

Methylene blue biosorption from aqueous solutions by yellow passion fruit waste

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Abstract

The yellow passion fruit (*Passiflora edulis* Sims. f. *flavicarpa* Degener) (YPFW) a powdered solid waste, was tested as biosorbent for the removal of a cationic dye, methylene blue (MB), from aqueous solutions. Adsorption of MB onto this low-cost natural adsorbent was studied by batch adsorption at 25 °C. The effects of shaking time, biosorbent dosage and pH on adsorption capacity were studied. In alkaline pH region the adsorption of MB was favorable. The contact time required to obtain the maximum adsorption was 48 h at 25 °C. Four kinetic models were tested, being the adsorption kinetics better fitted to pseudo-first order and ion exchange kinetic models. The ion exchange and pseudo-first order constant rates were 0.05594 and 0.05455 h⁻¹, respectively. The equilibrium data were fitted to Langmuir, Freundlich, Sips and Redlich–Peterson isotherm models. Taking into account the analysis of the normal distribution of the residuals (difference of $q_{\text{measured}} - q_{\text{model}}$), the data were best fitted to Sips isotherm model. The maximum amount of MB adsorbed on YPFW biosorbent was 44.70 mg g⁻¹.

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Keywords: Biosorbent; Low-cost adsorbent; Yellow passion-fruit waste; Methylene blue; Aqueous solution; Batch adsorption; Isotherm models

1. Introduction

The removal of color from aquatic systems caused by presence of synthetic dyes is extremely important from the environmental viewpoint because most of these dyes are toxic, mutagenic and carcinogenic [1]. The release of colored waters into the ecosystem is a source of aesthetic pollution, also causing perturbation to aquatic life [2]. Several methods have been developed to remove synthetic dyes from waters and wastewaters in order to decrease their impact on the environment. The processes developed consist in decolorizing by photocatalytic oxidation, microbiological or enzymatic decomposition and adsorption on inorganic or organic matrices [3]. The most commonly used adsorbent to remove dyes from waters and wastewaters is activated carbon [4], but due to the relatively high operating costs, such as regeneration of the used adsorbent had limited appli-

cation on a larger scale [5]. Thus, the use of an inexpensive adsorbent to remove dyes from waters and wastewaters, which does not require previous pre-treatment, has been object of study [5].

Non-conventional adsorbents, including natural materials such as waste from agro-industrial activities, have been used successfully, used as alternative low-cost adsorbents for the removal of several dyes from aqueous solution [6–11]. For example, several studies on the removal of methylene blue using various kinds of these non-conventional materials have been reported, such as: the adsorption on, chromium waste sludge [11], fibrous clay minerals [12], natural sepiolite [13], marine green alga [14], de-oiled-soya and bottom ash [15], fly ash [16], on Indian rosewood sawdust [17], on several agricultural wastes such as cotton hulls, coconut tree sawdust, sago waste, maize cobs and banana piths [18], cassava peel [19]; rice husk [20] and maize waste [21].

In a previous study [22], we reported of statistical design of experiments to optimize the best conditions for dye, methylene blue, removal from aqueous solution using yellow passion fruit waste (YPFW – *Passiflora edulis* Sims. f. *flavicarpa* Degener). This previous work was a base for optimizing the batch adsorption conditions carried out in this work, where basically all

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Nomenclature

Nomenclature

a_{RP}	the Redlich–Peterson constants $(\text{mg l}^{-1})^{-\beta}$
A^+	is the adsorbate
$[A^+]$	the molar concentration of the ions A^+
B	is the adsorbent matrix
C^+	is the ion released to the aqueous solution after exchange process
$[C^+]$	the molar concentration of the ions C^+
C_0	the initial dye concentration put in contact with the adsorbent (mg l^{-1})
C_e	the dye concentration at the equilibrium (mg l^{-1})
dq	differential of q
F	is the fraction attained of equilibrium at time t , obtained by ratio between the amount adsorbed (mg g^{-1}) at time t and at infinite time $(F = q_t/q_\infty)$
h_0	the initial sorption rate $(h_0, \text{ expressed in } \text{mg g}^{-1} \text{ h}^{-1})$
k_1 and k_2	are the forward and reverse specific rate constants (h^{-1})
k_f	pseudo-first order rate constant (h^{-1}) .
k_s	is the pseudo-second order rate constant $(\text{g mg}^{-1} \text{ h}^{-1})$.
K_F	the Freundlich constant related with adsorption capacity $[\text{mg g}^{-1} (\text{mg l}^{-1})^{-1/n}]$
K_L	the Langmuir affinity constant (l mg^{-1})
K_{RP}	Redlich–Peterson constants (l g^{-1})
K_S	the Sips constant related with affinity constant $(\text{mg l}^{-1})^{-1/n}$
m	the mass of adsorbent (g)
n	dimensionless exponents of Freundlich and Sips equations
n_{AB} and n_{BC}	the moles of A^+ and C^+ adsorbed on the adsorbent. $E = n_{AB} + n_{BC}$
q	amount adsorbed of adsorbate by the adsorbent (mg g^{-1})
q_e	is the adsorption capacity in the equilibrium (mg g^{-1})
q_t	is the amount of adsorbate adsorbed at time t (mg g^{-1})
Q_{\max}	the maximum adsorption capacity of the adsorbent (mg g^{-1})
S	the ion exchange constant rate (h^{-1})
t	time of contact (h)
V	the volume of dye put in contact with the adsorbent (l)

Greek letters

α	the initial adsorption rate $(\text{mg g}^{-1} \text{ h}^{-1})$ of Elovich equation
β	Elovich constant related to the extent of surface coverage and the activation energy involved in chemisorption (g mg^{-1})
β	The Redlich–Peterson exponent (dimensionless)

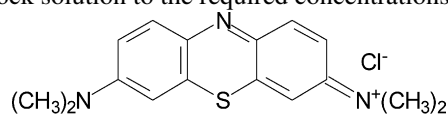
the parameters optimized using statistical tools were in agreement with the parameters optimized using univariate analysis, as already reported for several adsorption systems [23–26], however the kinetics and equilibrium studies were not shown in the previous study. The yellow passion fruit is cultivated on a large scale in Brazil and it has an agronomic importance because the fruits are widely used *in nature* or in a processed form as concentrated juice [27,28]. The by-products resulting from juice processing represent major disposal problem for industry and the environment. Thus, its reutilization is of great interest.

In this work, we are continuing our studies, exploring the potential use of yellow passion-fruit waste (YPFW) as a biosorbent to remove methylene blue (MB) dye from aqueous solutions. The important parameters such pH, kinetics and equilibrium isotherm studies were carried out to complement the usability of YPFW as an alternative and low-cost adsorbent.

2. Experimental procedure and methods

2.1. Solutions and reagents

The cationic dye, methylene blue (MB) (CI 52030, $C_{16}H_{18}N_3SCl$) was obtained from Sigma Chemical Co., USA, with analytical grade that was used without further purification. The stock solution was prepared by dissolving accurately weighted dye in distilled water to the concentration of 1000 mg l^{-1} . The working solutions were obtained by diluting the dye stock solution to the required concentrations.



Structural formula of methylene blue.

In order to adjust the pH solutions, 0.10 mol l^{-1} sodium hydroxide or hydrochloric acid solutions were used, using a pH-meter Digimed Model DM 20 for the measurements.

2.2. Preparation and characterization of biosorbent

Yellow passion-fruit were purchased at local market. The waste peel was removed and the collected biosorbent was extensively washed with water, dried under sunlight for 48 h. Afterwards, the yellow passion peel was crushed in a knife-mill. The resulting material was sieved, and the portion with particle diameter lower than $250 \mu\text{m}$, was subsequently washed with doubly distilled water for 10 min, and then dried in an oven at 60°C for 24 h. Powdered material was preserved in the desiccator and used in the adsorption studies.

Yellow passion-fruit waste (YPFW) was characterized by FTIR using a Shimadzu FTIR, model 8300 (Kyoto, Japan). The spectra were obtained with a resolution of 4 cm^{-1} , with 100 cumulative scans.

The specific surface area of biosorbent was determined by the Brunauer, Emmett and Teller (BET) multipoint technique,

Table 1
Physical and chemical properties of YFPW biosorbent

BET specific surface area (m ² g ⁻¹)	30.0
Total pore volume (cm ³ g ⁻¹)	0.07
BJH pore diameter (nm)	3.0
Zero charge pH	3.7
Elemental analysis	
C (%)	45.32
H (%)	12.67
N (%)	0.51
Acidic surface groups concentration	
Carboxylic groups (mmol g ⁻¹)	1.81
Carbonyl groups (mmol g ⁻¹)	0.70
Phenolic (mmol g ⁻¹)	0.02
Ashes content (%)	1.6
Total fiber (%)	21.4
Mineral composition on biosorbent	
Ca (%)	0.198
Fe (%)	0.059
Zn (%)	0.0094
Mn (%)	0.0339
Na (%)	0.0762
K (%)	0.104
Al (%)	0.207
Si (%)	0.480 ^a
Mg (%)	0.089
P (%)	0.314

^a dry ash.

obtained by the N₂ adsorption–desorption isotherm, determined at liquid nitrogen boiling point, using a homemade volumetric apparatus [29,30], connected to turbo molecular Edwards vacuum line systems, employing a Hg capillary barometer and also an active Pirani gauge [29,30]. The biosorbent material was previously degassed at 100 °C, in vacuum, for 1 h. The pore size distribution was made in the volumetric apparatus, cited above, using nitrogen probe [29,30]. The data analysis was made by using the Barret, Joyner and Halenda (BJH) method [29,30].

The surface functional groups on the YFPW were investigated by Boehm titration [32].

For determination of silica contents in the biosorbent, the YFPW was calcined in a muffle-furnace at 900 °C under air atmosphere during 4 h in order to obtain mineral ashes. For determination of major mineral components, a digestion procedure using nitric acid and hydrogen peroxide, as described elsewhere [33], was employed. The mineral composition of the biosorbent present in the digest of the biomaterial was determined by flame atomic absorption spectrometry using an Analyst 200 (Perkin-Elmer) spectrometer.

The fiber contents was evaluated as described elsewhere [34].

The elemental analysis of the biosorbent was carried out on a CHN Perkin-Elmer M CHNS/O Analyzer, Model 2400, after degassing treatment at 150 °C. The analyses were made in triplicate.

The zero point of charge of the YFPW was measured by the mass titration [35] methods.

The physical and chemical properties of biosorbent were presented in the Table 1.

2.3. Adsorption studies

All the experiments were carried out at 25 °C in order to avoid solubilization of organic groups present in the YFPW biosorbent [36].

The yellow passion-fruit waste (YFPW) adsorption capacity for MB was studied using the batch procedure performing all the experiments in triplicate. For this experiment, a fixed amount of biosorbent (0.100–1.00 g) was placed in a 125 ml Erlenmeyer flask containing 50.0 ml of dye solution (5.0–600.0 mg l⁻¹) at pH ranging from 2.0 to 11.0 and the contact time ranging from 0.08 to 72 h. Then, the Erlenmeyer flasks were shaken in a rotary orbital shaker at 60 rpm and 25 °C for 72 h. The biosorbent was separated from the liquid phase by the centrifugation at 3000 rpm for 10 min, as already reported in other works [12,37] and then, the dye remained in the solution was determined by spectrophotometry using a UV–Vis spectrophotometer (Shimadzu Model TCC240-A) with 1.0 cm path length cell. Absorbance measurements were made at the maximum wavelength of MB at 660 nm.

Batch desorption studies were carried out by agitating 50.0 mL of dye solution of 25.0 mg l⁻¹ and 0.500 g of biosorbent, the agitation time used was 56 h, and the supernatant dye solution was discarded. The amount dye loaded biosorbent, was firstly washed with water for removing non-adsorbed dye. Then, the dye-loaded biosorbent was agitated with 25.0 ml of aqueous solutions (0.010–0.30 mol l⁻¹ HCl or 0.050–0.50 mol l⁻¹ KCl) up to 1 h. The desorbed dye was separated and estimated as before.

The amount of dye uptaken by the biosorbent was calculated by applying the equation:

$$q = \frac{(C_0 - C_e)}{m} V \quad (1)$$

where q is the amount of dye uptaken by the adsorbent (mg g⁻¹); C_0 is the initial MB concentration put in contact with the adsorbent (mg l⁻¹), C_e is the MB concentrations (mg l⁻¹) after the batch adsorption, m is the mass of adsorbent (g) and V is the volume of dye put in contact with the adsorbent (l).

2.4. Statistical evaluation of the kinetic and isotherm parameters

In this work, the kinetic and equilibrium models were fitted employing the non-linear fitting method using the software Microcal Origin 7.0. In addition, the models were also evaluated by probability plot of the residuals (difference between the q_i model and q_i experimental) [25] by using the Minitab Statistical Software release 14.20.

Where $q_{i \text{ model}}$ is each value of q predicted by the fitted model and $q_{i \text{ experimental}}$ is each value of q measured experimentally.

3. Results and discussion

3.1. Characterization of biosorbent

The physical and chemical properties of yellow passion-fruit waste biosorbent were presented in the Table 1. The pore size dis-

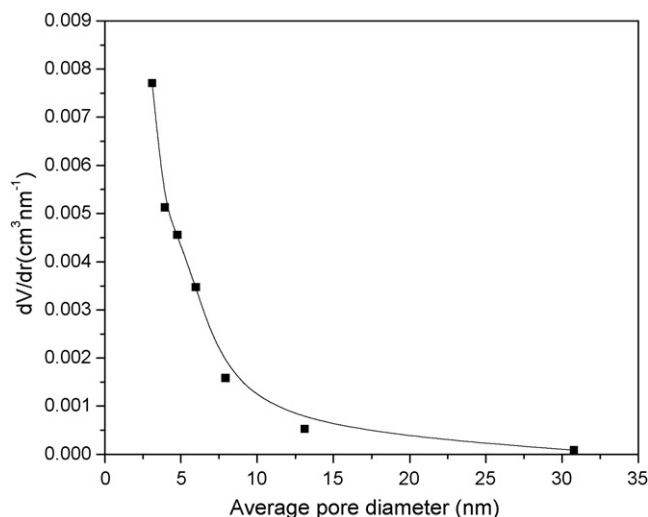


Fig. 1. Pore size distribution of yellow passion fruit obtained by BJH method.

tribution, obtained by BJH method, was presented in the Fig. 1. As can be seen, the distribution of average pore diameter curve is a descendent one, where the maximum presents an average pore diameter of 3 nm, and a small amount of pores ranging from 3 to 30 nm. Therefore, this material could be considered a mesoporous material [30] which is defined as a material that presents average diameter pore between 2 and 50 nm [30].

The YPFW is composed basically of polysaccharide lignin, and pectin, containing hydroxyl and carboxylate groups [28,36]. The Fig. 2 showed the FTIR spectrum of YPFW biosorbent. The absorptions with maxima at 3400 cm^{-1} was assigned to the stretching of O–H group and the band about 2900 cm^{-1} was assigned to stretching of C–H bond of methyl and methylene groups presented in the lignin structure [38]. The band observed at 1745 cm^{-1} was assigned to a carbonyl band (C=O) of unionized carboxylate stretching of carboxylic acid or pectin ester [38], while the peak at 1620 cm^{-1} was attributed to C=O stretching of carboxylic acid with intermolecular hydrogen bond [38]. The band at 1425 cm^{-1} is due to aromatic ring of lignin. The band in the 1250 cm^{-1} is due to the bending modes of O–C–H,

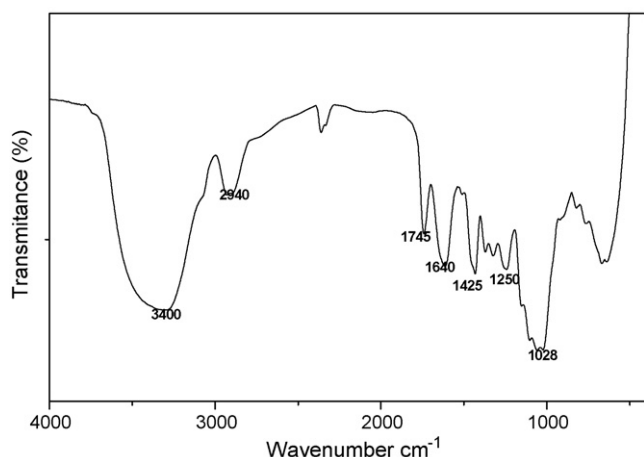


Fig. 2. FTIR spectrum of yellow passion-fruit waste.

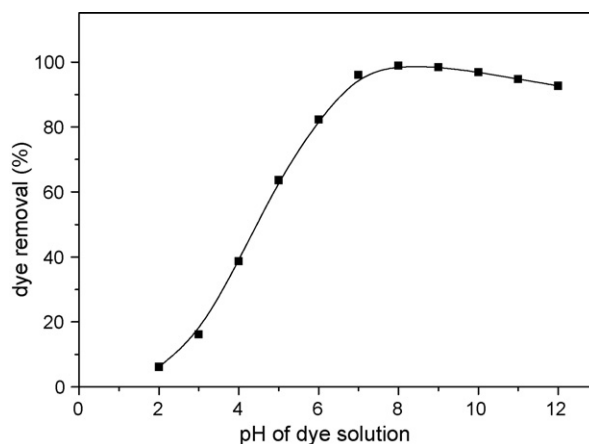


Fig. 3. Effects of pH on the removal of MB from aqueous solution, using an initial concentration of 28.7 mg l^{-1} , and the temperature was fixed at $25\text{ }^{\circ}\text{C}$.

C–C–H and C–O–H. The band at 1028 cm^{-1} was assigned to C–O stretching, also confirmed the lignin [36] presence on the yellow passion fruit. These FTIR results corroborated by the amount of carboxylic and carbonyl groups on the material and with the elemental analysis (see Table 1) indicated that the YPFW presented functional groups such as, OH, COO^- and CO, that could be potential adsorption sites for interaction with the cationic MB dye.

3.2. Acidity effects on the adsorption of methylene blue dye

Fig. 3 depicted the dependence of MB dye removal with the changes in pH solution. The removal of MB increased significantly with increases in the pH solutions ranging from 2.0 up to 7.0. For pH values higher than 7.0 and lower than 10.0, the amount of dye removal was kept practically constant (variations lower than 2.8%). For pH values higher than 10.0, it was observed a 5.8% decrease in the percentage of dye removal, that could be attributed to solubilization of organic groups present on the surface of biosorbent [27]. Therefore, the best pH range for adsorption of MB was from 7.0 to 10.0. This result could be explained considering the electrostatic interaction between the surface of the biosorbent, negatively charged, mainly due to COO^- species, since the pKa values of carboxylic acids range from 3.8 to 5.0 [39], with the cationic dye MB. At lower pH a possible protonation of COO^- occurs, precluding the electrostatic attraction with the MB dye, decreasing the adsorbate uptake. Thus, at pH values ranging from 7.0 to 10.0, the carboxylic groups are available to adsorb the positively charged dye, increasing the removal of MB from aqueous solution. In order to confirm these results, the zero charge potential of YPFW determined, whose value obtained was 3.7. At pH values lower than 3.7 the surface of YPFW is positively charged, precluding the electrostatic attraction of MB, a cationic dye. On the other hand, for pH values higher than 3.7, the MB adsorption is facilitated.

Similar trends, where the negative charge of the adsorbent surface were observed for MB adsorption on Fe(III)/Cr(III) hydroxide [40], malachite green on agro-industry waste [41] and MB on various carbon adsorbents [42].

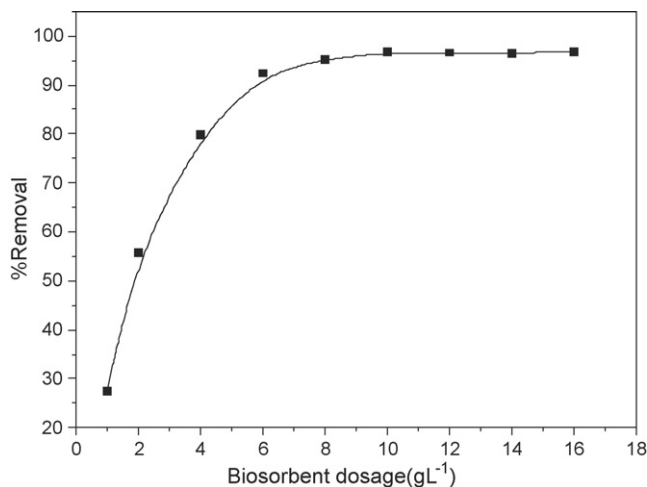


Fig. 4. Effects of adsorbent dosage on removal MB by YFPF; agitation time, 48 h, MB concentration 28.7 mg l⁻¹, temperature 25 °C, pH 8.0.

In order to continue this work, the solution pH was fixed at 8.0. At this pH value, it was not observed any variations in the solubility of organic compounds of biosorbent in the aqueous phase after contact times of 72 h. In addition, the MB dye solution ranging from 10 to 1000 mg l⁻¹ was not precipitate at pH 8.0, as already reported elsewhere [17].

3.3. Effects of adsorbent dosage

In Fig. 4 was shown the percentage of MB removal by YFPF biosorbent at different biosorbent doses (1.0–16.0 g l⁻¹). The results revealed that the color removal was increased up to a biosorbent dosage of 10.0 g l⁻¹ and then it remained almost constant. Increase in the percentage of dye removal with adsorbent dosage could be attributed to an increased in the adsorbent surface area, which increased the availability of more adsorption sites. In the further experiments the adsorbent dosage was fixed at 10.0 g l⁻¹.

3.4. Adsorption kinetics and desorption experiments.

Adsorption kinetic study is important in treatment of aqueous effluents as it provides valuable information on the reaction pathways and in the mechanism of adsorption reactions. In Table 2 are summarized some of the most important kinetic models which were employed in this work. For describing the adsorption of MB on YFPF biosorbent the four kinetic models

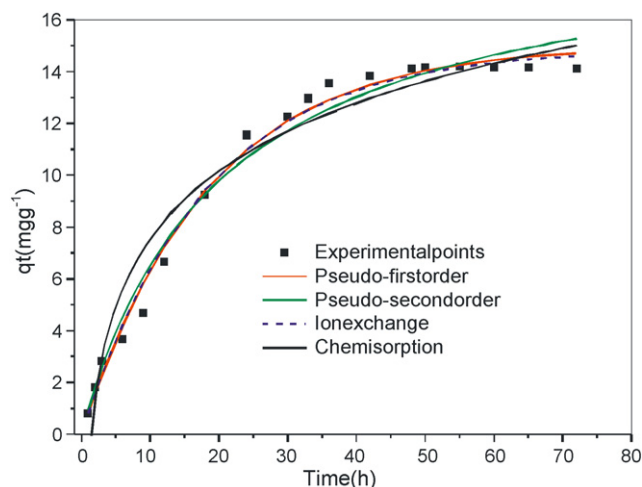


Fig. 5. Kinetic models for the removal of MB from aqueous solution using YFPF biosorbent. Conditions initial MB concentration of 28.7 mg l⁻¹, temperature was fixed at 25 °C, pH 8.0. and biosorbent dosage of 10.0 g l⁻¹.

presented on Table 2, were fitted (Fig. 5). The kinetic parameters of the fitted models were presented on Table 3. As can be seen, the pseudo-first order, the pseudo-second order, the ion exchange and the chemisorption models were suitably fitted, presenting good residual analysis [25], with low standard deviation of the residuals and an average of the residues close to zero, besides of presenting a probability higher than 0.05. From all these four kinetic models, the pseudo-first order kinetic model was a little bit better fitted when compared with the other three kinetic models, since it presented the lower standard deviation of the residues (<0.49 mg g⁻¹), which meant, that the *q* fitted by this model was closer to *q* experimentally measured for the all the experimental points. The residual analysis was also confirmed by the value of *R*² however the distribution of the residuals gives a better idea about the fitting of each individual point [25]. Therefore, the pseudo-first order, ion exchange, pseudo-second order, chemisorption models in decreasing order, should explain the adsorption of MB) by using YFPF biosorbent.

Based on these kinetic results and on the previously described results, there are several arguments to state that the adsorption mechanism of MB on YFPF biosorbent should follow an electrostatic mechanism, i.e., the negatively charged biosorbent at pH values higher than 7.0 (carboxylates present on the YFPF, see Fig. 2 and Table 1), should attract the positively charged

Table 2
Kinetic adsorption models

Kinetic model	Differential equation	Integrated equation	Non-linear equation	Refs.
Pseudo-first order	$\frac{dq}{dt} = k_f(q_e - q_t)$	$\ln(q_e - q_t) = \ln(q_e) - k_f t$	$q_t = q_e [1 - \exp(-k_f t)]$	[43]
Pseudo-second order	$\frac{dq_t}{dt} = k_s(q_e - q_t)^2$	$qt = \frac{k_s q_e^2 t}{1 + q_e k_s t}$	$h_o = k_s q_e^2$ initial sorption rate	[44]
Ion exchange	$\frac{dn_{AB}}{dt} = k_1[A^+][BC] - k_2[C^+][AB]$	$n_{AB} = \frac{k_1[A^+]E}{k_1[A^+] + k_2[C^+]} \{1 - \exp(-St)\} = q_t$	$F = 1 - \exp(-St)$	[45]
Elovich	$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)$	$q_t = \frac{1}{\beta} \ln(t + t_0) - \frac{1}{\beta} \ln(t_0)$	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$	[46]

Table 3
Kinetic parameters

Kinetic parameter	
Pseudo-first order	
k_f (h^{-1})	0.05455
q_e (mg g^{-1})	15.01
R^2	0.9906
Residual analysis	
Average of residuals	0.01623
Standard deviation	0.4866
Probability	0.579
Pseudo-second order	
k_s ($\text{g mg}^{-1} \text{h}^{-1}$)	0.002580
q_e (mg g^{-1})	19.49
h_0 ($\text{mg g}^{-1} \text{h}^{-1}$)	0.9803
R^2	0.9800
Residual analysis	
Average of residuals	0.04475
Standard deviation	0.7096
Probability	0.744
Ion exchange model	
S (h^{-1})	0.05594
R^2	0.9905
Residual analysis	
Average of residuals	-0.003740
Standard deviation	0.4913
Probability	0.502
Chemisorption model	
α (g mg^{-1})	2.760
β ($\text{mg g}^{-1} \text{h}^{-1}$)	0.2637
R^2	0.9485
Residual analysis	
Average of residuals	4.289×10^{-6}
Standard deviation	1.138
Probability	0.294

Conditions initial MB concentration of 28.7 mg l^{-1} , temperature was fixed at 25°C , pH 8.0. and biosorbent dosage of 10.0 g l^{-1} .

methylene blue. The contact time to reach the equilibration is about 48 h (see Fig. 5).

In order to confirm the electrostatic attraction of the negatively charged biosorbent at pH values higher than 7.0 with the positive charged MB dye, desorption experiments were carried out. Several solutions containing $0.01\text{--}0.30 \text{ mol l}^{-1}$ of HCl and $0.05\text{--}0.50 \text{ mol l}^{-1}$ of KCl were tested for regeneration of the loaded biosorbent (see Fig. 6). It should be mentioned that the addition of solutions with concentrations higher than 0.1 mol l^{-1} HCl desorbed the MB uptaken by the YPFW immediately, on the other hand, the quantitative recoveries of the biosorbent using KCl as regenerating solution took about 1 h of agitation.

Based on all the results discussed therein, a proposed mechanism for MB removal from aqueous solution is depicted on Scheme 1.

First of all, for initiating the adsorption process, the pH of the solution should be adjusted to values higher than 7.0, in order to remove the proton of the carboxylic acids present on the biosorbent surface. The second step depicted the adsorption mechanism, is the electrostatic attraction of the positively

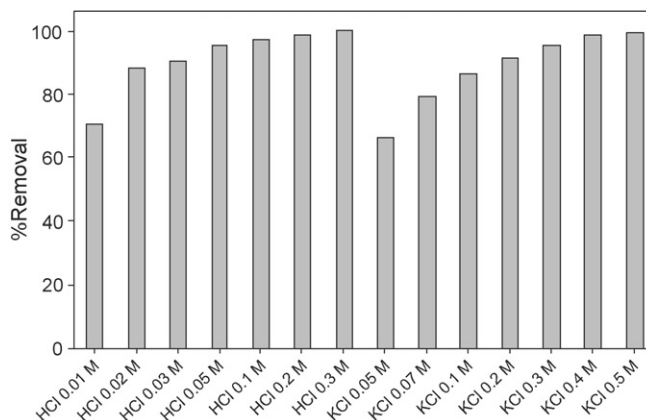


Fig. 6. Desorption of loaded biosorbent with HCl and KCl. Desorption experiments were carried out at 25°C during 1 h.

charged MB with the negatively charged biosorbent ($\text{pH} \geq 7.0$). The complete regeneration of the loaded biosorbent takes place using 0.50 mol l^{-1} of KCl after about 1.0 h of contact time or with 0.3 mol l^{-1} of HCl almost immediately (step 3).

3.5. Equilibrium isotherm

Adsorption isotherms are basic requirements for designing any adsorption system. Isotherm expresses the relation between the amounts of adsorbate (mg) removed from the liquid phase by unit of mass of adsorbent (g) at constant temperature.

An accurate mathematical description of equilibrium adsorption capacity is indispensable for reliable prediction of adsorption parameters and quantitative comparison of adsorption behavior for different adsorbent system or for varied conditions within any given systems. These parameters of equilibrium isotherms often provide some insight into both sorption mechanism and surface properties and affinity of the adsorbent. Therefore, it is important to establish the most suitable correlation of equilibrium curves in order to optimize the condition for designing adsorption systems. There are many equations for analyzing experimental adsorption equilibrium data. In this work, the Langmuir, Freundlich, Sips and Redlich–Peterson isotherm models were tested [47]. These equations are given in Table 4.

The isotherms of adsorption of MB on YPFW were performed, using the best experimental conditions, pH 8.0, contact time of 56 h, and temperature fixed at 25°C .

In this work, the adsorption experiments were fitted to Langmuir, Freundlich Sips and Redlich–Peterson isotherm models

Table 4
Isotherm models

Isotherm model	Equation	Refs.
Langmuir	$q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e}$	[47]
Freundlich	$q_e = K_F C_e^{1/n}$	[48]
Sips	$q_e = \frac{Q_{\max} K_S C_e^{1/n}}{1 + K_S C_e^{1/n}}$	[49]
Redlich–Peterson	$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^\beta}$ where $\beta \leq 1$	[50]

(see Fig. 7 and Table 4). The data of the fitted models were presented on Table 5. Based on the residual analysis, the equilibrium data fitted very well all the isotherm models for both adsorbents, with the exception of Freundlich model, which presented an average of residuals of 4.832 mg g^{-1} with a standard deviation of 2.531 mg g^{-1} . It was observed that slightly better isotherm fitting, based on the residual analysis, was the Sips isotherm model, however the other models should also be taken into account, since they were properly fitted, presenting an aver-

age of the residuals close to zero, a small standard deviation and a probability higher than 0.05, as previously observed [25].

In addition, it should be highlighted that the residual analysis is very important to interpret the isotherm fittings since the unique value of R^2 given in the non-linear fitting could be misleading. Although the Freundlich fitting presented a R^2 value of 0.9812, it is observed that almost all the residuals were systematically dislocated to the positive values (see Fig. 7) on the other hand, for all other isotherm models, the residuals distri-

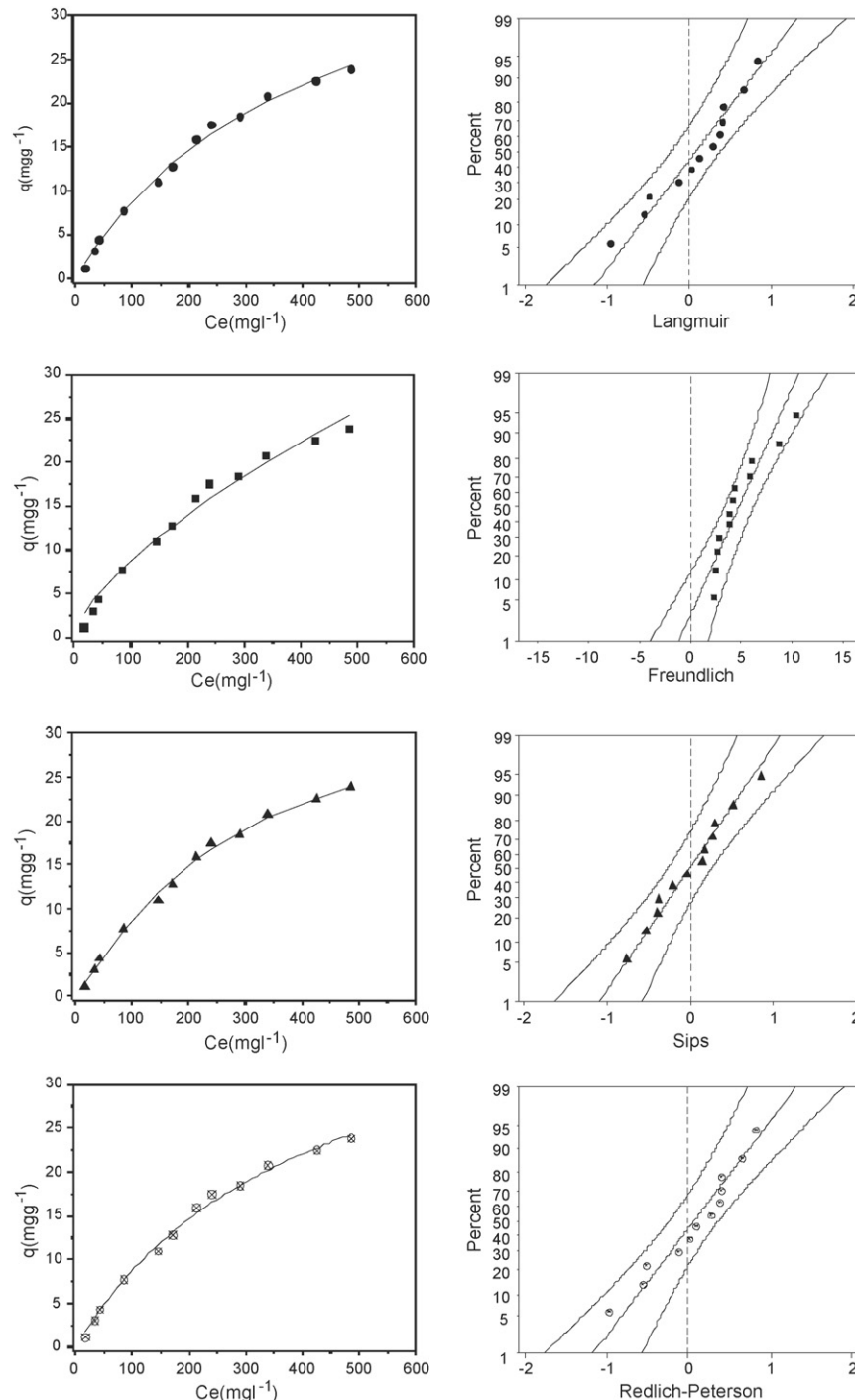
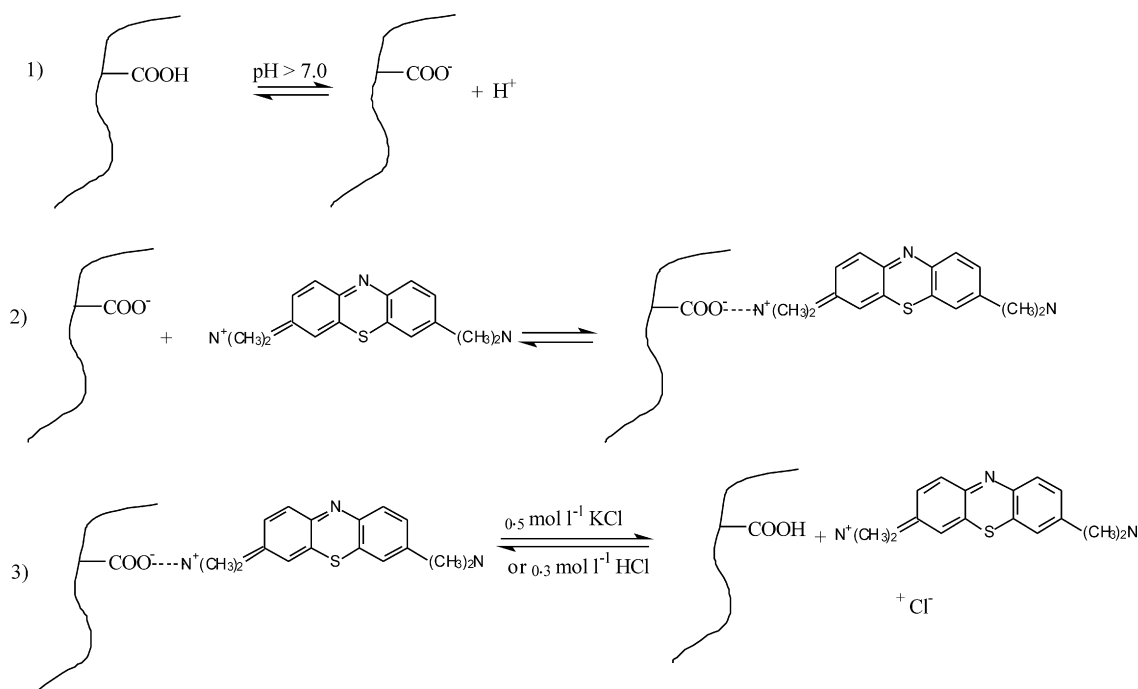


Fig. 7. Adsorption isotherm models MB from aqueous solution on biosorbent using batch adsorption procedure at 25 °C, and using a contact time of 56 h.



Scheme 1. Adsorption and removal of MB on YPFW biosorbent.

Table 5
Isotherm parameters

Isotherm	Value
Langmuir	
Q_{\max} (mg g^{-1})	44.70
K_L (l mg^{-1})	0.00244
R^2	0.9952
Residual analysis	
Average of residuals	0.07995
Standard deviation	0.5330
Probability	0.524
Freudlich	
K_F ($\text{mg g}^{-1}(\text{mg l}^{-1})^{-1/n}$)	0.4039
N	1.4949
R^2	0.9812
Residual analysis	
Average of residuals	4.832
Standard deviation	2.531
Probability	0.050
Sips	
Q_{\max} (mg g^{-1})	36.96
K_S ($(\text{mg l}^{-1})^{-1/n}$)	0.00158
N	0.8758
R^2	0.9964
Residual analysis	
Average of residuals	-0.004641
Standard deviation	0.4718
Probability	0.930
Redlich–Peterson	
K_{RP} (l g^{-1})	0.1090
a_{RP} (mg l^{-1}) $^{-\beta}$	0.00244
β	1.00
R^2	0.9952

Table 5 (Continued)

Isotherm	Value
Residual analysis	
Average of residuals	0.06952
Standard deviation	0.5345
Probability	0.511

bution followed a normal pattern. This result reinforces the use of residual analysis, instead of using just the R^2 to compare different isotherm fittings, as already observed [25].

In addition, it was also observed that the Langmuir and Redlich–Peterson isotherm models closely agreed with the Sips isotherm model. It is also notably that the Redlich–Peterson exponent (β) presented a value of 1.00, therefore this isotherm was reduced to Langmuir isotherm model. By dividing K_{RP} parameter by a_{RP} parameter of Redlich–Peterson isotherm, it gives the maximum coverage of the adsorbate per gram of adsorbent, whose value is 44.67 mg g^{-1} . This value is approximately the Langmuir maximum adsorption capacity (44.70 mg g^{-1}). Based on these explanations, it can be inferred that the maximum adsorption capacity of the yellow passion fruit waste for MB removal from aqueous solution was 44.70 mg g^{-1} since the Langmuir model was suitably fitted when compared with the other isotherm models.

4. Conclusions

The yellow passion-fruit waste (YPFW) is a locally available and low-cost material that can be used as an alternative biosorbent for removal the cationic dye MB from aqueous solutions, without any laborious pre-treatment.

The biosorbent was characterized by FTIR spectroscopy indicating the presence of $-\text{COOH}$, $\text{C}=\text{O}$, and $\text{O}-\text{H}$ groups. These data were also confirmed by conventional titrations where quantitative values of carboxylic groups were measured (1.81 mmol g^{-1}) in the biosorbent.

The adsorption of MB depended on pH and shaking time. The optimum pH for the adsorption of MB was in the range 7.0–10.0 and the contact time necessary for equilibrium was 48 h. There are several indicatives that the mechanism of adsorption of methylene blue by yellow passion-fruit waste should be an electrostatic attraction of negatively charged biosorbent at $\text{pH} \geq 7.0$ (since the carboxylic acids of the biosorbent should lose a proton at this pH value) with positively charged methylene blue. The ion exchange kinetic model was properly fitted, presenting good residual analysis when compared with other kinetic models. In addition, the almost instantaneous recovery of methylene blue from loaded biosorbent by addition of 0.30 mol l^{-1} of HCl, corroborate that the adsorption mechanism should be electrostatic attraction.

The isotherm models were suitably fitted employing Langmuir, Sips and Redlich–Peterson isotherm, presenting a standard deviation of the residual lower than 0.54 mg g^{-1} . Therefore, the maximum adsorption capacity of the yellow passion-fruit waste for adsorption of methylene blue was 44.70 mg g^{-1} .

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