 mol L^{-1} NaCl as eluent. The use of AS biosorbent for the treatment of simulated industrial textile effluents presents fair good performance by removing at least 66.8% of the mixture of dyes in a medium containing high saline concentrations.

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