Removal of the pesticide methomyl contained in simulated effluent from equipment washing by adsorption in residual orange bagasse

Remoção do pesticida metomil de efluentes simulados de lavagem de equipamentos por meio de adsorção em bagaço de laranja

Eliminación del plaguicida metomilo contenido en el efluente simulado del lavado de equipos por adsorción em bagazo de naranja residual

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Abstract

This work consists of the study of methomyl removal, an extremely toxic carbamate pesticide, contained in aqueous solutions synthesized, by adsorption in residual orange bagasse from industrial juices processing. The adsorption kinetics was studied by obtaining the best fit for the model of pseudo-second order (R^2= 0.949). The Langmuir isotherm model adjusted better to the experimental data confirming the adsorption in monolayers, without interaction among the adsorbate molecules. The scanning electron microscopy (SEM) revealed that particulate adsorbents have rather irregular surface, but with rigid structure and virtually no internal pores. The characterization of the functional groups by infrared spectroscopy (FTIR) revealed the presence of hydroxyl, Carbonyl and carboxylic groups on the adsorbents particles surface. Central composite rotational design 2x2 (DCCR 2x2) was used for the statistical study of the effects of pH and solid/liquid ratio (R) on the methomyl adsorption capacity in orange bagasse particles. The obtained mathematical model adjusted well to the experimental data (R^2= 95%). In the studied intervals the highest values of adsorption capacity (q) were 3.73 and 3.43 (mg.g^{-1}), obtained under the conditions of pH 6.0 with R 0.017 g.mL^{-1} and pH 4.5 with R 0.015 g.mL^{-1}, respectively. Thus, it was possible to conclude that there was a greater adsorption in assays containing greater adsorbent mass in pH slightly acid.

Keywords: Adsorption; Pesticide; Methomyl; Orange bagasse; Lignocellulosic biomass.

Resumo

Este trabalho consiste no estudo da remoção de metomil, um pesticida carbamato extremamente tóxico, contido em soluções aquosas sintetizadas em laboratório, por adsorção em bagaço de laranja residual do processamento de sucos industriais. A cinética de adsorção foi estudada obtendo-se o melhor ajuste para o modelo de pseudo-segunda ordem (R^2= 0,949). O modelo de isoterma de Langmuir se ajustou melhor aos dados experimentais confirmando a adsorção em monocamadas, sem interação entre as moléculas do adsorbato. A microscopia eletrônica de varredura (MEV) revelou que os adsorventes particulados apresentam superfície bastante irregular, porém com estrutura rígida e praticamente sem poros internos. A caracterização dos grupos funcionais por espectroscopia de infravermelho (FTIR)

revelou a presença de grupos hidroxila, carbonila e carboxílicos na superfície das partículas adsorventes. O delineamento central composto rotacional 2x2 (DCCR 2x2) foi utilizado para o estudo estatístico dos efeitos do pH e da razão sólido / líquido (R) na capacidade de adsorção de metomil em partículas de bagaço de laranja. O modelo matemático obtido se ajustou bem aos dados experimentais (R^2= 95%). Nos intervalos estudados os maiores valores de capacidade de adsorção (q) foram 3,73 e 3,43 (mg.g^{-1}), obtidos nas condições de pH 6,0 com R 0,017 g.mL^{-1} e pH 4,5 com R 0,015 g.mL^{-1}, respectivamente. Assim, foi possível concluir que houve uma maior adsorção em ensaios contendo maior massa adsorvente em pH levemente ácido.

Palavras-chave: Biossorção; Pesticida; Metomil; Bagaço de laranja; Biomassa lignocelulósica.

Resumen

Este trabajo consiste en el estudio de la remoción de metomilo, un plaguicida carbamato extremadamente tóxico, contenido en soluciones acuosas sintetizadas, por adsorción en bagazo de naranja residual del procesamiento de jugos industriales. Se estudió la cinética de adsorción obteniendo el mejor ajuste para el modelo de pseudo-segundo orden (R^2= 0,949). El modelo de isoterma de Langmuir se ajustó mejor a los datos experimentales confirmando la adsorción en monocapas, sin interacción entre las moléculas de adsorbato. La microscopía electrónica de barrido (SEM) reveló que los adsorbentes de partículas tienen una superficie bastante irregular, pero con una estructura rígida y prácticamente sin poros internos. La caracterización de los grupos funcionales por espectroscopía infrarroja (FTIR) reveló la presencia de grupos hidroxilo, carbonilo y carboxílico en la superficie de las partículas adsorbentes. El diseño rotacional compuesto central 2x2 (DCCR 2x2) se utilizó para el estudio estadístico de los efectos del pH y la relación sólido / líquido (R) sobre la capacidad de adsorción de metomilo en partículas de bagazo naranja. El modelo matemático obtenido se ajustó bien a los datos experimentales (R^2= 95%). En los intervalos estudiados los valores más altos de capacidad de adsorción (q) fueron 3.73 y 3.43 (mg.g^{-1}), obtenidos en las condiciones de pH 6.0 con R 0.017 g.mL^{-1} y pH 4.5 con R 0.015 g.mL^{-1}, respectivamente. Así, se pudo concluir que existía una mayor adsorción en los ensayos que contenían mayor masa adsorbente en pH ligeramente ácido.

Palabras clave: Adsorción; Pesticida; Metomilo; Bagazo de naranja; Biomasa lignocelulósica.

1. Introduction

The widespread use of pesticides in agriculture can cause soil pollution through different forms, both by spraying, leaching and overland flow, and by point sources such as accidental spills, equipment or washing machine leaks and contaminated containers (Carter, 2000; De Wilde et al., 2007). Once present in the soil, the pesticides act as a source of air and water bodies contamination, because they can spread through the soil and contaminate surface and groundwater waters (El Bakouri & Morillo, 2007; El Bakouri et al., 2008, 2010). The pesticide residues present in vegetables and drinking water have a great potential to cause long-term harmful effects, such as cancer (Bolognesi et al., 2000; Pimentel et al., 2006; Arrebola et al., 2015; Rivero et al., 2015; Yoshida et al., 2015; Caron-Beaudoin et al., 2016).

Methomyl, $C_5H_{10}N_2O_2S$, S-methyl-1-N-(methyl carbamoyl oxy) thioacetamide, is a high-risk toxicological pesticide (Fernandes et al., 2011), of the group of N-methylcarbamate of oximes, which has insecticide and acaricide activity (Lewis et al., 2016). It is considered by the U.S. Environmental Protection Agency (EPA) as restricted use due to its residual accumulation in soil, agricultural products and aquatic systems (EPA, 1998; El-Fakharany et al., 2011; Caetano et al., 2013). The effects of environmental contamination by methomyl were described mainly on aquatic organisms as carp (Cyprinus carpio), Daphnia magna, ostracods, algae, daphnids (Rao et al., 1984; Farré et al., 2002; Todd & Leeuwen, 2002; Boran et al., 2007; Wang et al., 2015; Toumi et al., 2016a; Toumi et al., 2016b; Meng et al., 2016) and amphibians (Lau et al., 2015; Saleem, 2019), due to the long half-life of methomyl in surface waters, 6 days, and in groundwater (Farré et al., 2002), 50 weeks. Its toxicological potential was also demonstrated in other species, such as mice (El-Demerdash et al., 2013; Trachantong et al., 2017).

The adsorption is one of the most effective physical processes for the pesticides removal in wastewater. The process has advantages such as operation and simple designs; compounds removal in very low concentrations (micro-pollutants); applicability in continuous and discontinuous processes; ability to remove toxic compounds; low investment cost; environmental benefit; and the probability of reuse and regeneration of adsorbents (Torrelas et al., 2016; Bhatnagar & Anastopoulos, 2017). Among the commercial adsorbents, activated charcoal is the most widely used, because it has high adsorption capacity of several organic pollutants. However, it has a relatively high cost and difficulties in regeneration processes (Fernandes et al., 2011); thus, there is a growing demand for efficient adsorbents with low cost, which is why the use of wastes from the agro industry becomes attractive, due to the

wide material availability and the possibility of contributing to the wastes elimination or reduction (Rojas et al., 2015; Pap et al., 2017).

Among the materials used in recent studies are: banana peels (Almeida & Santos, 2020), coconut fiber (Cardoso et al., 2020), sawdust (Tavares et al., 2020), orange peel (Pandiarajan et al., 2018), plum pit (Pap et al., 2017), limes peel and corn cobs (Singh et al., 2017), peanut hulls (Cui et al.,2017), eucalyptus bark, corn cobs, bamboo chips, rice husk and straw (Mandal et al., 2017), peat and coconut fiber (Chwastowski et al., 2017), seeds of sweet cherry (Pap et al., 2016), solid waste from tomatoes processing (Saygili et al., 2016), wood wastes (Hajati et al., 2015; Largitte et al., 2016), forest biological waste (Kim et al., 2015), processing waste (Saygili et al., 2016), pistachio peels (Nowicki et al., 2015), and coffee residues (Kyzas et al., 2012; Berhe et al., 2015).

The orange bagasse corresponds to the residue obtained after the extraction of juice, whose mass corresponds to 50% of the mass of the fruit, thus being a low-cost material that contains valuable compound such as pectin, soluble sugars, proteins, appreciable quantities of fibers (cellulose and hemicelluloses) and lignin (Tsukamoto et al., 2013).

This work aims to characterize the adsorption process of the pesticide methomyl, present in simulated effluent from rinsates, in residual orange bagasse using kinetic models of pseudo-first order, pseudo-second order and Elovich model, and the model of Langmuir and Freundlich isotherms, and apply the rotational central composite design (DCCR) 2x2 to evaluate the effects of pH and solid-liquid ratio (R) on the process.

2. Material and Methods

2.1 Adsorbent preparation

The adsorbent material was prepared from orange bagasse originated from the juice industry Gyn Fruit, located in Goiânia. The collected residues were subjected to washing in running drinking water, cut into pieces of 3 x 3 cm and dried in an oven with air circulation at 50 $^{\circ}$C for 24 hours (Seolatto et al., 2012). Subsequently, the biomass was crushed in knife mill and passed in granulometric sieve, and the particles were selected with a mean diameter of 1.275 mm, thereby avoiding the use of sprayed material, or very large particles in the adsorption trials.

2.2 The adsorbent characterization (SEM and FTIR)

To characterize the adsorbent particles analyzes of scanning electron microscopy (SEM) were conducted with the microscope Jeol JSM - 6610, equipped with Thermo Scientific EDS NSS Spectral Imaging, 5 kV electrical voltage, and Fourier Transform (FTIR) infrared absorption spectroscopy analysis in the Perkin Elmer Spectrum model 400 spectrophotometer. The samples were prepared in a 1% KBr mass, and the spectra were obtained in the range 400 to 4000 cm^{-1} (mid-infrared region), with 128 scans.

2.3 Contaminated waters

The contaminated waters used in this work were prepared as solutions in the laboratory from the commercial product *Lannate*, *DU PONT* manufacturer, with active ingredient methomyl.

2.4 Analysis of pesticide concentrations in the solutions

The methomyl concentrations in solutions were determined by HPLC (Shimadzu Prominence LC-20AD), with UV-VIS detector, and analytical column C18 Core-Shell phenomenex, 5 µm, 4.6 x 250 mm, according to methodology developed by Silva (2018). The running was held with injection volume 5 µL, flow of 1.0 mL.min^{-1} and detection at 230 nm. Mobile phase water: methanol (% v/v) was used, with exploratory gradient (90:10 to 0:100) during the period from 0 to 20 minutes, column cleaning (0:100) from 21 to 35 minutes, return to the initial condition (0:100) from 36 to 40 minutes and stabilization of the initial condition (90:10) from 41 to 55 minutes. The methomyl analytical standard was purchased from Sigma-Aldrich.

2.5 Adsorption assays

All the adsorption assays were performed in 250-mL Erlenmeyer flasks, using 1.0 g of adsorbent and 100 mL of an aqueous solution of the pesticide. For the study of the adsorption kinetics, samples were analyzed at different contact times, with the maximum of 48 hours and solutions to the concentration of 400 mg.L^{-1} of methomyl. In all the adsorption assays, the flasks were kept in an incubator at 30 $^{\circ}$C, with orbital shaking at 150 rpm (Seolatto et al.,

2012). The solutions used in the assays were prepared with ultrapure water. The adsorption capacity in balance q_e (mg.g^{-1}) was calculated using the mass balance equation:

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

Where,

q_e is the adsorption capacity in balance (mg.g^{-1}),

C_0 is the initial solution concentration (mg.L^{-1}),

C_e is the solution concentration in balance (mg.L^{-1}),

V is the volume of the solution used in the assay (L),

m is the mass of adsorbent used in the assay (g).

2.5.1 Adsorption kinetics

The adsorption kinetics study aimed to elucidate the mechanisms that controlled the adsorption process, allowing the effectiveness of the adsorbent to be evaluated according to the contact time necessary to achieve the balance. The mathematical models of pseudo-first order, pseudo-second order, and the Elovich model were adjusted to the experimental data, using the equations (2) to (4), whose parameters were obtained graphically.

The equation of the pseudo-first order model, of Lagergren (Lagergren, 1898):

$$ln(q_e - q_t) = ln\,(q_e) - k_1 \cdot t$$
(2)

The equation of the pseudo-second order model (McKay, 1999):

$$\frac{1}{q_t} = \frac{1}{k_2 \cdot q_e{}^2} + \frac{t}{q_e}$$
(3)

The Elovich equation model (Aharoni & Ungarish, 1976):

$$q_t = \frac{1}{\beta} \cdot ln(\alpha \cdot \beta) + \frac{1}{\beta} \cdot ln(t)$$
(4)

Where,

q_t is the quantity of adsorbate adsorbed on the solid phase (mg.g^{-1}),

q_e is the adsorption capacity in balance (mg.g^{-1}),

K_1 is the constant rate of adsorption of pseudo-first order (min^{-1}),

K_2 is the constant rate of adsorption of pseudo-second order (min^{-1}),

β is the constant of Elovich (mg.g^{-1}),

α is the constant related to the initial adsorption rate (mg.g^{-1}.min^{-1}).

2.5.2 Adsorption isotherms

2.5.2.1 The Langmuir isotherm model

Langmuir isotherm (Langmuir, 1918) was developed assuming that the adsorption process is reversible, and occurs in monolayers, in a fixed number of active sites, which have equivalent energy and contain only one molecule adsorbed, and may be represented by Equation (5).

$$\frac{C_e}{q_e} = \frac{1}{q_{máx}} \cdot C_e + \frac{1}{q_{máx} \cdot K_L} \tag{5}$$

Where q_e (mg.g^{-1}) corresponds to the amount of solute adsorbed per gram of adsorbent in balance, q_{max} (mg.g^{-1}) is the maximum capacity of adsorption, K (L.mg $^{-1}$) is the constant of adsorbate/adsorbent study, and C_e is the adsorbate in balance (mg.L^{-1}). Knowing the interception values (linear coefficient) and the inclination (angular coefficient), it is possible to calculate the values for the parameters q_{max} and K_L.

2.5.3 The Freundlich isotherm model

The model proposed by Freundlich constitutes a model with empirical characteristics that can be applied to systems that are not ideal, in heterogeneous surfaces, with the occurrence of several active adsorption sites, with different adsorptive energies and interaction among the adsorbate molecules, resulting in multilayer adsorption (Chakraborty et al., 2012; Dada et al., 2011; McKay, 1996). The Freundlich equation (6), represents a quantitative relationship in which the solute adsorption increases indefinitely with the increase of the concentration.

$$log(q_e) = log(K_F) + \left(\frac{1}{n}\right) \cdot log C_e \tag{6}$$

Where q_e (mg.g^{-1}) corresponds to the amount of solute adsorbed per gram of adsorbent in balance, Ce is the adsorbate concentration in balance (mg.L^{-1}), 1/n is a constant related to the heterogeneity of the surface, and K_F is the constant of Freundlich adsorption capacity $(g^{-1}.L^{1/n}.mg^{(1-1/n)})$.

2.6 Influence of pH and solid/liquid ratio (R) on the adsorption capacity

According to Anastopoulos et al., (2017) the critical experimental conditions that affect the adsorption capacity of a solid are the initial concentration, the pH of the aqueous solution, the contact time, the temperature, the biomass dosage, and the coexistence of other pollutants. The solution pH plays an important role on the control of the adsorbent surface charge, the ionization degree of the adsorbate in the solution, as well as on the decoupling of several functional groups present in the active sites of the adsorbent (Banerjee & Chattopadhyaya, 2013).

The biomass dosage is positively correlated with the adsorption capacity, since the greater the adsorbent mass, the greater the surface area and, consequently, the greater the availability of active sites. However, the excess mass can cause the aggregation/agglomeration of adsorbent particles, leading to a decrease in surface area and, consequently, the active sites available (Belay & Hayelom, 2014).

The statistical study of the methomyl adsorption in orange bagasse was performed with the *R Studio* software, with the objective to evaluate the effects of the parameters pH and adsorbent weight/volume ratio of solution (g.mL^{-1}), called "R" on the biomass adsorption capacity. This was used for the rotational central composite design (DCCR) 2^2, containing four central points and four axial points, resulting in 12 (twelve) trials (Lazic', 2004), in which the pH values ranged from 3.9 to 8.1 and the R values from 0.003 to 0.017 (g.mL^{-1}), with α orthogonality of 1.41, according to the experimental matrix presented in Table 3. The analysis of variance (ANOVA) of the experimental data was performed with a confidence interval of 95%, and multiple regressions were used to adjust a mathematical model to the experimental data and, therefore, obtain a surface response to the region of the evaluated sample.

3. Results and Discussion

3.1 Characterization of the adsorbent particles

The surface morphology of the adsorbent particles of orange bagasse was characterized by Scanning Electron Microscopy (SEM). The images with an increase of 50 and 150 times allowed to observe a rather irregular surface, different formats, formation of elevations, small cavities and surface pores, while more expanded images (500 and 1500 times) allowed the visualization of areas with few irregularities, without pores or internal cavities, indicating high particles rigidity, as shown by Figures 1 a – d.

The absorption spectroscopy in the infrared region was performed to characterize the functional groups present in the adsorbent structure. Bands in 1059, 1258, 1420, 1635, 2930 and 3395 cm^{-1} were observed in the spectrum represented in Figure 2. The large and intense band in 3395 cm^{-1} was attributed to the vibrational stretch of the bond O-H, group characteristic of the cellulose present in the sample. The band at 2930 cm^{-1} was related to the vibrational elongation of the bond C-H.

The bands in 1635 and 1420 cm^{-1} were related to the vibrational elongation of the carbonyl groups connection (C=O) and to the presence of carboxylic groups in lignin and hemicellulose. The band at 1258 cm^{-1} is related to the harmonic vibration of the stretch C-O of carboxylic acids and alcohols. The spectrum obtained for the adsorbent particles of orange bagasse was similar to the literature. Bhattacharjee & Biswas (2019) described bands in 3317, 2936, 1711, 1609, 1514, 1458, 1357, 1217 and 1114 cm^{-1}, upon characterizing the orange bagasse used as raw material in the pyrolysis reactor. Safari et al., (2019) upon characterizing nanoparticles synthesized from orange peels, obtained bands in 690, 1070, 1650, 2950 and 3450 cm^{-1}. Guiza (2017) observed the presence of hydroxyls, carbonyls, and amines in orange peels (CWOP). Therefore, the presence of these functional groups on the orange bagasse surface demonstrates the ease of intermolecular interactions with methomyl, once the pesticide chemical structure favors the hydrogen bonds formation with the adsorbent due to the presence of hydrogen acid and basic groups.

3.2 Adsorption kinetics

The curves of the experimental analyzes and adjusted models of pseudo-first order, pseudo-second order and Elovich are presented in Figure 3.

Figure 3 shows that the rapid adsorption in the initial stages, from 0 to 60 minutes, occurred due to the large number of active sites available on the adsorbent surface, allowing many species of adsorbate to be physically adsorbed within a short time interval (physisorption). Over time, after 60 minutes, depending on the availability of active sites free decreased, the chemical bonds between adsorbent and adsorbate began to control the process (chemisorption), until it reached the balance (Inyang et al., 2015; Yan et al., 2015). Thus, it was observed that the process may have occurred through these two main steps to control the balance in 480 minutes. This hypothesis is corroborated by the adjustment of models of pseudo-first and pseudo-second order presented in Table 1, which also shows the values of the kinetic parameters, the constant k_1 being the rate of adsorption of pseudo-first order (min^{-1}), k_2 the constant rate of adsorption of pseudo-second order (g.mg^{-1}min^{-1}) and β the constant of Elovich (mg.g^{-1}).

From the kinetic parameters, it was observed that the model of pseudo-second order is better adjusted to the experimental data showing the greatest value of R^2 (0.999) compared to Elovich models ($R^2 = 0.949$) and pseudo-first order ($R^2 = 0.917$), indicating that the methomyl adsorption rate in orange bagasse was controlled predominantly by the chemisorption step (Feng et al., 2015; Ahmed et al., 2016; Jia et al., 2017; Danish & Ahmad, 2018). The satisfactory adjustment of the model of pseudo-first order ($R^2 = 0.917$) also indicated the occurrence and the importance of the physisorption for the process (Yan et al., 2002; Kolodynska et al., 2012).

El-Geundi et al. (2013) investigated the adsorption of methomyl solutions at 43.7 and 125.1 mg.L^{-1}, on activated carbon originated from cotton stalks (Cotton Stalk Activated Carbon - CSAC). The researchers reported that the methomyl removal was fast in its early stages and decreased gradually with the contact time, reaching the balance in 150 minutes at 25 °C, for both concentrations, with maximum of 87.9% for the highest concentration. El-Geundi et al. (2012) also reported the methomyl adsorption in particles of carbonized natural clay at the same balance time.

The methomyl adsorption was also evaluated in activated charcoal in a fixed bed reactor (HGRPB) with balance after 420 minutes (Chang & Lee, 2012), and in marine sediments after 600h of reaction (Yang et al., 2005), at 25 °C, in a quite specific two-step process, with a fast adsorption up to 300 minutes, followed by a slow process until the balance. The stage of internal diffusion was responsible for the control of the mass transport mechanism.

3.3 Adsorption isotherms

The curve of the adsorbed quantities was built (q) as a function of the equilibrium concentration (EC) and adjusted the Langmuir and Freundlich models to the experimental data, obtaining the parameters of the equations of each model.

3.3.1 The Langmuir isotherm model

The adjustment of the model to the experimental data is given by the magnitude of the correlation coefficient for the regression and is much closer to the unit according to the best adjustment of the model. The Langmuir equation is considered important for both theories of physical adsorption, as well as for the theories of chemical adsorption. In general, efficient adsorbents have high values of q_{max} and K_L (Chakraborty et al., 2011; Dada et al., 2012).

3.3.2 The Freundlich isotherm model

In general, a favorable adsorption presents n (Freundlich constant) between 1 and 10 (Hameed et al., 2009). The greater its value (less than 1/n), the stronger will be the interaction between the adsorbate and the adsorbent. On the other hand, when 1/n is equal to 1, it indicates that the adsorption is linear, i.e. the energies are identical for all the adsorption sites. When 1/n is greater than the unit, the adsorbent has greater affinity for the solvent, suggesting that there is a strong intermolecular attraction between both of them (Kumar & Gaur, 2011). Thus, the kinetic parameters obtained by the Freundlich model, allow concluding that the adsorption was favorable, because the value of n (3.3852) is between 1 and 10. The parameters calculated from the adjustment by linear regression of the equations of the Langmuir and Freundlich models to the experimental data are presented in Table 2.

According to Table 2, the Langmuir model showed the best fit ($R^2 = 0.989$), confirming the adsorption hypothesis in monolayer and without interaction among the methomyl molecules. This result agrees with the result obtained by El-Geundi et al. (2013), as the researchers also affirmed that the Langmuir model was better adjusted to the experimental data of the methomyl adsorption in activated charcoal from cotton stalks. Considering the Langmuir model, the values of the parameters q_{max} and K_L, obtained by linear regression, were 10.776 and $6.19.10^{-3}$, respectively.

Figure 4 allowed viewing the adjustments of the Langmuir and Freundlich models to

the experimental points. Among the concentrations from 200 to 600 mg.L^{-1} the q value increased at a constant rate apparently. After 600 mg.L^{-1}, the adsorbent saturation was reached.

3.4 Influence of pH and solid/liquid ratio (R) on the adsorption capacity

The effects of the independent variables pH and R were evaluated (solid-liquid ratio) on the adsorption methomyl capacity in orange bagasse [q (mg*g^{-1}), dependent variable]. The obtained data were treated by multiple regressions for the construction of a mathematical model and then visualized on a surface response. The results of the 12 assays carried out in accordance with the DCCR 2^2, with four axial points and four repetitions of the central point, are presented in Table 3.

Table 3 shows that the best responses were obtained in experiments 2 and 8, with the adsorption capacity of 3.426 and 3.733 mg*g^{-1}, respectively. In these experiments, the R values were high, 0.015 and 0.017, at pHs 4.5 and 6.0, respectively. Thus, it was noted the trend of better answers to larger values of R in more acidic pH. The comparison of the assays 1 and 3, at pH 7.5, with different levels of R, shows that the best answer (q = 2.028 mg*g^{-1}) was obtained for the lowest R-value (0.005). However, in the assays 2 and 4, at pH 4.5, the highest adsorption capacity (q = 3.426 mg*g^{-1}) was obtained for the lowest R-value (0.015). Thus, a strong interaction was observed between the parameters pH and R, but with opposite behaviors in acidic or basic solutions. This evidence was also proven by experiment 5, which presented the second lowest answer (q = 0.369 mg*g^{-1}), even at low pH, with R values at zero level (0.010 g*mL $^{-1}$). The repetition assays in central points 9 to 12, presented adsorption capacities very close, proving the repeatability of experiments.

The analysis of variance (ANOVA) and the coefficients obtained for the mathematical model from multiple regression are presented in Table 4.

ANOVA was performed with a confidence interval of 95%. Therefore, the effects for P greater than 0.05 (5%) were not considered significant, i.e. only the effect of the term "pH" of first degree was considered statistically not significant for the methomyl adsorption process in orange bagasse.

The main effects were related to the interaction pH*R and the term R, whose coefficients were -1.003 and +0.8103, respectively, as the highest coefficients were related to the influence factors on the adsorption. The experimental data showed good fit to the regression model (R^2 = 0.938). Thus, the Equation (7) was used in the surface response

construction, as shown by Figure 5.

$$q(pH, R) = 1{,}249 + 0{,}810 \cdot (R) - 1{,}003 \cdot (pH \cdot R) - 0{,}295 \cdot (pH^2) + 0{,}639 \cdot (R^2) \quad (7)$$

The application of central composite design (DCCR rotational 2x2) to evaluate the methomyl adsorption process, with the parameters pH and R (ratio of adsorbent mass/volume of adsorbate) resulted in a surface response (Figure 8) with two regions of better answers of adsorption capacity (q), indicating a strong interaction between the parameters pH and R. The best responses were obtained for low pH and high R, or high pH and low R, and in the region assessed the best answer (q = 3.733 mg.g^{-1}) was obtained for low pH (6.0) and high R (0.017 g.mL^{-1}). In the region of high pH, it was observed the release of organic matter in the solution, negatively affecting the adsorption. Therefore, it was concluded that there was a greater efficiency of methomyl adsorption in acidic high R, that is, with larger quantities of adsorbent particles of orange bagasse.

Yang et al., (2005) reported that the methomyl adsorption in marine sediments decreased with the increase in pH. The authors stated that the increase in pH may have caused greater release of organic matter of the sediments in the solution, negatively affecting the pesticide adsorption. The release of organic acids may have negatively affected the methomyl adsorption in orange bagasse in assays with greater mass of adsorbent and basic pHs. Consequently, smaller quantities of biomass may have resulted in lower release of organic acids, resulting in greater methomyl adsorption capacity.

Gupta et al., (2006) stated that the alterations of the solution pH can also change the pesticides molecule properties and, consequently, its adsorption. Rengaraj et al., (2002) stated that pH affects the sorbent surface properties. In very low pHs, the sorbent surface would be surrounded by hydronium ions, which could increase the interaction of sorbate with the binding sites of the sorbent by forces of attraction and, therefore, improve its adsorption capacity.

The best results of methomyl adsorption in orange bagasse for solutions with lower pH values seem to confirm the effect of hydronium ions over the attraction forces among the pesticide molecules and the biomass. Thus, it was concluded that the methomyl adsorption in orange bagasse must be carried out in solutions with acid pH in order to obtain greater interaction forces between the molecules of the sorbate and the adsorbent, in addition to avoiding the release of organic material in the solution. Therefore, the experimental conditions with high R in acid pH were considered the best for the methomyl adsorption in

orange bagasse.

4. Conclusions

The studies of the methomyl adsorption kinetics in the biomass of orange bagasse demonstrated that the model of pseudo-second order is better adjusted to the experimental data, suggesting the predominance of chemisorption as a controlling step of the process. The Langmuir isotherm model adjusted better to the experimental data, confirming the adsorption in monolayers, without interaction among the adsorbate molecules. The evaluation of the Freundlich isotherm model indicated that the adsorption was favorable, because the parameter n was >1.

The adsorbent particles produced from orange bagasse did not have many pores and internal cavities, resulting in the predominance of active superficial sites, as seen in the images obtained by SEM. The infrared spectroscopy with Fourier Transform (FTIR) allowed observing that the main organic functions present on the adsorbent particles surfaces of orange bagasse were the carbonyl, carboxylic and hydroxylic groups, highlighting the ease to form intermolecular interactions with the pesticide.

The best responses were obtained for low pH and high R, or high pH and low R, and in the region assessed, the best answer with a value of $q = 3.733$ mg.g^{-1} was obtained for low pH (6.0) and high R (0.017 g.mL^{-1}), suggesting that the biosorbent proved to be a good alternative for removing the pollutant from effluents contaminated with the methomyl pesticide.

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