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Punica granatum husk (PGH), a powdered biowaste material for the adsorption of methylene blue dye from aqueous solution

Marilice S. Bretanha[a], Mariene C. Rochefort[a], Guilherme L. Dotto[b], Eder C. Lima[c], Silvio L.P. Dias[c], Flávio André Pavan[a,*]

[a]*Research of Program of Post-graduate in Engineering-PPEng, Institute of Chemistry, Federal University of Pampa, UNIPAMPA, 96412-420, Bagé, RS, Brazil, Tel. +55 53 32472367; email: flavio.pavan@unipampa.edu.br (F.A. Pavan)*
[b]*Chemical Engineering Department, Federal University of Santa Maria, UFSM, Santa Maria, RS, Brazil*
[c]*Institute of Chemistry, Federal University of Rio Grande do Sul, UFRGS, Porto Alegre, RS, Brazil*

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ABSTRACT

In this study, *Punica granatum* husk (PGH), an agricultural powdered biowaste, was used as adsorbent for the removal of methylene blue (MB) dye from aqueous solutions. The effects of initial pH of solution, adsorbent dosage, contact time, and initial dye concentration on the MB adsorption were evaluated in batch adsorption mode at 298 K. Kinetic data were evaluated by pseudo-first-order, pseudo-second-order, and Elovich models. The equilibrium adsorption was evaluated by Langmuir, Freundlich, and Sips isotherm models. The applicability of PGH was also evaluated for simulated effluents. The results revealed that pseudo-second-order model agreed well with the experimental kinetic data. The adsorption of MB onto PGH was better fitted using Sips isotherm. The maximum adsorption capacity obtained by Sips model was 68.40 mg g^{-1}. Regeneration of PGH adsorbent was possible using 1.0 mol L^{-1} of HCl as eluent. PGH adsorbent is adequate for removal of MB from simulated textile and river effluents. The results obtained in this work show that PGH can be used as alternative adsorbent for MB removal from effluents.

Keywords: Punica granatum husk; Methylene blue; Textile effluents; Batch adsorption

1. Introduction

Methylene blue (MB) is a cationic dye widely used for dying cotton, silk, and wood [1]. The discharge of colored effluents containing MB is undesirable for several reasons such as: causes eyes burn, allergy, skin irritation, ingestion may cause nausea, vomiting, and mental confusion, also reduces light penetration precluding the photosynthesis of aqueous flora [2,3]. Thus, the treatment of MB containing effluents is necessary to avoid the negative impacts in the water quality caused by this dye. Several traditional treatment processes have been applied for the removal of MB dye from waters and wastewaters in order to decrease their impact on the environment. The processes developed consist basically in decolorizing by electrochemical combined with biological treatment [4], photocatalytic oxidation [5], Fenton treatment [6], nanofiltration [7], sonocatalytic degradation [8], biological treatment [9], and adsorption on activated carbon [10]. Activated carbon is most popular adsorbent used for metals, pesticide, and dye removal. The excellent

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*Corresponding author.

ability of activated carbon for dye removal is well known and undisputed, but its high cost precludes the practical use [11]. In this way, the search for cheaper and efficient adsorbents, such as, low-cost agricultural wastes, to replace activated carbon has gained attention in recent years [12].

Agricultural wastes are abundant, requires a little processing and its physicochemical characteristics are adequate for adsorption purposes [13,14]. Agricultural wastes such as yellow passion fruit waste [15], *Jatropha curcas* shells [16], sugarcane bagasse [17], peanut husk [18], papaya seeds [19], tea waste [20], meranti sawdust [21], and pretreated lignocellulosic materials [22] were successfully employed as adsorbent for dyes removal from water and wastewaters. In this field, the present paper report an investigation about the ability of *Punica granatum* husk (PGH), a solid agricultural waste, to remove MB dye from aqueous solutions. PGH is a biowaste of the pomegranate juice factories which is used for treatment of diseases, as an antioxidant and anitimutagenic [23]. It contains various organic compounds such as cellulose, lignin, hemicelluloses, hydroxyl, and carboxyl. These groups can be able to bind dye molecules through different mechanisms [24].

The utilization of PGH as adsorbent for dye removal is still very scarce in the current literature. In a recent study, Senthilkumar et al. [25] reported the use of activated carbon produced from *Punica granatum* peel to remove C.I. Reactive Orange 4 from aqueous solutions. Other study reported by Ay et al. [26] showed the use of *P. granatum* peel to remove Acid blue 40 from wastewater. Since, PGH was little investigated as dye adsorbent the utilization of this agricultural biowaste as adsorbent for MB dye is still a novelty in the current literature.

Based on the above mentioned, the main goal of this investigation was to explore the potential of PGH as an alternative adsorbent for the removal MB dye from aqueous effluents. In this context, batch assays were carried out in order to investigate the influences of initial pH of solution, adsorbent dosage, contact time, and initial dye concentration on MB adsorption. Kinetic and equilibrium studies were performed at 298 K and the adsorbent regeneration was investigated. Furthermore, the potential of PGH for the removal of MB from simulated textile and river effluents was tested.

2. Materials and methods

2.1. Solutions and reagents

The cationic dye, MB (3,7bis (dimethylamio)-phenothiazin-5-ium chloride; C.I. 52030; molecular formula $C_{16}H_{18}N_3SCl$, and molecular weight 319.8 g mol^{-1}) was obtained from Merck Ltda., Brazil, with analytical grade and was used without further purification. The dyes cibacron brilliant yellow (5-dichloro-4-[(4E)-4-[[5-[[4-chloro-6-(4-sulfonatoanilino)-1,3,5-triazin-2-ylamino]-2-sullfonatophenyl] hydrazinylidene]-3-methyl-5-oxopyrazol-1-yl] benzenesulfonate-trisodium); C.I. 18972; molecular formula $C_{25}H_{19}C_{13}N_9NaO_{10}S_3$, molecular weight 831.0 g mol^{-1}) and reactive black 5 (2-(4-Aminophenylsulfonyl) ethyl hydrogen sulfate 4-Amino-5-hydroxynaphthalene-2,7-disulfonic acid); C.I. 20505, molecular formula $C_{26}H_{21}N_5Na_4O_{19}S_6$; molecular weight 991.82 g mol^{-1}) were obtained from Sigma-Aldrich, Brazil, Ltda. The salts, NaCl, $Na_2CO_{3,}$ $CaCl_{2,}$ $Mg_2SO_{4,}$ KCl, $(NH_4)_2HPO_4$, and CH_3COOH were purchased from Synth, Brazil. The sodium hydroxide (NaOH) and hydrochloride acid (HCl) used were from Merck Ltda., Brazil. The stock MB solution (1,000.0 mg L^{-1}) was prepared and used for to obtain different initial dye concentrations. The solutions pH were adjusted with 0.10 mol L^{-1} NaOH or HCl solutions using a pH meter (Digimed, DM 20, Brazil) for the measurements. Deionized water was used for all experiments.

2.2. Adsorbent preparation

Pomegranate fruit (*P. granatum L.*) was obtained at the local market, in Bagé, RS, Brazil. The husk was removed manually from fresh pomegranate fruit, washed with distilled water for the removal of color and dust, and dried at 333 K for 48 h (Sterilifer, SX450A, Brazil). After, the husk was crushed (Quimis, Q298A21, Brazil) and sieved to the 250 μm sieve. Finally, the husk was washed with distilled water and then oven dried at 333 K (Sterilifer, SX450A, Brazil) for 12 h. The powdered biomass obtained was then denoted PGH.

2.3. Adsorbent characterization

The specific surface area and porosity of PGH were determined by the Brunauer, Emmett and Teller (BET) and Barret Joyner and Halenda (BJH) methods, using N_2 adsorption technique with a surface area analyzer (Quantasorb, QS-7, USA). PGH was previously degassed at 393 K in vacuum for 2 h. N_2 analysis was carried out using a bath at temperature of 75 K.

The active sites (carboxyl, lactonic, and phenolic) on PGH surface were determined by Boehm titration method [27]. The elemental analysis of carbon, hydrogen, and nitrogen on PGH was determined using a CHN PerkinElmer M CHNS/O analyzer Model 2400, Brazil. The point zero of charge (pH_{PZC}) of PGH was determined according to the procedure described by Khormaei et al. [28].

The main functional groups of PGH before and after the adsorption process (more adequate condition) were identified by Fourier transform infrared (FT-IR) spectroscopy (Shimadzu, 8300, Japan). Amounts of 50.0 mg of the sample were pressed with dried potassium bromide. The spectra were obtained with a resolution of 4 cm^{-1} with 100 cumulative scans over the range of 4,000–500 cm^{-1}.

The PGH textural characteristics were observed by scanning electron microscopy (SEM) in a Jeol electron microscope (Model JSM 5800, USA), with working voltage of 20.0 kV at magnification of 2,500 times.

2.4. Batch adsorption and desorption studies

The effects of important parameters that affecting the adsorption capacity of PGH, such as, initial pH solution, adsorbent dosage, initial dye concentration, and contact time, were studied using batch contact adsorption at 298 K (Quimis, G225M, Brazil). These experiments were performed with 50.0 mL of MB solution (initial concentration 50.0 mg L^{-1}) at different contact times (0.08–24.0 h), adsorbent dosage (0.1–1.0 g), and pH values (2.0–12.0). For adsorption equilibrium studies, 0.6 g adsorbent was placed in a series of conical flasks (125.0 mL) each one containing 50.0 mL of different initial dye concentrations (5.0–500.0 mg L^{-1}) at pH 5.0. The conical flasks were shaken in a rotary orbital shaker at 150 rpm for 5.0 h (Quimis, G225M, Brazil). The adsorbent was separated from the liquid phase by centrifugation (Quimis, Q222T216, Brazil) and the remaining dye in the solution was then determined by UV–vis spectrophotometer (Varian, Cary 50 Bio, USA) with 1.0 cm path length cell. Absorbance measurements were made at 660 nm. All experiments were made in triplicate ($n = 3$) and blanks were performed. The amounts of MB adsorbed per gram of adsorbate at equilibrium (q_e) and at any time (q_t) were obtained by the Eqs. (1) and (2), respectively:

$$q_e = \frac{C_0 - C_e}{m} V \tag{1}$$

$$q_e = \frac{C_0 - C_t}{m} V \tag{2}$$

where C_0 is the initial MB concentration (mg L^{-1}), C_e is the equilibrium MB concentration (mg L^{-1}), C_t is the MB concentration at any time (mg L^{-1}), m is the adsorbent amount (g), and V is the volume of dye solution (L).

Desorption studies were made aiming to regenerate the adsorbent. HCl was used as eluent. 0.6 g of MB-loaded PGH were mixed with 50.0 mL of HCl (0.1, 0.2, 0.5, 0.8, and 1.0 mol L^{-1}) in Erlenmeyer flasks. The mixture was agitated with rotator shaker (Tecnal, TE-141, Brazil) at 150 rpm for 5.0 h. Subsequently, samples were centrifuged at 5,000 rpm for 20 min (Centribio, 80-2B, Brazil). The dye concentration released in the desorbing solution was determined by UV–vis spectrophotometer (Varian, Cary 50 Bio, USA) at 660 nm. The desorption results were presented in terms of desorption percentage [29].

2.5. Applications of PGH adsorbent on simulated effluents

Textile and river simulated effluents were prepared and used to test the potential of PGH adsorbent for MB removal. The effluents were prepared as previously described [13]. The simulated textile effluent (pH 9.8) contains the following substances: NaCl (80.0 mg L^{-1}), Na_2CO_3 (50.0 mg L^{-1}), CH_3COOH (50.0 mg L^{-1}), cibacron brilliant yellow (5.0 mg L^{-1}) and reactive black 5 (5.0 mg L^{-1}). The simulated river effluent (pH 5.8) contains the following substances: $CaCl_2$ (294.0 mg L^{-1}), NaCl (216.1 mg L^{-1}), Mg_2SO_4 (86.2 mg L^{-1}), KCl (9.7 mg L^{-1}), and $(NH_4)_2HPO_4$ (7.3 mg L^{-1}). The removal of MB from the simulated effluents proceeded as follows: 0.6 g of PGH adsorbent was placed into conic flask containing 50.0 mL of the simulated effluents in the presence of 10.0 mg L^{-1} of MB. The mixture was stirred at 150 rpm for 5.0 h. Then, the solid phase was separated by centrifugation and the MB concentration on supernatant was determined.

2.6. Kinetic and equilibrium models

In the kinetic study, the adsorption of MB onto PGH was evaluated by pseudo-first-order [30], pseudo-second-order [31] and Elovich [32] models. To know the equilibrium relation, the models namely Langmuir [33], Freundlich [34], and Sips [35] were fitted with the experimental data. The kinetic and equilibrium models were presented in Table 1.

The kinetic and equilibrium models were fitted by Levenberg–Marquardt method and the interactions were calculated by the simplex method. The fit quality was statistically evaluated by Chi-square (χ^2), determination coefficient (R^2), and adjusted determination coefficient (R^2_{adj}) [36].

Table 1
Kinetic and isotherm models

Kinetic models	Equation
Pseudo-first order	$q_t = q_e\,[1 - \exp(-k_f\,t)]$
Pseudo-second order	$q_t = \frac{k_s\,q_e^2\,t}{1 + q_e\,k_s\,t}$
Elovich	$q_t = \frac{1}{\beta}(\alpha\beta) + \frac{1}{\beta}(t)$
Isotherm models	
Langmuir	$q_e = \frac{Q_{max} K_L\,C_e}{1 + K_L\,C_e}$
Freundlich	$q_e = K_F\,C_e^{1/n_F}$
Sips	$q_e = \frac{Q_S K_S\,C_e^{1/n}}{1 + K_S\,C_e^{1/n}}$

Notes: k_f: Pseudo-first order rate constant (h^{-1}); q_e: equilibrium adsorption capacity ($mg\,g^{-1}$); k_s: pseudo-second order rate constant ($g\,mg^{-1}\,h^{-1}$); α: initial adsorption rate ($mg\,g^{-1}\,h^{-1}$); β: desorption constant ($mg\,g^{-1}$); Q_{max}: maximum adsorption capacity from Langmuir model ($mg\,g^{-1}$); K_L: Langmuir constant ($L\,mg^{-1}$); K_F: Freundlich constant ($mg\,g^{-1}\,(mg\,L^{-1})^{-1/nF}$); nF: constant relative to the adsorption intensity; K_S: Sips Constant ($(g\,L^{-1})^{-1/n}$); n: Sips exponent; Q_S: maximum adsorption capacity from Sips model ($mg\,g^{-1}$).

3. Results and discussion

3.1. Characterization of PGH adsorbent

The specific surface area of PGH (obtained by BET method) was 37.5 $m^2\,g^{-1}$. The average pore diameter found by BJH method was 43 Å. These values are relatively high for agricultural residues [37], indicating the good potentiality of PGH as adsorbent. The concentrations of active sites on PGH were 1.89 $mmol\,g^{-1}$ of carboxylic groups, 0.84 $mmol\,g^{-1}$ of carbonyl groups, and 0.09 $mmol\,g^{-1}$ of phenolic groups. The elemental analysis results indicated the chemical composition was carbon (42.90%), hydrogen (4.1%), and nitrogen (0.33%). The point of zero charge (pH_{ZPC}) of PGH was 4.1.

3.2. FT-IR and SEM analysis

FT-IR vibrational spectra of PGH before and after MB adsorption are shown in Fig. 1(a) and (b), respectively. The main vibrational frequencies before adsorption were found at 3,429, 2,927, 1,637, 1,433, 1,062, and 580 cm^{-1} (Fig. 1(a)). The band at 3,429 cm^{-1} can be assigned to the –N–H and –O–H groups on PGH surface. The frequency at 2,927 cm^{-1} can be attributed the stretching vibration of $-CH_3$ or $-CH_2$ groups. The band at 1,637 cm^{-1} can be attributed to the –C=O stretching of carboxylic acid with intermolecular hydrogen bond. The bands at 1,433 and 1,062 cm^{-1} were assigned to –C–O group. FT–IR analysis indicated the presence of functional groups such as –N–H, –O–H, –C=O, and –C–O on the surface of PGH adsorbent. The –O–H, –C=O, and –C–O functional groups on PGH adsorbent surface were also confirmed by Boehm tritation analysis (see Section 3.1).

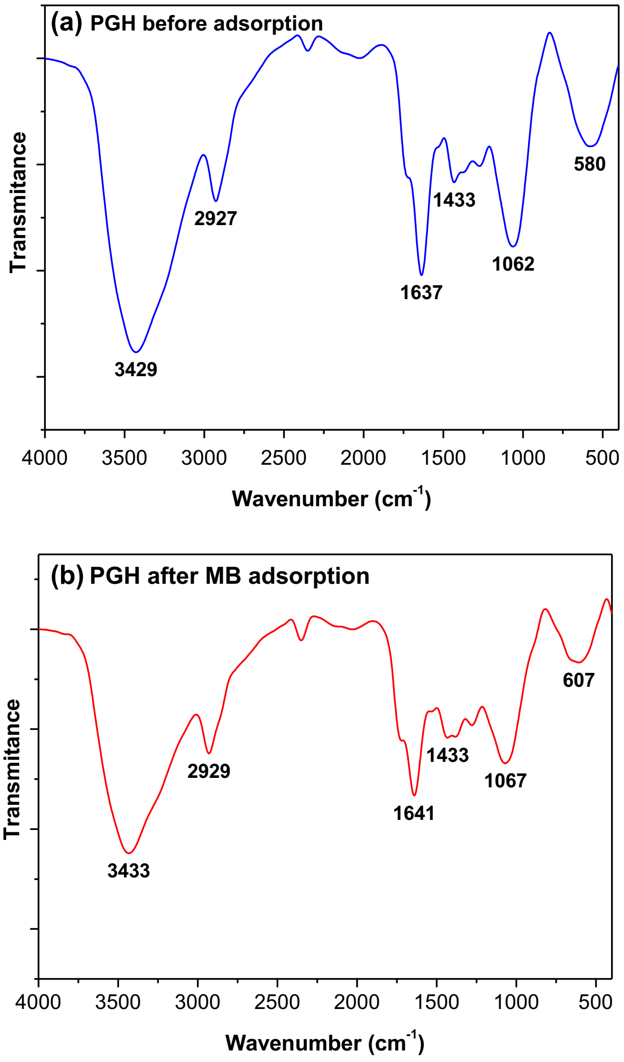

Fig. 1. FT-IR spectra of (a) PGH before adsorption and (b) PGH adsorbed with MB (more adequate conditions).

After the adsorption process (Fig. 1(b)), some changes were observed in the vibrational frequencies of –N–H, –O–H, –C=O, and –C–O functional groups (in relation to Fig. 1(a)). The bands at 3,429 and 1,637 cm^{-1} shifted to 3,433 and 1,641 cm^{-1}, respectively. The band at 1,062 cm^{-1} shifted to 1,067 cm^{-1}. Furthermore, it was observed in the FT-IR spectrum of loaded PGH adsorbent (Fig. 1(b)) that the intensity of stretching vibrational bands at 3,433, 1,641, and 1,067 cm^{-1} decreased. These differences between the FT-IR spectra of PGH before and after MB adsorption suggest that the amines, hydroxyl, and carboxyl groups onto PGH adsorbent were involved in the interactions with MB dye. Similar results were

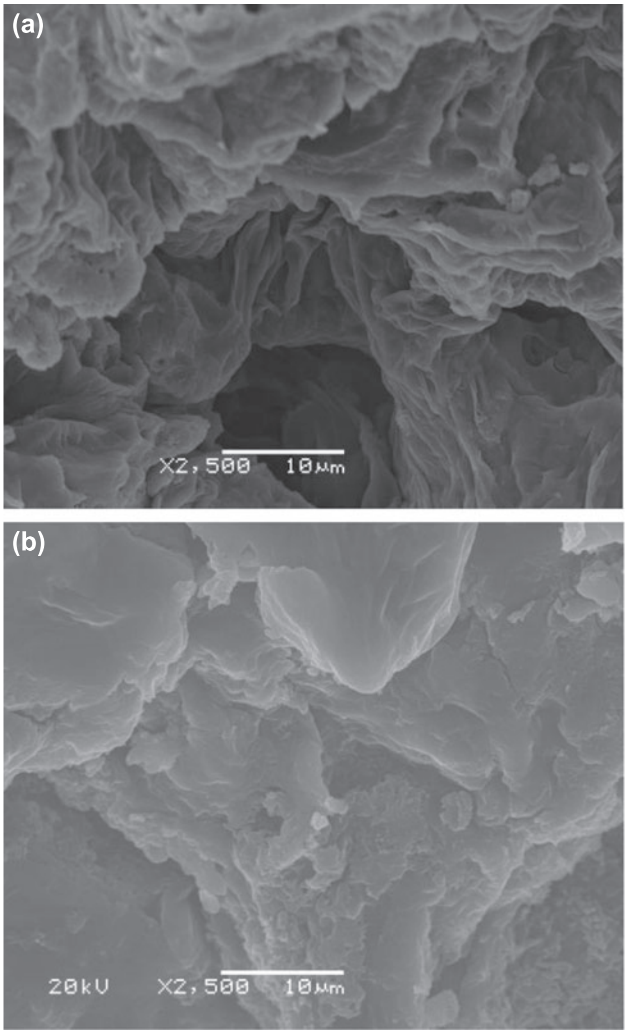

Fig. 2. SEM micrographics of PGH. (a) before MB incorporation and (b) after MB incorporation.

obtained using *P. granatum* L. peels for removal of Acid Blue 40 [26].

The SEM images of PGH and dye-loaded PGH are shown in Fig. 2(a) and (b), respectively. It can be observed (Fig. 2(a)) that native PGH have an irregular and non-compacted surface with cavities and protuberances. These textural characteristics can help MB adsorption, because there is a possibility for MB molecules take up these spaces [38]. After incorporation of MB (Fig. 2(b)), the cavities and protuberances of the PGH surface disappeared indicating that the adsorption phenomena occurred. [19].

3.3. pH effect

The pH effect on MB adsorption onto PGH adsorbent was investigated in the range from 2.0 to 12.0 (initial pH of solution) and the results are shown in Fig. 3. It was found in Fig. 3 that when the pH values increased from 2.0 to 5.0, the adsorption capacity increased about 75%. A new increase from 5.0 to 12.0 was not significant ($p < 0.05$) regarding the adsorption capacity (Fig. 3). These results show that the more adequate pH range for MB adsorption on PGH is from 5.0 to 12.0. This result is particularly important since PGH maintain its adsorption capacity in a wide range of pH. This behavior can be explained in $\mathrm{pH_{ZPC}}$ on the basis of PGH (4.1). At pH values lower than 4.1, the surface of PGH is positively charged, hindering the electrostatic attraction with dye molecules consequently, lower adsorption was observed. However, at pH values higher than 4.1 the MB adsorption is facilitated because the adsorbent surface is negatively charged, and so, attract the cationic molecules of MB [19,39]. This behavior was also verified by Ahmad and Kumar [40] using treated ginger waste for the removal of Malachite green from aqueous solution and by Prasad and Santhi [41] in the adsorption of cationic dyes by *Acacia nilotica* leaves. Based on the above results, pH 5.0 was selected as the more adequate for MB adsorption on PGH.

3.4. Effect of adsorbent dosage

The effect of adsorbent dosage (from 0.1 to 1.0 g/50 mL) on the MB adsorption onto PGH was verified at 298 K, initial MB concentration 50.0 mg L^{-1} and pH 5.0. The results (Fig. 4) indicated that an increase in the adsorbent dosage from 0.1 to 0.6 g cause an increase on dye adsorption percentage from 47.8 to 92.6%. This increase is attributed to the

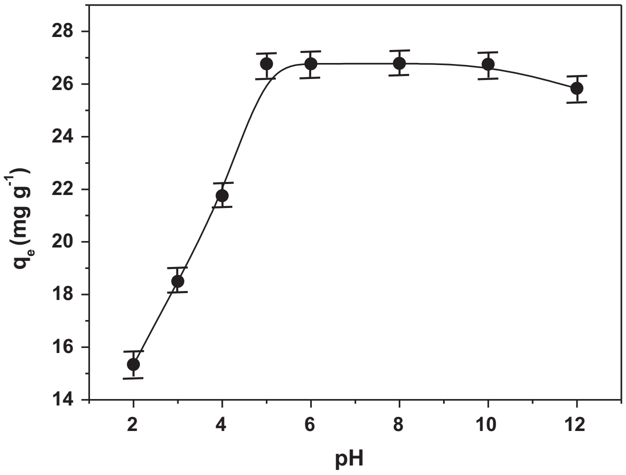

Fig. 3. Effect of pH on adsorption of MB by PGH ($C_0 = 50.0$ mg L^{-1}, $T = 298$ K, and adsorbent dosage = 0.6 g).

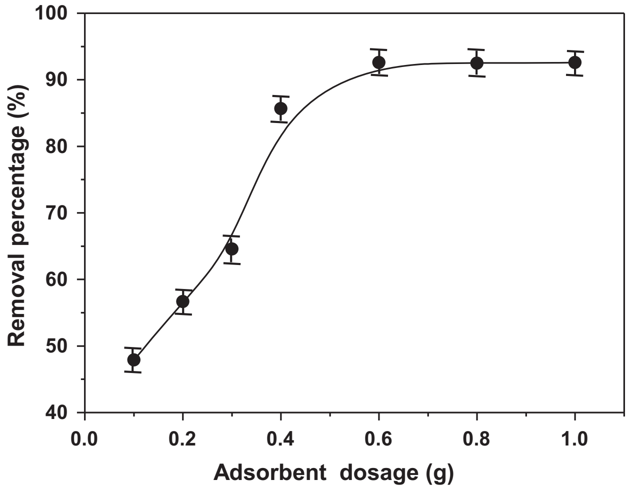

Fig. 4. Effect of adsorbent dosage on the adsorption of MB by PGH ($C_0 = 50.0$ mg L^{-1}, $T = 298$ K, and pH = 5.0).

increase in amount of surface area and number of vacant binding sites [19]. A new increase from 0.6 to 1.0 g of adsorbent caused no effect on the MB removal percentage (Fig. 5). This behavior could be attributed to the aggregation of adsorbent particles at a fixed volume of solution [42]. Thus, the adsorbent dosage selected for subsequently adsorption experiments was 0.6 g/50.0 mL.

3.5. Effects of contact time and initial dye concentration

The effects of contact time (0.08–24.0 h) and initial dye concentration (10.0, 20.0 and 50.0 mg L^{-1}) on the adsorption of MB onto PGH are show in Fig. 5(a). It was found that, the adsorption of MB onto PGH was faster in the first 2.0 h, after, the adsorption rate decreased and the equilibrium was attained in 5.0 h. This behavior occurred because at initial adsorption stages the concentration gradient between the bulk solution and adsorbent external surface is high, facilitating the mass transport. Furthermore, at initial stages there is a large available surface area [43]. After the initial stages, the saturation of adsorption sites on the external surface of adsorbent occurred and the dye molecules were adsorbed on the internal surface, consequently, the adsorption rate was slow. Similar behavior was reported by Gupta et al. [44] using chemically modified *Ficus carica* as adsorbent for removal of MB. Therefore, 5.0 h was selected as adequate contact time for MB adsorption. Regarding to the initial MB concentration effect (Fig. 5(a)), it was found that an increase from 10.0 to 50.0 mg L^{-1} increased the adsorption capacity from 9.8 to 42.5 mg g^{-1}. This result could be attributed to the driving force that overcomes the mass transfer resistance [45].

3.6. Kinetic evaluation

From the kinetic viewpoint, the adsorption of MB onto PGH was evaluated by pseudo-first-order, pseudo-second-order and Elovich models. The kinetic parameters are summarized in Table 2. Fig. 5(b)–(d) show the fit of kinetic models for MB adsorption on PGH at initial dye concentrations of 10.0, 20.0, and 50.0 mg L^{-1}, respectively. The high values of R^2 and R^2_{adj} and the low values of χ^2 (Table 2) show that the pseudo-second-order model was the more adequate to represent the adsorption kinetics of MB onto PGH. Table 2 shows that k_s (pseudo-second-order rate constant) decreased with the increase in initial MB concentration, while h_0 (initial adsorption rate) and q_e (equilibrium adsorption capacity) increased. This indicates that at the initial stages, more dye was adsorbed faster, at higher MB concentrations. Similar trend was found by Wang and Li [46].

3.7. Equilibrium study

The equilibrium study was performed by the fit of Langmuir, Freundlich, and Sips models (Table 1) with the experimental data. The equilibrium experimental curve was obtained in the following conditions: 298 K, pH of 5.0, contact time 5.0 h, and adsorbent dosage 0.6 g/50.0 mL The initial MB concentration ranged from 5.0 to 500.0 mg L^{-1}. The equilibrium parameters are shown in Table 3, and the experimental fitted curve is presented in Fig. 6. Fig. 6 shows that both Langmuir and Sips isotherm models adequately describe the adsorption of MB. The Sips isotherm model present highest values of R^2 and R^2_{adj} and the lowest values of χ^2 (Table 3) when compared with Langmuir isotherm model. The experimental data obtained did not agree with Freundlich isotherm model. These results indicated that Sips model is more adequate to represent the adsorption equilibrium of MB onto PGH.

The maximum adsorption capacity from the Sips model (Q_S) was 68.40 mg g^{-1}. This value was compared with other adsorbents used to remove MB from aqueous solutions as follows: peanut hull 68.03 mg g^{-1} [47], yellow passion fruit waste 44.70 mg g^{-1} [15], olive pomace 42.3 mg g^{-1} [48], gypsum 36.00 mg g^{-1} [49], rice husk 28.00 mg g^{-1} [50], cereal chaff 20.3 mg g^{-1} [51], and hazelnut shell 38.22 mg g^{-1} [52]. The above comparison shows that PGH is an advantageous adsorbent over many other adsorbents used for MB removal.

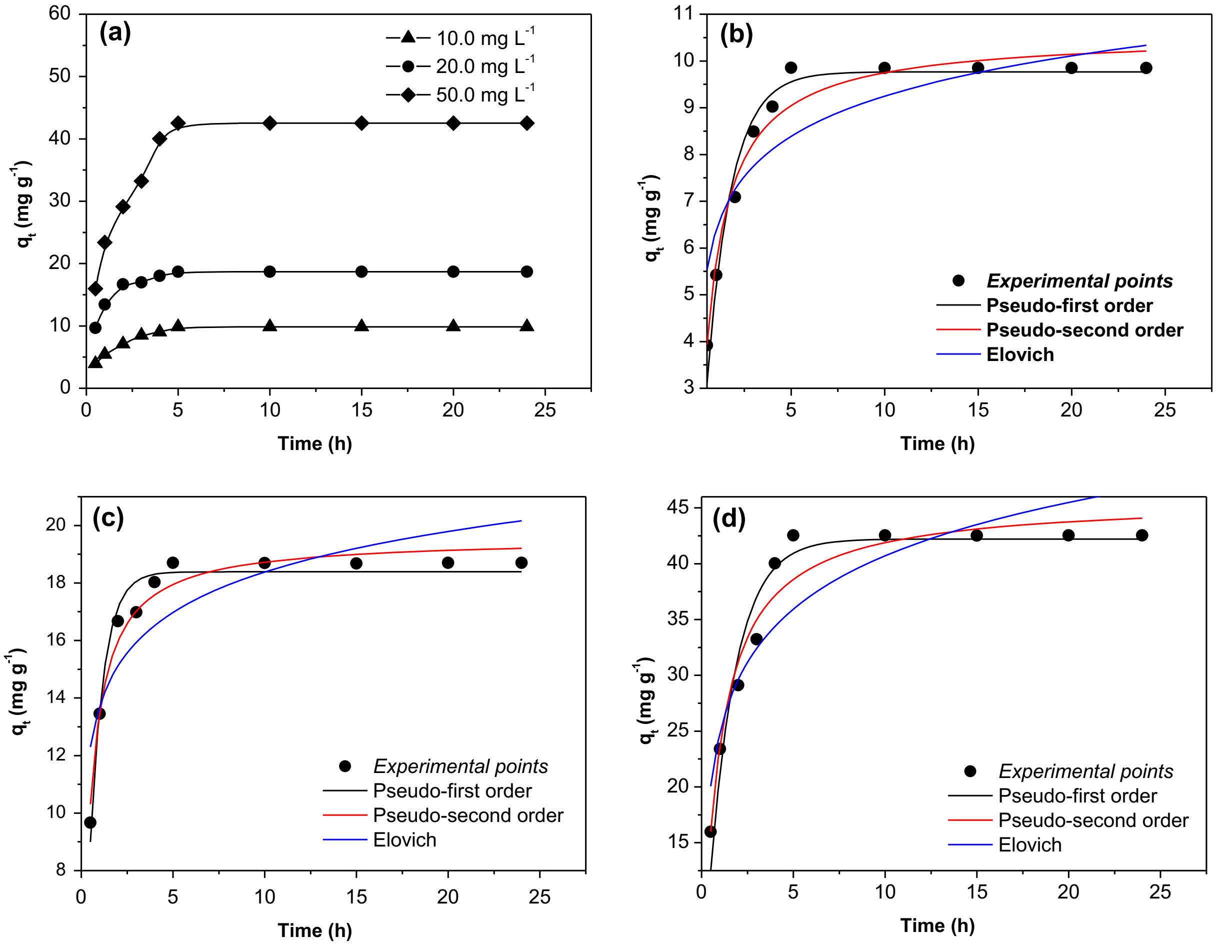

Fig. 5. Effect of contact time: (a) Kinetic curves for the adsorption of MB on PGH; (b) C_o = 10.0 mg L^{-1}; (c) C_o = 20.0 mg L^{-1} and (d) C_o = 50.0 mg L^{-1} (T = 298 K, pH = 5.0, and adsorbent dosage = 0.6 g).

3.8. Desorption studies

Desorption studies were performed to evaluate the possibility of adsorbent regeneration. HCl, a strong inorganic acid, is commonly used for to desorb of dyes molecules from the adsorbent. The results of MB desorption onto PGH adsorbent as a function of eluent (HCl) concentration (0.1, 0.2, 0.5, 0.8, and 1.0 mol L^{-1}) are shown in Fig. 7. Fig. 7 shows that the desorption percentage increased with increasing concentrations of HCl. The explanation for these results is that with increase in concentration of HCl, an increase in hydrogen ions concentration on solution occurs. This increase of hydrogen ions solution leads to increase in the exchange of hydrogen ions presents in solution by dye molecules adsorbed onto adsorbent, and consequently, the desorption rate increase. The more adequate desorption condition was obtained with 1.00 mol L^{-1} of HCl, where 92.1% of MB was desorbed. Similar behavior was observed for MB desorption onto sawdust adsorbent [47]. The good desorption obtained at strongly acid solution suggest that MB adsorption onto PGH is governed by electrostatic interactions [44]. These data agree with previously published results [15,19].

3.9. Application of PGH for MB adsorption from simulated effluents

In order to verify the applicability of PGH for MB adsorption in real conditions, simulated textile and river effluents and were prepared. Distilled water containing only MB dye was used for to compare the removal efficiency.

The simulated effluents employed in these studies contain various compounds, such as inorganic salts, dyes, and organic molecules (see Section 2.5), commonly present in industry and environmental waters [13,52]. It is know that these compounds when present

Table 2
Kinetic parameters for MB adsorption on PGH at the more adequate conditions

	C_0 (mg L^{-1})		
Model	10.0	20.0	50.0
Pseudo-first order			
k_{f} (h^{-1})	0.765	1.344	0.692
q_{e} (mg g^{-1})	9.76	18.38	42.26
R^2	0.966	0.969	0.950
R^2_{adj}	0.962	0.965	0.944
χ^2	0.336	1.461	1.360
Pseudo-second order			
k_{s} (g mg^{-1} h^{-1})	0.114	0.112	0.023
q_{e} (mg g^{-1})	10.57	19.56	45.79
h_0 (mg g^{-1} h^{-1})	15	16	20
R^2	0.971	0.973	0.958
R^2_{adj}	0.968	0.970	0.953
χ^2	0.200	0.100	1.020
Elovich			
α (mg g^{-1} h^{-1})	77.128	1,724.767	239.725
β (g mg^{-1})	0.654	0.492	0.147
R^2	0.843	0.761	0.841
R^2_{adj}	0.825	0.734	0.823
χ^2	0.682	0.800	3.190
q_{e} (experimental) (mg g^{-1})	9.98	19.86	44.04

Table 3
Isotherm parameters for MB adsorption on PGH at the more appropriate conditions

Langmuir	
$q_{\max}$ (mg g^{-1})	66.50
K_{L} (L mg^{-1})	0.262
R^2	0.994
R^2_{adj}	0.993
χ^2	0.240
Freundlich	
K_{F} (mg g^{-1} (mg $\mathrm{L}^{-1})^{-1/n\mathrm{F}}$)	22.51
nF	4.47
R^2	0.903
R^2_{adj}	0.893
χ^2	2.698
Sips	
$q_{\max}$ (mg g^{-1})	68.40
K_{S} ((g $\mathrm{L}^{-1)-1/n}$)	0.296
n	1.16
R^2	0.996
R^2_{adj}	0.995
χ^2	0.109
q_{e} (experimental) (mg g^{-1})	68.23

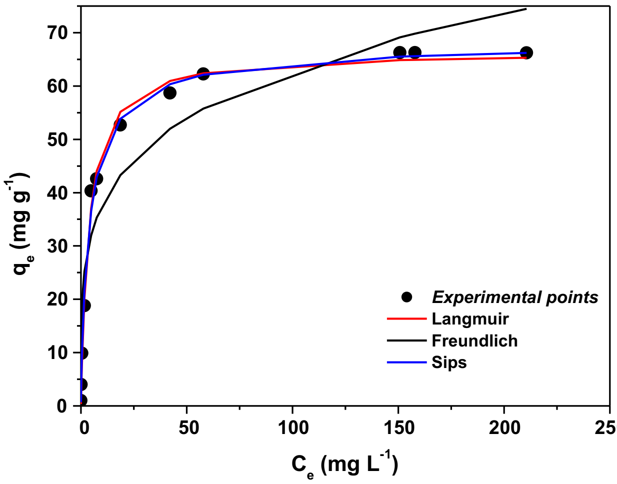

Fig. 6. Equilibrium isotherm for the adsorption of MB by PGH (T = 298 K, adsorbent dosage = 0.6 g/50 mL, pH = 5.0, and contact time = 5.0 h).

in waters can affect significantly the dye molecules adsorption and limiting the potential applications of adsorbent. Fig. 8 shows the visible spectra (from 500

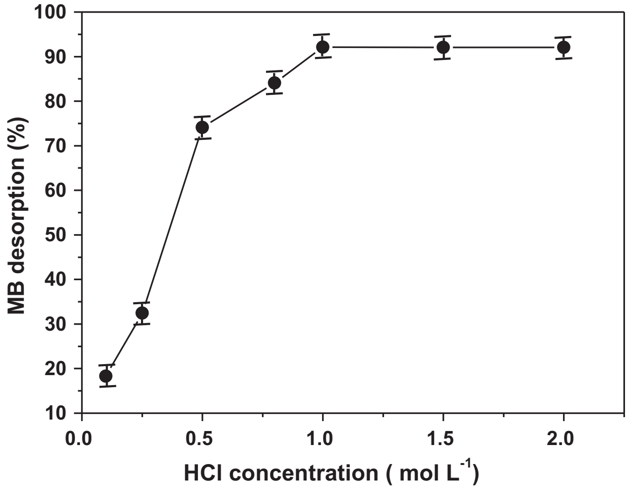

Fig. 7. Desorption results.

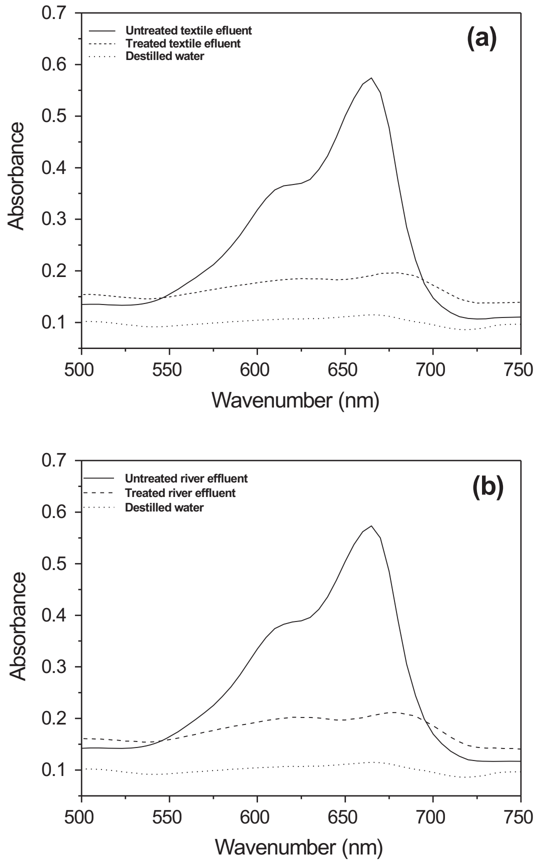

Fig. 8. Visible spectra of simulated effluents before and after treatment with PGH adsorbent at best adsorption conditions: (a) textile effluent and (b) river effluent.

to 750 nm) of untreated and treated textile (Fig. 8(a)) and river (Fig. 8(b)) effluents. The intensity of band at 650.0 nm was used for to verify the dye percentage removal of simulated effluents. Fig. 8 shows that after the treatment with PGH adsorbent, the bands of dye practically disappeared, indicating good efficiency of adsorbent for treating textile and river effluents. Based on quantitative analysis, the removal efficiencies for simulated textile effluent, simulated river effluent, and distilled water at $C_0 = 10.0\ \mathrm{mg\,L^{-1}}$ of MB were 90.3, 93.2, and 98.9% respectively. These results are quite satisfactory considering the amounts of inorganic salts and organic molecules presents in the simulated effluents, which are potentially able to inhibit the MB adsorption. Thus, the PGH adsorbent has great potentialities to remove MB from textile and river effluents.

4. Conclusion

In this work, PGH was tested as adsorbent for the removal of MB from aqueous solutions. The effects of initial pH of solution, adsorbent dosage, contact time, and initial dye concentration were evaluated. Kinetic and equilibrium studies were performed. The potential of PGH to treat simulated effluents was verified. The results obtained by FT-IR indicate that carboxyl and hydroxyl groups are responsible to uptake MB molecules. The more adequate pH for the adsorption of MB was in the range from 5.0 to 12.0. The equilibrium was attained in 5.0 h of contact time using 0.6 g/50.0 mL of adsorbent. The adsorption kinetics of MB onto PGH can be well described by pseudo-second-order model. The Sips isotherm model is more appropriate to explain the adsorption of MB on PGH. Based on Sips isotherm model, the maximum adsorption capacity was $68.40\ \mathrm{mg\,g^{-1}}$. Desorption studies showed that PGH adsorbent can be regenerated using 1.0 M HCl solution as an eluent. PGH was adequate to treat simulated textile and river effluents, since the MB removal percentages were 90.3 and 93.2%, respectively. Based on these results, it can be concluded that PGH can be used as an alternative adsorbent for the removal of MB from aqueous systems.

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Symbols

C_0 — initial MB concentration ($\mathrm{mg\,L^{-1}}$)
C_e — dye concentration at equilibrium ($\mathrm{mg\,L^{-1}}$)
C_t — MB concentration at any time ($\mathrm{mg\,L^{-1}}$)

m — adsorbent amount (g)
V — volume of dye solution (L)
χ^2 — Chi-square
R^2 — determination coefficient
R^2_{adj} — adjusted determination coefficient
pH_{PZC} — point zero of charge
k_{f} — pseudo-first-order rate constant (h^{-1})
q_{e} — equilibrium adsorption capacity (mg g^{-1})
k_{s} — pseudo-second-order rate constant ($\text{g mg}^{-1}\ \text{h}^{-1}$)
α — initial adsorption rate ($\text{mg g}^{-1}\ \text{h}^{-1}$)
β — desorption constant (mg g^{-1})
$Q_{\max}$ — maximum adsorption capacity from Langmuir model (mg g^{-1})
K_{L} — Langmuir constant (L mg^{-1})
K_{F} — Freundlich constant ($\text{mg g}^{-1}\ (\text{mg L}^{-1})^{-1/n\text{F}}$)
$n\text{F}$ — constant relative to the adsorption intensity
K_{S} — Sips constant ($(\text{g L}^{-1})^{-1/n}$))
n — Sips exponent
Q_{S} — maximum adsorption capacity from Sips model (mg g^{-1})
PGH — *Punica granatum* husk
nm — nanometer
MB — methylene blue

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