

APPLICATION OF POMEGRANATE PEEL WASTE ON BIOSORPTION OF METHYLENE BLUE FROM AQUEOUS SOLUTIONS.

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ABSTRACT: Pomegranate peel waste (PPW), a solid waste, was prepared and tested as biosorbent for the removal of a cationic dye, methylene blue (MB), from aqueous solutions by batch procedure. The effects of pH of solution, biosorbent dosage, contact time, and dye initial concentration on biosorption capacity were studied. MB uptake was favorable at pHs ranging from 5.0 to 12.0. The contact time required to obtain the maximum biosorption was 5 h at 25 °C using 0.6 g of biosorbent. Two kinetic equations models, pseudo-first-order and pseudo-second-order, were used to study the mechanism of dye biosorption. The pseudo-second-order kinetic model should better explain the biosorption process of MB taken up by PPW biosorbent. MB biosorption onto PPW was analyzed by Langmuir, Freundlich, and Sips isotherm models. The best data were fitted to Sips isotherm model. It was found that the Sips model is appropriate to explain the biosorption isotherm. The maximum amount of MB biosorbed on PPW was 68.42 mg dye g⁻¹ at 25 °C. The results in this study indicated that PPW, is an attractive candidate for removing MB from aqueous solutions.

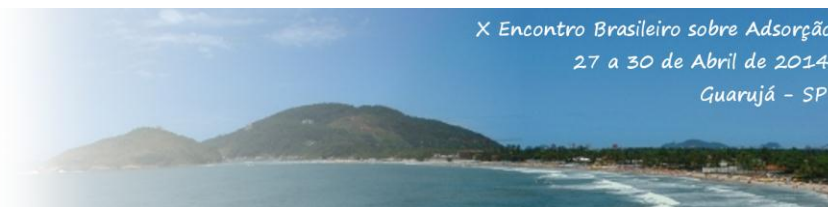
KEYWORDS: biosorption; equilibrium; kinetics; methylene blue; pomegranate peel waste.

1. INTRODUCTION

High volumes of aqueous effluents contaminated with textile and food dyes are generated by different industries. Such effluents belong to class of contaminant that is one of the most important hazardous species found in industrial wastewaters. The treatment of these effluents is necessary because the presence of dyes in water reduces light penetration precluding the photosynthesis of aqueous flora (de Lima et al, 2007). The removal of dyes from an aquatic ecosystem is extremely important from the healthiness point of view (Tsuboy et al, 2007; Birhanli & Ozmen, 2005; Caritá & Marin-Morales, 2008) since most of them are toxic, cause allergy and skin irritation, and are mutagenic and/or carcinogenic (Tsuboy et al, 2007; Birhanli & Ozmen, 2005; Caritá & Marin-Morales, 2008). Several methods have been developed to remove 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 (Santos et al, 2007; Hao et al, 2000; Martinez-Huitle & Brillias, 2009). However, these processes in general are expensive and incapable of the complete removal of dyes from solutions. Adsorption using activated carbon has shown be competitive for removal dyes from aqueous solution but, the higher cost of this adsorbent has limits its use (Robinson et al, 2001). So, this has led many researchers to search for alternatives and inexpensive materials to minimize costs in adsorption processes.

Several botanic materials or agro-industrial wastes have been used as potential adsorbents for removal dyes from aqueous solutions. These adsorbents include yellow passion fruit waste (Pavan et al, 2008), coir pith, peanut hull (Gong et al, 2005), papaya seeds (Hammed, 2009), granular



kohlrabi peel (Gong et al, 2007), leaf powder (Ponnusami et al, 2008), rice husk (Chandrasekhar & Pramada, 2006), and Brazilian pine-fruit shell (Lima et al, 2008).

The species *Punica granatum* (Punicaceae) has been widely used by traditional medicine in America, Asia, Africa and Europe for the treatment of different types of diseases (Malik et al, 2005). Increasing interest in the consumption of pomegranates both in fresh and processed forms could be attributed to their beneficial health effects and, as a result, many food products containing pomegranates and pomegranate juice are currently consumed (Malik et al, 2005). Due to the high consumption of pomegranate fruit, increasingly higher amounts of the residues are disposed, causing an environmental problem. To the best of our knowledge, up to now no study on the use of pomegranate peel waste (PPW) as an adsorbent to the removal of methylene blue (MB) from aqueous solution has been reported. In the present work, the PPW was used to remove the MB dye from aqueous solutions. The purpose of the present work was to exploit a utilize new low cost biosorbent for to reduce the cost of wastewater treatment. The PPW sample was characterized by using different experimental techniques such as Fourier transform infrared (FTIR) spectroscopy, Elemental analysis, Nitrogen adsorption-desorption isotherms, Surface area (BET), Average pore diameter (BJH method) and Bohem tritration. Batch adsorption mode was carried out to investigate the effect of operational parameters such as pH, contact time, dosage biosorbent, and initial dye concentration on the biosorption capacity. Kinetic and equilibrium data were processed to understand the biosorption of MB onto PPW.

2 MATERIALS AND METHODS

2.1 Solution and reagents

De-ionized water was used throughout for solution preparations. 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. The cationic dye, MB (CI 52030; C₁₆H₁₈N₃SCl, was obtained from Sigma

Chemical Co., USA, with analytical grade that was used without further purification. The stock solution was prepared by dissolving accurately weighed dye in distilled water to the concentration of 500 mg L⁻¹. Working solutions were obtained by diluting the dye stock solution to the required concentrations.

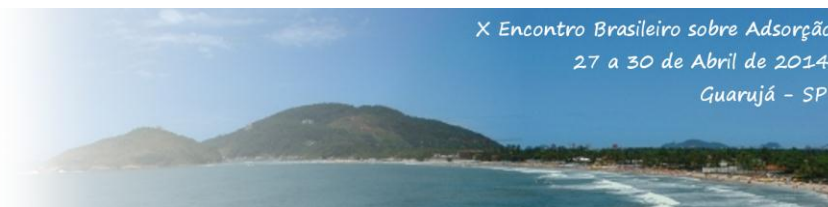
2.2 Biosorbent preparation

Pomegranate fruit (*Punica granatum*) were purchased at local market. The peel was removed and the collected biosorbent was extensively washed with water and dried at 60 °C for 48 h. Afterwards, the peel was crushed and sieved to the 250 µm size. Subsequently, the biosorbent was washed with doubly distilled water for 10 min, and then dried in an oven at 60°C for 24 h. PPW was preserved in the desiccator and used in the biosorption studies.

2.3 Biosorbent characterization

The specific surface area of biosorbent was determined by the Brunauer, Emmett and Teller (BET) multipoint technique, obtained by the N₂ adsorption-desorption isotherm. The adsorbent 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. Data analysis was made by using the Barret, Joyner and Halenda (BJH) method. PPW was characterized by Fourier transform infrared (FTIR) spectroscopy using a Shimadzu FTIR, model 8300 (Kyoto, Japan). Amounts of 50 mg of the sample were pressed with dried KBr and the spectra were obtained with a resolution of 4 cm⁻¹, with 100 cumulative scans. The surface functional groups on the PPW were investigated by Boehm titration (Boehm, 1994). The PPW morphological properties were analyzed by scanning electron microscopy. The point zero of charge (pH_{pzc}) of the biosorbent was determined by using Bohem tritration.

Table 1: Physical and chemical properties of PPW biosorbent.



| | |
|--|------|
| Specific surface area – BET (m ² .g ⁻¹) | 32.5 |
| Average pore volume (cm ³ .g ⁻¹) | 0.08 |
| BJH average pore diameter (nm) | 4.3 |
| Point of zero charge (PH _{pcz}) | 4.1 |
| Acidic surface groups concentration | |
| Carboxylic groups (mmol.g ⁻¹) | 1.89 |
| Carbonyl groups (mmol.g ⁻¹) | 0.84 |
| Phenolic (mmol.g ⁻¹) | 0.09 |

2.4 Batch biosorption studies

All the experiments were carried out at 25 °C. The PPW biosorption capacity for MB was studied using the batch procedure biosorption. 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 (1.0 to 500.0 mg L⁻¹) at pH values ranging from 2.0 to 12.0 and the contact time ranging from 0.08 to 12 h. Then, Erlenmeyer flasks were shaken in a rotary orbital shaker at 60 rpm and 25 °C for 12 h. The biosorbent was separated from the liquid phase and, then, the remaining dye in the solution was determined by 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. The amount of dye taken up by the biosorbent was calculated by applying the equation:

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

where, q is the amount of dye taken up by the biosorbent (mg g⁻¹); C₀ is the initial MB concentration put in contact with the biosorbent (mg L⁻¹), C_e is the MB concentrations (mg L⁻¹) after the batch biosorbent, m is the mass of biosorbent (g) and V is the volume of dye put in contact with the biosorbent.

2.5 Batch desorption studies

Batch desorption studies were carried out by agitating 50.0 ml of dye solution of 25.0

mg L⁻¹ and 0.6 g of biosorbent, the agitation time used was 5 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 1M HCl up to 5 h. The desorbed dye was separated and estimated as explained above. The amount of dye uptaken by the biosorbent was calculated by applying the equation:

$$\% \text{ MB desorption} = (C_a - C_f) / C_0 \times 100 \quad 2)$$

where, C_a is dye concentration adsorbed on PPW and C_f dye concentration desorbed from the biosorbent by 1M HCl solution in batch mode.

2.6 Kinetic models

Biosorption kinetic study is important in the treatment of aqueous effluents as it provides valuable information on the reaction pathways and in the mechanism of adsorption reactions. To study the mechanism of dye biosorption, the kinetic data were fitted using the pseudo-first-order and pseudo-second-order kinetic equation models. The equations are given in Table 2.

Table 2: kinetics and isotherm biosorption models.

| Kinetics model | Non-linear Equations |
|---------------------|--|
| Pseudo-first-order | $q_t = q_e \cdot [1 - \exp(-k_f \cdot t)]$ |
| Pseudo-second-order | $q_t = \frac{k_s \cdot q_e^2 \cdot t}{1 + q_e \cdot k_s \cdot t}$ |
| Isotherm model | |
| Langmuir | $q_e = \frac{Q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}$ |
| Freundlich | $q_e = k_f \cdot C_e^{1/n}$ |
| Sips | $q_e = \frac{Q_{\max} \cdot K_s \cdot C_e^{1/n}}{1 + K_s \cdot C_e^{1/n}}$ |

2.7 Equilibrium models

In order to describe the equilibrium between biosorption capacity and adsorbate



concentration at constant temperature, the Langmuir, Freundlich, and Sips isotherm models were employed.

2.8 Statistical evaluation of the kinetic and isotherm parameters

In this work, the kinetic and equilibrium models were fitted employing the nonlinear fitting method using the nonlinear fitting facilities of the software Microcal Origin 7.0 (Lima et al, 2008).

$$F_{\text{error}} = \sqrt{\frac{\sum_{i=1}^p \left(\frac{q_i \text{ model} - q_i \text{ experimental}}{q_i \text{ experimental}} \right)^2}{p-1}} \quad 3)$$

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, and p is the number of experiments performed.

3 RESULTS AND DISCUSSION

3.1 Surface area and pore size distribution

The specific surface area and average pore volume of PPW obtained by the BET (Brunauer, Emmet, Teller) method were 32.5 m²/g and 0.08 cm³/g, respectively. The average pore diameter found by the BJH method was 4.3 nm, which is a characteristic of mesoporous materials.

3.2 FT-IR analysis

The presence of functional groups on PPW surface potentially able to bind dye was investigated by the infrared spectroscopy technique. The FTIR spectrum of the biosorbent is shown in Figure 1. The band with maxima at 3417 cm⁻¹ was assigned to the stretching of O-H group and the band about 2943 cm⁻¹ was assigned to the stretching of C-H bond of methyl and methylene groups (Pavia et al, 1996). The band observed at 1728 cm⁻¹ was assigned to a carbonyl band (C=O) of unionized carboxylate stretching of carboxylic acid (Pavia et al, 1996), while the peak at 1632 cm⁻¹ was attributed to C=O stretching of

carboxylic acid with intermolecular hydrogen bond (Pavia et al, 1996). The bands in the 1352-1229 cm⁻¹ are due to the bending modes of O-C-H, C-C-H and C-O-H (Pavia et al, 1996). The band at 1063 cm⁻¹ was assigned to C-O (Pavia et al, 1996). The FTIR analysis indicated the presence of functional groups such as OH, COO⁻ and CO on the adsorbent that could be responsible for the interaction of MB with adsorbent. These data were also confirmed by conventional titrations where quantitative values of carboxylic and phenolic groups (see Table 1) were measured in the adsorbent.

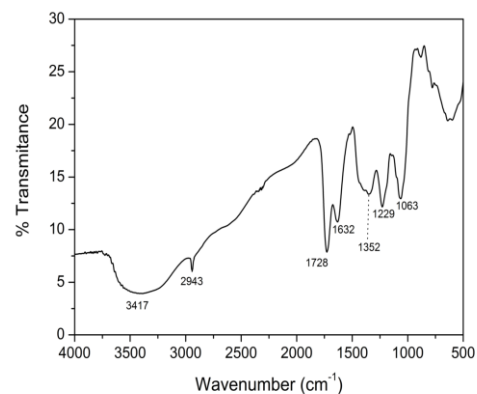
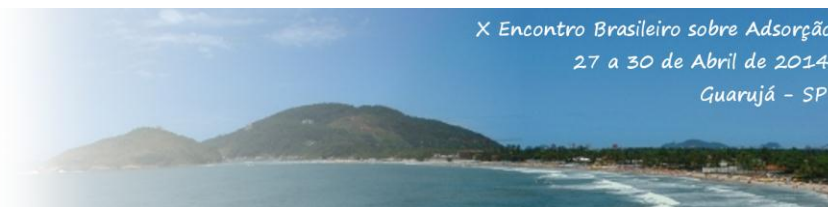


Figure 1. FTIR spectrum of PPW biosorbent.

3.4 Effect of acidity

Figure 2 shows the dependence of MB biosorption on pH change. The removal of MB increased significantly as the pH solutions increased from 2.0 to 5.0. The percentage removal of MB was not significantly altered when the pH was increased from 5.0 to 12.0. This result could be interpreted as an electrostatic interaction between the surface of the adsorbent, negatively charged, and the cationic dye MB. At lower pH values, a possible protonation of COO⁻ occurs, preventing the electrostatic attraction with the MB dye from solution, and in turn, a decrease of the adsorbate uptake is observed. Thus, at pH values ranging from 5.0 to 12.0, the carboxylic groups are available to adsorb the positively charged dye, increasing the removal



of MB from the aqueous solution. The point of zero charge value of the biosorbent confirms this behavior (Table 1). At pH values lower than 4.1, the surface of PPW is positively charged, hindering the electrostatic attraction of MB, a cationic dye. At pH values higher than 4.1 the MB adsorption is facilitated because the surface of biosorbent is negatively charged.

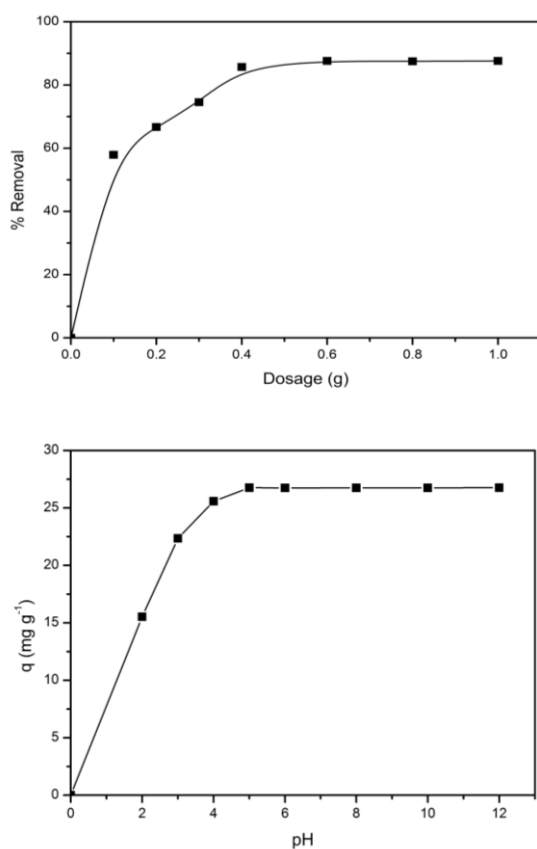


Figure 2. Effects of pH and dosage.

3.5 Effect of the biosorbent dosage

The influence of the biosorbent dosage on MB biosorption is shown in Figure 2. The increase in the concentration of the biosorbent, up to 0.6 g, results in a slight increase in the percentage of MB uptake (0 to 87.6%). As the amount of biosorbent increases, the number of active sites also increases and, consequently, a higher biosorption occurs. Above 0.6 g of biosorption, the percentage of MB uptake remains constant.

3.6 Contact time, initial dye

concentration, and kinetic studies

The effect of the contact time has been evaluated with different initial dye concentrations (10.0, 20.0 and 50.0 mg L⁻¹) at pH 5, with biosorbent dosage 0.6g and 25 °C temperature on adsorption MB onto PPW. Results show that the equilibrium states were attained with 5 h of contact time. After an equilibrium time of 5 h, no more dye was adsorbed. In further experiments the contact time between the biosorbent and bioadsorbate was fixed at 5 h.

To describe the adsorption of MB onto PPW adsorbent two non-linear kinetic models, pseudo-first-order and pseudo-second-order were employed. The kinetic parameters of the fitted models are summarized in Table 2.

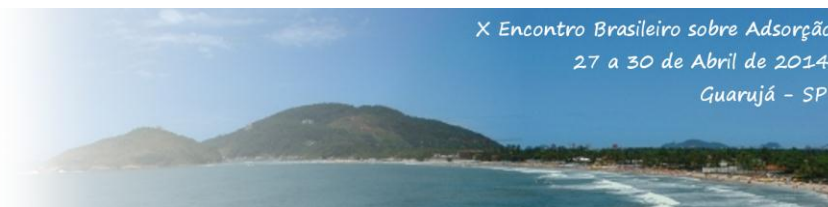
The values of coefficient correlation (r^2) and the pseudo-second order rate constant (K_s) are presented in Table 3. As can be seen, the pseudo-second-kinetic order was suitably fitted, presenting low error function values and high r^2 values, for the 10.0, 20.0 and 50.0 mg L⁻¹ initial concentration levels of the dye. It is possible to observe in Table 3 that the pseudo-second order rate constant (K_s) decreases with the increase of initial concentration from 0.10 to 0.02 (g mg⁻¹ h⁻¹), while q_e increased with the increase of initial concentration. Based on these kinetic results, the biosorption mechanism of MB onto PPW is more likely to be governed by chemisorption.

Table 3. Kinetic parameters for MB, using PPW

| | C_o (mg L ⁻¹) | | |
|-----------------------------|-----------------------------|--------|--------|
| | 10 | 20 | 50 |
| Pseudo-first order | | | |
| k_f (h ⁻¹) | 0.825 | 1.18 | 0.762 |
| q_e (mg g ⁻¹) | 9.87 | 18.7 | 42.9 |
| r^2 | 0.9971 | 0.9902 | 0.9879 |
| F_{error} | 0.108 | 0.480 | 0.572 |

3.7 Equilibrium studies

A biosorption isotherm describes the relationship between the amount of adsorbate taken up by the biosorbent and the adsorbate concentration remaining in solution. The analysis of the equilibrium data is an important



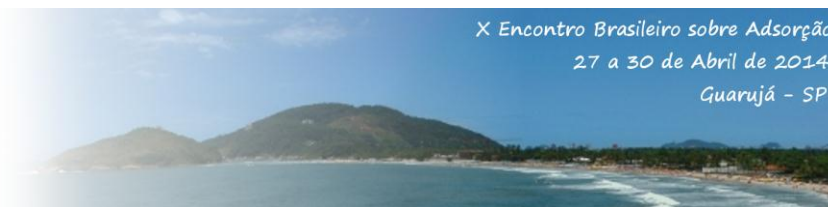
reliable prediction of adsorption parameters and quantitative comparison of biosorption behaviors for different adsorbent systems. In the present study, the non-linear Langmuir, Freundlich and Sips isotherm models were tested to investigate the adsorption behavior of MB on PPW adsorbent at 25 °C. These equations are given in Table 4.

Table 4. Isotherm parameters for MB biosorption, using PPW as biosorbent. Conditions: temperature was fixed at 25 °C, biosorbent dosage 0.6 g, contact time was fixed at 5 h, and pH was fixed at 5.0

| Langmuir | Values |
|--|--------|
| Q_{\max} (mg.g ⁻¹) | 66.50 |
| K_L (L.mg ⁻¹) | 0.262 |
| r^2 | 0.9946 |
| F_{error} | 0.240 |
| Freudlich | |
| K_F (mg.g ⁻¹ .(mg.L ⁻¹) ^{-1/n}) | 22.5 |
| n_F | 4.47 |
| r^2 | 0.9034 |
| F_{error} | 2.698 |
| Sips | |
| Q_{\max} (mg g ⁻¹) | 68.42 |
| K_S ((g.L ⁻¹) ^{-1/ns}) | 0.2965 |
| N_s | 1.1593 |
| r^2 | 0.9961 |
| F_{error} | 0.109 |

The Langmuir isotherm model assumes that the adsorption occurs on a homogenous adsorbent surface of identical sites that are equally available and energetically equivalent with each site carrying equal numbers of adsorbed species. The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of biosorption over the surface. It is characterized by the heterogeneity factor 1/n. The amount of adsorbed material is the summation of biosorption on all sites. The Sips isotherm is a

combination of the Langmuir and Freundlich isotherm type models. At low adsorbate concentrations it effectively reduces to a Freundlich isotherm, while at high adsorbate concentrations it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm. The isotherm of adsorption of MB on PPW biosorbent was performed using the best experimental conditions, pH 5, biosorbent dosage 0.6 g, and a constant temperature 25°C. The data of the three different equilibrium biosorptions, relative error functions, and the model parameters obtained from these nonlinear regressions are listed in Table 4. Correlation coefficients, calculated by fitting the experimental equilibrium data to Langmuir, Freundlich and Sips isotherms, are shown in Table 4. The correlation coefficient obtained from Langmuir isotherm was 0.994. This correlation coefficient value is higher than those obtained for the Freundlich isotherm. The high value of correlation coefficient for Langmuir isotherm is an indication of homogeneous surface of the biosorbent. The R_L value (0.262) obtained from Langmuir model for $C_o = 500$ mg.L⁻¹ MB indicate a favorable biosorption of MB on PPW. The maximum biosorption capacity obtained from the Langmuir isotherm was 66.48 dye mg per gram of adsorbent. The correlation coefficient for the Freundlich isotherm was 0.903. The low value of the correlation coefficients showed the poor agreement of the Freundlich model with the experimental data. The values for Freundlich constants k_F and n were found to be 22.5 (mg.g⁻¹.(mg.L⁻¹)^{-1/n}) and 4.47, respectively. The high value of n is also an indication that there is a good affinity between dye and biosorbent. The correlation coefficient for the Sips isotherms was 0.9961. The high value of the correlation coefficient showed the good agreement with the Sips model according to the experimental data. The maximum MB uptake obtained with Sips isotherm model was 68.42 dye mg per gram of biosorbent. The Sips model provided slightly higher values of maximum uptake than those obtained with the



Langmuir model. Considering the F_{error} values given in the Table 4, the Sips model presented the lowest value for F_{error} , ($F_{\text{error}} = 0.10$) compared with Langmuir ($F_{\text{error}} = 0.240$) and Freundlich ($F_{\text{error}} = 2.698$) isotherm models. The results obtained showed that the Sips model produced the best fitting isotherm parameters values for all the cases studied, and the lowest relative error values.

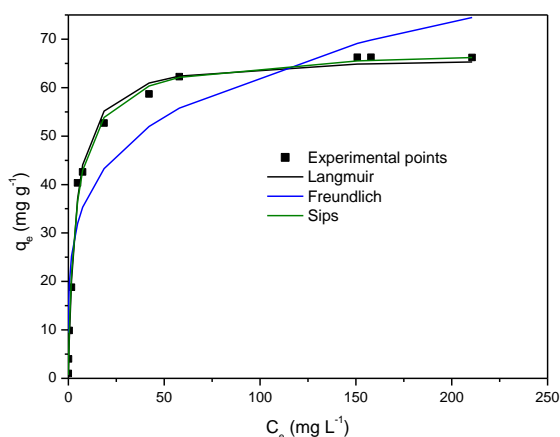


Figure 3. Langmuir, Freundlich and Sips biosorption

3.8 Desorption studies

The MB- biosorbed PPW in a batch experiment was washed with distilled water to elute the remaining dye. Then, the sample was desorbed with a solution containing 1M of HCl for regeneration of adsorbent. The results obtained show that the MB desorption is relatively fast after 70 min and that the percentage of MB desorbed from MB-biosorbed PPW was quite high ca 90.5%. main biosorption mechanism of MB on PPW.

4 Conclusions

The PPW can be used as an alternative biosorbent for the removal of the cationic dye MB from aqueous solutions. The advantages of this adsorbent were low cost, availability in high quantities and good adsorption capacity. The optimum pH for the biosorption of MB was in the range 5.0-12.0. The adsorption of MB by PPW should be an electrostatic

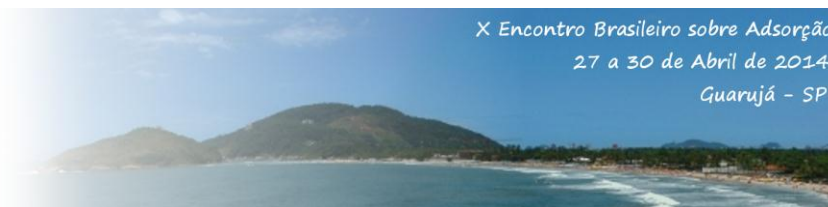
attraction of negatively charged biosorbent at $\text{pH} \geq 5.0$ with positively charged MB. The equilibrium was attained in 5h. The kinetics of MB to the adsorbent can be well described by the pseudo-second-order equation. The applicability of the three isotherm models for the present data follows the order: Sips > Langmuir > Freundlich. The good recovery (90.5 %) of MB from loaded PPW by 1M of HCl corroborates that the biosorption mechanism should be an electrostatic attraction. The Sips isotherm model is more appropriate to explain the adsorption of MB on PPW. Based on the Sips isotherm model the amount of dye uptake (mg/g) was $68.42 \text{ mg dye g}^{-1}$.

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