Carbohydrate Polymers 101 (2014) 954–960

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Removal of pigments from aqueous solution by a calcium alginate–grape marc biopolymer: A kinetic study

M. Perez-Ameneiro, X. Vecino, L. Barbosa-Pereira, J.M. Cruz, A.B. Moldes*

Chemical Engineering Department, University of Vigo, School of Industrial Engineering (EEI), Campus As Lagoas, Marcosende, 36310 Vigo, Pontevedra, Spain

ARTICLE INFO

Article history:
Received 7 August 2013
Received in revised form
18 September 2013
Accepted 24 September 2013
Available online 4 October 2013

Keywords:
Grape marc
Adsorption
Biopolymer
Kinetics
Dyes

ABSTRACT

In this work, the potential use of a biopolymer based on grape marc entrapped in calcium alginate beads for the removal of pigments from an agro industrial effluent was evaluated. The parameters that affect the pigment adsorption such as pH (3.5–7.0), temperature (10–40 °C) and initial pigment concentration (6.9–55.1 mg/L) were studied by applying an incomplete factorial design. The dependent variables evaluated consisted of color effluent parameters from CIELAB and Tristimulus system, as well as the concentration of pigments in the wastewater after the adsorption treatment. The most significant independent variables tested were the pigments concentration followed by pH, whereas temperature had a negligible effect on the adsorption process. Moreover, at the optimal operational conditions (pH 3.5 and room temperature) kinetic studies were carried out by applying pseudo-first order, pseudo-second order, Chien–Clayton and intraparticle diffusion models, observing a good agreement between theoretical and experimental results.

1. Introduction

Adsorption technologies using activated carbon are widely used to remove certain types of contaminants, like dye compounds and pigments, from different agro industrial wastewaters (Sanghi & Verma, 2013). However, the use of activated carbon possesses both economic and environmental limitations, mainly associated with its high cost and the absence of ecofriendly technologies for its activation. Thus, activated carbon can be obtained by thermal activation, usually using temperatures higher than 600 °C, depending on whether the thermal activation is carried out in presence or absence of O_2. Moreover, carbon can be subjected to a chemical activation in order to reduce the operation time needed for activation.

Therefore, it is necessary to make efforts in order to explore the possibility of using ecofriendly and low-cost alternatives to obtain biodegradable, abundant and readily available biopolymers that can be used as adsorbents for the treatment of contaminated waters. From this point of view many carbonaceous materials such as corn cobs, globe artichoke leaves, marine algae, coconut coir, bamboo waste, orange peel, rice husk and peanut shell and spent tea leaves (Sanghi & Verma, 2013) were proposed in the literature for the production of commercial activated carbons; although, in most of the cases, they also have been submitted to different activation processes involving high temperatures or the utilization of alkalis or acids.

On the other hand, some authors have proposed the utilization of agricultural residues as green adsorbents, without any activation, such as barley husk, wheat husk, coffee husk, rice husk, rice straw, rice hull, cotton seed hull, pumpkin seed hull, palm ash, wheat shells, wheat straw, sugar cane dust, broad bean peels, spent corn cob, peanut hull, hazelnut shell, pine fruit shells, fruit seed, pine sawdust or grass waste (Sanghi & Verma, 2013), or also grape marc (Paradelo, Moldes, & Barral, 2009) and peat (Vecino, Devesa-Rey, Cruz, & Moldes, 2013). In comparison to activated carbon, these kinds of polymeric adsorbents, due to their low cost, can be disposed of after their utilization without an expensive regeneration, but their adsorption capacities are lower than those carbonaceous materials that have been subjected to an activation process.

Recently, the immobilization of activated carbon in calcium alginate beads has received great attention, because the use of such techniques in wastewater treatment offers a promising way of improving the efficiency of the adsorption process, especially in solving the problems associated with solid–liquid separation in settling tanks (Annadurai, Juang, & Lee, 2002; Devesa-Rey, Bustos, Cruz, & Moldes, 2011; Vecino, Devesa-Rey, Moldes, & Cruz, 2012; Kumar, Tamilarasan, & Sivakumar, 2013). Thus, Vecino et al. (2013) have demonstrated that entrapped peat in calcium alginate beads is a useful adsorbent for the elimination of pigments from water. The most significant tested variables in the formulation of entrapped

* Corresponding author. Tel.: +34 986812215; fax: +34 986812201.
E-mail addresses: mp.ameneiro@uvigo.es (M. Perez-Ameneiro), xanel.vecino@uvigo.es (X. Vecino), letriciapereira@uvigo.es (L. Barbosa-Pereira), jmcruz@uvigo.es (J.M. Cruz), amoldes@uvigo.es (A.B. Moldes).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.09.091

peat for the elimination of colored compounds from vinasses were the concentration of peat and the concentration of calcium chloride, whereas the sodium alginate concentration, in most of the dependent variables assayed, did not have a significant effect; but the commercialization of peat as plant growth media can prevent its utilization in the formulation of polymeric adsorbents.

On the contrary, grape marc is a waste product from winery industry that is available in abundance, with a great potential as inexpensive adsorbent. Hence, in previous works we have demonstrated that grape marc compost was able to remove 78.5% of colored compounds from wastewater (Paradelo et al., 2009). Grape marc is a polymer composed by cellulose, hemicellulose and lignin and during composting the cellulosic and hemicellulosic fraction is partially mineralized given a more stable product as a result.

Consequently, renewable raw materials based on agricultural residues, like grape marc, could be interesting substrates to formulate new ecofriendly adsorbents.

Thus, this work deals with the utilization of grape marc that underwent a biological activation, through composting, in order to obtain a biopolymeric adsorbent. Following, in order to increase the adsorption capacity of the adsorbent, this was encapsulated in calcium alginate beads. The influence of pH, temperature and pigment concentration on adsorption capacity of calcium alginate–grape marc biopolymer was studied. Moreover, at the optimal operational conditions, the dynamics of adsorption by using pseudo-first order, pseudo-second order rate equations, Chien–Clayton and intraparticle diffusion models were studied.

2. Materials and methods

2.1. Grape marc

Grape marc was obtained from local winery industries and subjected to a spontaneous biodegradation of the organic matter for a period of 3 months in vessels 29 cm in diameter and 24 cm high, following the protocol carried out in previous works (Moldes, Vázquez, Domínguez, Díaz-Fierros, & Barral, 2007).

2.2. Analytical methods for grape marc characterization

For all analyses, fresh grape marc samples were sieved to <20 mm and homogenized. The samples were air-dried and milled prior to carbon, and nitrogen analysis. The analyses of the main fractions (cellulose, hemicelluloses and Klason lignin) of raw grape marc and biodegraded grape marc, were carried out by performing a quantitative acid hydrolysis in two-stages, acid treatment (the first step with 72% sulfuric acid at 30 °C during 1 h, and the second one after dilution of the media to 3% sulfuric acid at 121 °C during 1 h, according to Vázquez, Lage, Parajó, & Vázquez,1992). The solid residue after hydrolysis was considered as Klason lignin and the liquid phase was analyzed by HPLC using an Interaction ION-300 column (mobile phase, H_2SO_4 0.01 M; flow rate, 0.4 mL/min; IR and UV detection). This method allowed the direct determination of glucose and xylose in the hydrolyzates that were converted to percentage of cellulose and hemicellulose in grape marc.

2.3. Vinasses

Vinasses were collected from local winery industries and kept at 4 °C for a month, until use.

2.4. Biopolymer formulation

The biopolymer composition was established on the basis of the protocol followed in previous works for other carbonaceous polymers like activated carbon or peat (Devesa-Rey et al., 2011; Vecino et al., 2012, 2013). Thus, the biopolymer evaluated in the current work was formulated using 2% of biodegraded grape marc, 2% of sodium alginate and calcium chloride 0.58 mol/L. Before adsorption experiments, the biopolymer was washed several times with distilled water at 60 °C for 25–30 min in order to remove excess $CaCl_2$.

Table 1
Independent and dependent variables used in the study.

(a) Independent variables

Variable	Nomenclature	Units	Range of variation
Pigment concentration	C_0	mg/L	6.9–55.1
Temperature	T^a	°C	10–40
pH	pH	–	3.5–7.0

(b) Dimensionless coded independent variables

Variable	Nomenclature	Definition	Range of variation
Dimensionless concentration	x_1	$(C_0 - 31.0)/24.1$	(−1,1)
Dimensionless temperature	x_2	$(T^a - 25)/15$	(−1,1)
Dimensionless pH	x_3	(pH – 5.25)/1.75	(−1,1)

(c) Dependent variables

Variable	Nomenclature	Units
Lightness (L^*)	y_1	–
x	y_2	–
y	y_3	–
C equivalent (C_{equiv})	y_4	mg/L

2.5. Morphological characterization of calcium alginate–grape marc biopolymer

The biopolymer was washed with sodium cacodylate 0.1 mol/L buffer and fixed with 2.5% of glutaraldehyde in cacodylate 0.1 mol/L buffer during 2–4 h at 4 °C. Following, the samples of biopolymer were introduced in 1% OsO_4 in cacodylate 0.1 mol/L buffer during 1 h at 4 °C. Dehydration was carried out with ethanol using a different graded series (30% – 15 min; 50% – 2× 15 min; 70% – 2× 15 min; 80% – 2× 15 min; 90% – 2× 15 min; 100% – 3× 15 m min) and amylacetate:ethanol in an ordered series (1:3 – 2× 15 min; 2:2 – 2× 15 min; 3:1 – 2× 15 min; amylacetate 100% – 3× 15 m min) in order to replace the ethanol for a phase miscible with liquid CO_2. The samples were then dried at the chamber critical point, cut with liquid N_2, covered with gold and observed using a scanning electron microscope (SEM).

The biodegraded grape marc powder undergoes no dehydration process. The powder was covered with gold and observed by SEM.

2.6. Adsorption studies

Adsorption experiments were carried out in 250 mL Erlenmeyer flasks, under different operational conditions following Box–Behnken (1960) factorial design (see Table 1). The independent variables studied consisted of T^a, pH and pigment concentration, whereas the evaluated dependent variables consisted of the color measurements by using CIELAB and Tristimulus system (Vecino et al., 2012), as well as the concentration of pigments at the equilibrium as equivalents of amaranth dye.

The experimental data obtained were analyzed by the Response Surface Method with Statistic 7.0 software (Version 5.1 Statistica for Windows; StatSoft, Inc., USA), which is a useful tool to study the synergic effect of independent variables over the selected dependent variables (Bezerra, Santelli, Oliveira, Villar, & Escaleira, 2008). Table 1 shows the range of independent variables studied as well as

their standardized (coded) dimensionless values. Coded variables were then assigned values of −1, 0 and +1, corresponding to the lowest, central and maximum limits of variation for each variable. The response surface graphic obtained from the coded variables is, therefore, not influenced by the magnitude of each variable, which allows combination of the factors on a dimensionless scale.

In addition, at the optimal operational conditions predicted by the model, a kinetic study was carried out and the experimental data obtained were adjusted to four kinetic models: pseudo-first order (Lagergren, 1898), pseudo-second order (Ho & McKay, 1999), Chien–Clayton (Chien & Clayton, 1980) and intraparticle diffusion (Weber & Morris, 1962). This kinetic study was developed using different initial concentrations of pigments (24.7 mg/L; 16.5 mg/L; 11.3 mg/L and 8.8 mg/L) obtained by dilution of the raw vinasse. The amount of pigment in the effluent was calculated as equivalents of amaranth dye, which gives similar color parameters and absorbance values than the vinasses used in this work.

2.7. Color measurement of aqueous effluent

Color of vinasses was evaluated in a double beam spectrophotometer (Jasco V-650). Color measurements were analyzed by considering the CIE 1976 (L^*, a^*, b^*) or CIELAB color system, which is widely accepted by both the scientific community and industry, since it is the most 'perceptually uniform' of the color spaces (Berns, 2000; Völz, 2001). Moreover, color measurements were carried out using Tristimulus system. A convenient way of visually representing Tristimulus values is the use of chromaticity co-ordinates, which maps all colors into a two-dimensional space, called CIE chromaticity diagram. This space has two axes x and y. The CIE chromaticity diagram provides a color map on which the chromaticities of all colors are plotted. Analyses of samples were carried out with filtration through a membrane of 0.45 μm pore size before analysis.

2.8. Analysis of pigment concentration

Vinasses are composed by a mixture of pigments that have a peak of absorbance at the same wavelength (520 nm) than commercial amaranth dye. Thus, the amount of pigments in vinasses was measured as equivalents of amaranth dye. Eq. (1) shows the relationship between the absorbance at 520 nm and the concentration of dye amaranth.

$$C_i = 23.6327 \times Abs_{520,i} - 0.0889 \quad (1)$$

Eq. (1) was used to convert the absorbance at 520 nm of samples into pigment concentration, as equivalents of amaranth dye.

3. Results and discussion

3.1. Characterization of calcium alginate–grape marc biopolymer

3.1.1. Chemical composition

Grape marc obtained from winery industry was composed of 18.5% of cellulose, 56.4% of lignin and 8.2% of hemicelulloses. After composting, the polymeric fraction of grape marc reduced the hemicellulosic and cellulosic polymers up to 9.5% and 2.8%, respectively, and increased the amount of lignin to 65.6%. Elemental analysis showed that biodegraded grape marc was composed by 3.9% N, 42.7% C and 5.5% H. The C/N ratio of grape marc decreased from 24.0 to 10.9 after the spontaneous biodegradation, indicating that grape marc was biodegraded giving a more stable product. The biodegradation of grape marc was carried out spontaneously, during 3 months. During this time no changes in temperature were observed in the reactors. This fact can be attributed to the high concentration of complex polymeric sugars in grape marc that are slowly degraded by the microorganisms (Moldes et al., 2007). After 3 months of biodegradation it was obtained a stable biopolymer, which was encapsulated in calcium alginate beads in order to increase its adsorption capacity. In addition, the encapsulation of grape marc gave a more manageable adsorbent that can be easily separated from the settling tanks, once the adsorption process is finalized, which represents an important advantage in comparison to other non-immobilized adsorbents.

3.1.2. SEM studies

The SEM images of the biodegraded grape marc powder and the calcium alginate–grape marc biopolymer are shown in Fig. 1.

Figs. 1a–c show the external morphology of biodegraded grape marc powder at different magnifications; ×160, ×700 and ×1000, respectively.

Figs. 1d–f show the external morphology of calcium alginate–grape marc biopolymer at different magnifications; ×30, ×250, ×1000, respectively; whereas Figs. 1g–i show the internal composition of the biopolymer, in a cross section, at the same magnifications. It can be observed that this is a heterogeneous biopolymer.

3.2. Adsorption studies

3.2.1. Optimization of operational conditions

Adsorption parameters such as pH, temperature and pigment concentration are important in the adsorption process as they affect the pigment adsorption capacity of the adsorbent. Thus, in this work a biopolymer composed by biodegraded grape marc and calcium alginate was submitted to different operational conditions. The dependent variables consisted of color parameters: $L^*(y_1)$, $x(y_2)$, $y(y_3)$ and $C_{equiv}(y_4)$; whereas the independent variables studied were pH, temperature and pigment concentration. The ranges of variation for the independent variables are included in Table 1.

It is important to point out that winery effluents are composed of different types of colored compounds. Thus, different absorbance measurements should be taken into account in order to measure the decrease in colored compounds concentration. Therefore, it can be considered that the utilization of CIELAB and Tristimulus system could help to quantify the elimination of dyes and pigments from wastewater.

Table 2 shows the set of adsorption experiments carried under different operational conditions, as well as the experimental results achieved for variables y_1 to y_4 after treatment. Thus, after the statistical treatment of data, a quadratic function can be obtained for all the dependent variables studied (Eq. (2)).

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 \quad (2)$$

where y is the dependent variable, β denotes the regression coefficients (calculated from experimental data by multiple regressions using the least-squares method) and x denotes the independent variables.

Moreover, Table 2 shows the values of the dependent variables tested in vinasses before being treated with the biopolymer, for the maximum (raw vinasse 1), central (raw vinasse 2) and lower concentration of pigments (raw vinasse 3).

The coefficients and the significance of each coefficient (p-values) for the variables y_1 to y_4, corresponding to the dependent variables tested, are shown in Table 3. Replacing these coefficients in Eq. (2), different equations can be created in order to determine the values of the dependent variables studied, within the ranges tested. Thus, simpler equations could be obtained by including in the equations only those coefficients whose combination of independent variables gave $p < 0.05$.

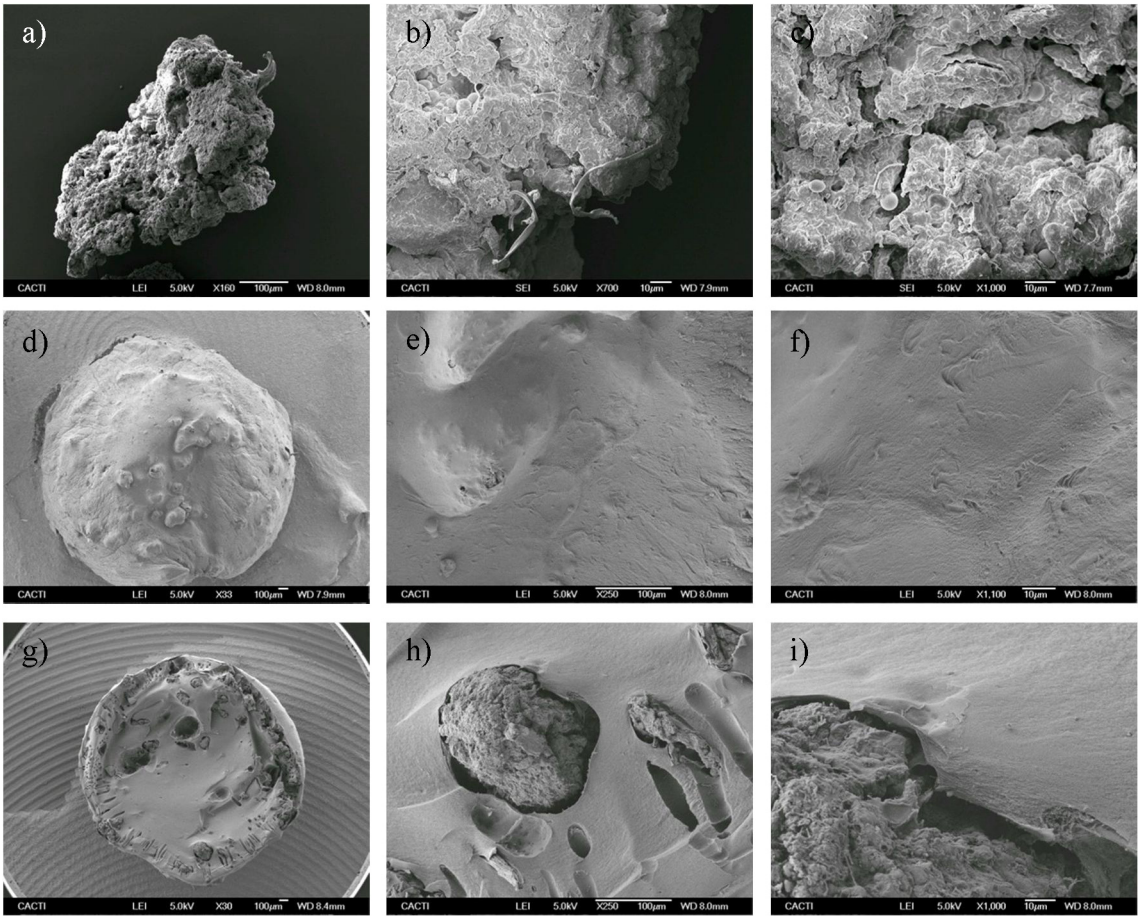

Fig. 1. SEM micrographs of calcium alginate–grape marc biopolymer.

For all the dependent variables studied in the ranges tested, the most important independent variable was the concentration of pigment, followed by the pH and the temperature. Fig. 2 shows maximum L^* values predicted by the model of 99.7, 90.7 and 82.6 after treatment with calcium alginate–grape marc biopolymer for the minimum (Fig. 2a), medium (Fig. 2b) and maximum (Fig. 2c) concentration of colored compounds in vinasses, respectively. The CIELAB color system is organized with three axes in a spherical form: L^*, a^*, and b^*. The L^* axis is associated with the lightness of the color and moves from top (value 100, white) to bottom (value 0, black); whereas the a^* and b^* axes are associated with changes in redness–greenness and in yellowness–blueness; both move in the axes that form a plane orthogonal to L^*, and do not have specific numerical limits. In this work, only L^* values of the CIELAB system were included because they are the most representative of the elimination of pigment compounds form the aqueous phase. L^*

Table 2
Operational conditions considered in this study (expressed in terms of the coded independent variables) and experimental results achieved for the dependent variables y_1 to y_4.

Exp.	Independent variables			Dependent variables			
	x_1	x_2	x_3	y_1	y_2	y_3	y_4
1	0	−1	−1	86.12	0.346	0.345	5.0
2	0	1	−1	89.27	0.346	0.354	3.9
3	0	−1	1	82.55	0.373	0.373	7.0
4	0	1	1	86.36	0.364	0.370	5.4
5	−1	−1	0	95.36	0.324	0.340	1.5
6	−1	1	0	96.08	0.330	0.347	1.4
7	1	−1	0	68.60	0.391	0.367	12.4
8	1	1	0	75.10	0.386	0.373	9.7
9	−1	0	−1	97.30	0.322	0.340	0.9
10	−1	0	1	95.33	0.330	0.346	1.6
11	1	0	−1	78.74	0.370	0.353	8.2
12	1	0	1	72.11	0.420	0.395	12.4
13	0	0	0	82.71	0.356	0.359	6.3
14	0	0	0	82.57	0.358	0.361	6.4
15	0	0	0	82.85	0.354	0.358	6.2
Raw vinasse 1	1	–	–	25.61	0.660	0.320	55.1
Raw vinasse 2	0	–	–	44.13	0.543	0.348	31.0
Raw vinasse 3	−1	–	–	83.37	0.359	0.341	6.9

Table 3
Regression coefficients and their statistical significance for variables y_1 to y_4.

	y_1	p_{y1}	y_2	p_{y2}	y_3	p_{y3}	y_4	p_{y4}
b_0	82.710000	0.000001*	0.356000	0.000011*	0.359333	0.000006*	6.274064	0.000113*
b_1	−11.190000	0.000020*	0.032625	0.000469*	0.014375	0.001408*	4.656832	0.000077*
b_{11}	0.435000	0.026925*	0.002500	0.138273	−0.002292	0.102213	0.210138	0.072795
b_2	1.772500	0.000779*	−0.001000	0.292893	0.002375	0.048015*	−0.691429	0.003460*
b_{22}	0.640000	0.012713*	−0.000750	0.546010	−0.000292	0.748876	−0.241250	0.056692
b_3	−1.885000	0.000689*	0.012875	0.003003*	0.011500	0.002198*	1.058558	0.001481*
b_{33}	2.725000	0.000714*	0.002000	0.194613	0.001458	0.208015	−0.725943	0.006767*
b_{12}	1.445000	0.002338*	−0.002750	0.110703	−0.000250	0.774506	−0.657958	0.007595*
b_{13}	−1.165000	0.003591*	0.010500	0.008949*	0.009000	0.007125*	0.860146	0.004465*
b_{23}	0.165000	0.142495	−0.002250	0.153351	−0.003000	0.059125	−0.119617	0.173774

* Significant coefficients, $p < 0.05$.

values around 100 mean that the effluent has a white color and all the dye compounds were removed from the water (Vecino et al., 2012).

On the other hand, a convenient way of visually representing Tristimulus values could be the use of chromaticity co-ordinates, which maps all colors into a two-dimensional space, called CIE chromaticity diagram. This space has two axes x and y. The CIE chromaticity diagram provides a color map on which the chromaticities of all colors are plotted (Vecino et al., 2012). From Table 2, it can be observed that x gave values from 0.32 to 0.42, whereas y gave values between 0.34 and 0.40. Thus, in the range tested, the adsorption treatment produced values for x and y in the white color regions on CIE chromaticity diagram, under all the evaluated experimental conditions. From this data, it can be concluded that the utilization of CIE chromaticity diagram is not adequate to evaluate the elimination of pigments from wastewater; whereas the results obtained by using the CIELAB system (variable y_1) are in concordance with the results obtained by measuring the concentration of pigments in water as equivalents of amaranth dye (variable y_4). Thus, Figs. 2d–f show maximum C_{equiv} after treatment with calcium alginate–grape marc biopolymer for the minimum, medium and maximum concentration of colored compounds in vinasses, respectively.

It can be observed that those conditions that produced L^* values around 100, which corresponds to white color, gave also lower concentrations of pigments in water after treatment. In addition, in Table 3 it can be observed a high concordance between the number of significant coefficients for variables y_1 and y_4.

Regarding the concordance between experimental results and the data predicted by the model, the coefficient of determination, R^2, yielded values from 0.98 to 0.99 for all the dependent variables studied. The theoretical data, in the range tested, can be calculated by replacing the coefficients of Table 3 in Eq. (2), observing a good agreement between experimental results and the data predicted by the model.

The results obtained in this work are in concordance with those reported by other authors. Thus, Paradelo et al. (2009) suggested that during the grape marc biodegradation, the concentration of humic and fulvic substances increases, which can improve the adsorbent properties of biodegraded grape marc. In addition, Arvanitoyannis, Ladas, & Mavromatis (2006) indicated that winery wastes are good adsorbents of metals, mainly due to

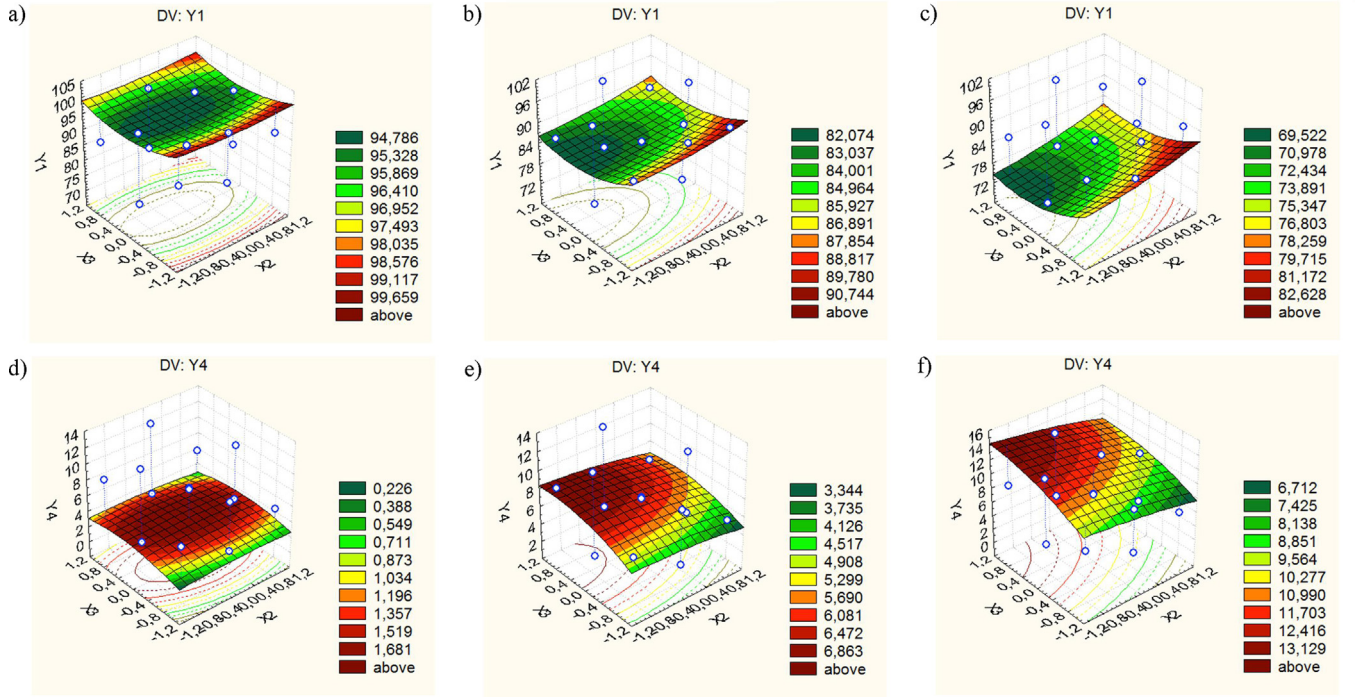

Fig. 2. Surface response variation in $L^*(y_1)$ and $C_{equiv}(y_4)$ with the temperature and the pH, for the minimum, medium and maximum concentration of pigments in vinasses, respectively.

Table 4
Comparison of kinetic parameters for pseudo-first order, pseudo-second order, Chien–Clayton and intraparticle diffusion kinetic models.

C_0	Pseudo-1st order kinetic model				Pseudo-2nd order kinetic model				Chien–Clayton kinetic model			Intraparticle diffusion model		
(mg/L)	K_1 (L/g min)	q_e exp (mg/g)	q_e calc (mg/g)	R^2	K_2 (L/g min)	q_e exp (mg/g)	q_e calc (mg/g)	R^2	α (mg/g min)	β (g/mg)	R^2	K_P (mg/g min$^{0.5}$)	C	R^2
24.7	0.044	0.76	0.35	0.99327	0.421	0.76	0.76	0.99616	4.99	11.19	0.96996	0.068	0.325	0.99216
16.5	0.039	0.53	0.22	0.97462	0.730	0.53	0.52	0.99746	5.21	17.10	0.98803	0.044	0.241	0.98719
11.3	0.034	0.36	0.13	0.93491	1.337	0.36	0.35	0.99860	6.57	27.17	0.98069	0.030	0.172	0.98765
8.8	0.046	0.28	0.10	0.98164	1.667	0.28	0.28	0.99851	6.66	34.44	0.99076	0.024	0.143	0.98862

their proteins, carbohydrates and phenolic compounds that have carboxyl, hydroxyl, sulfate, phosphate and amino groups that can bind metal ions, although the grape marc used in this work was not immobilized.

3.2.2. Kinetic studies

The optimal operational conditions for removing pigment compounds from vinasses using calcium alginate–grape marc biopolymer were determined. Following, batch adsorption experiments were conducted at 25 °C and pH 3.5, in order to develop kinetic studies.

Pseudo-first order, pseudo-second order, Elovich equation modified by Chien and Clayton (1980), and intraparticle diffusion models were considered to investigate the adsorption process of pigments onto the calcium alginate–grape marc biopolymer.

Eq. (3) shows the linear form of the pseudo-first order model (Lagergren, 1898), where q_e (mg pigments/g adsorbent) and q_t (mg pigments/g adsorbent) are the amount of adsorbed pigments at equilibrium and at a defined time t (min), respectively, and K_1 (1/min) is the rate constant of pseudo-first order adsorption.

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \tag{3}$$

Moreover, sorption kinetics may be described by a pseudo-second order model following Eq. (4) (Ho & McKay, 1999), where K_2 (g/mg min) is the equilibrium rate constant of pseudo-second order adsorption. Eq. (4) does not have the problem of assigning an effective q_e. If the pseudo-second order kinetic equation is applicable, the plot of t/q_t against t should give a linear relationship, from which q_e and K_2 can be determined from the slope and intercept of the plot, and there is no need to know any parameter beforehand.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \tag{4}$$

Adsorption kinetics can also be adjusted to the Elovich equation (Elovich and Larionov, 1962a, 1962b). Notwithstanding this model was initially applied to adsorption kinetics of gases on solids, there are also examples for the removal of solutes from liquid solutions (Atkinson, Hingston, Posner, & Quirk, 1970) (Eq. (5)).

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{5}$$

Chien and Clayton (1980) proposed the simplification of Eq. (5) by assuming $\alpha\beta t \gg 1$, and considering the boundary conditions $q_t = 0$ for $t = 0$ and $q_t = q_t$ at $t = t$. In the Chien–Clayton expression (Eq. (6)), α (min mg/g) is the initial sorption rate, and β (g/mg) is

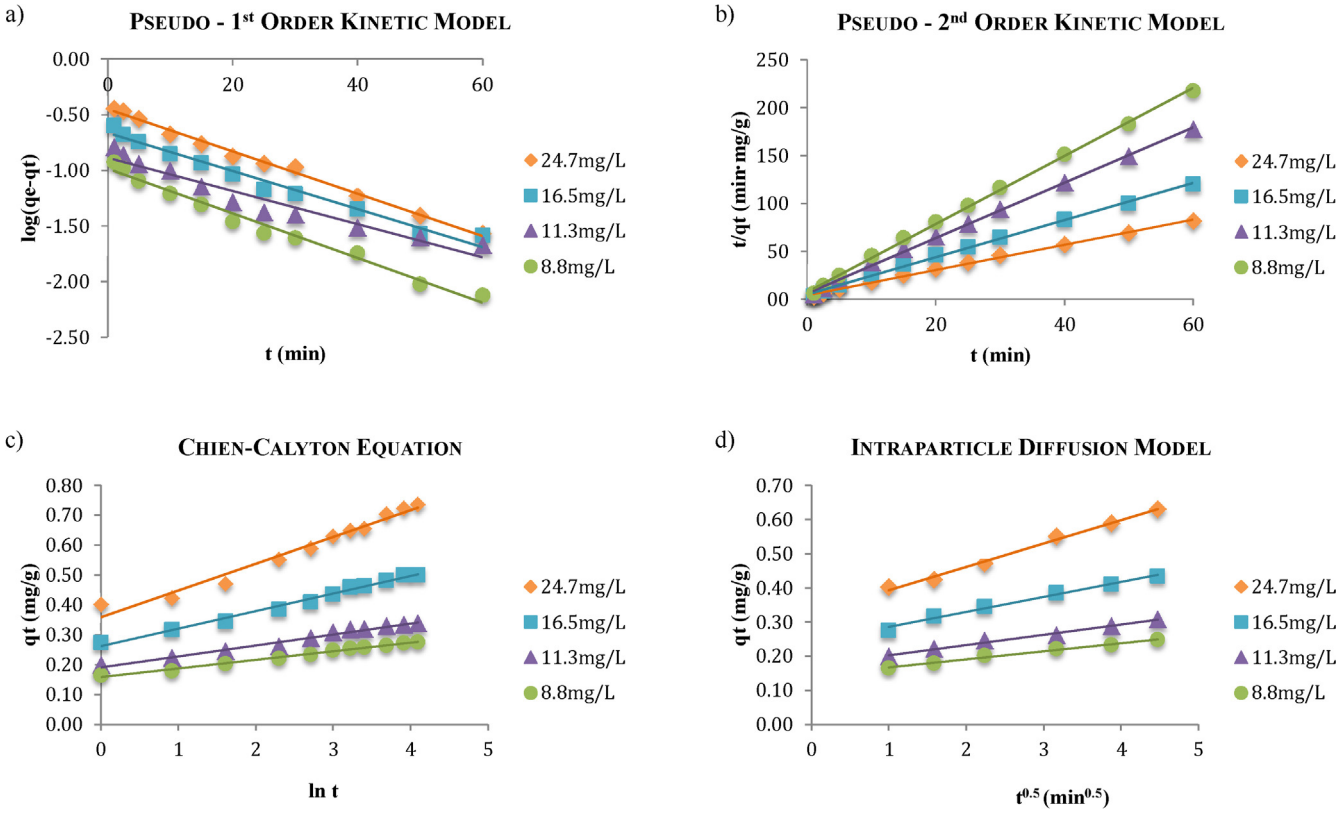

Fig. 3. Kinetic plots for the adsorption of pigments onto a calcium alginate–grape marc biopolymer.

related to the extent of surface coverage and activation energy for chemisorption.

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad (6)$$

Furthermore, experimental data have been fitted to the intraparticle diffusion model (Weber & Morris, 1962) in order to determine whether the adsorption process is governed only by intraparticle diffusion or if it is more complex and involves more than only one diffusive resistance. The intraparticle diffusion model can be expressed using Eq. (7).

$$q_t = K_P t^{0.5} + C \quad (7)$$

where K_P is the intraparticle diffusion rate constant (mg/g min$^{0.5}$) and C is the intercept (mg/g), and it is related to the thickness of the boundary layer. The slope of the linear part of the curve of q_t vs. $t^{0.5}$ – K_P – indicates the rate of adsorption controlled by intraparticle diffusion. When the intercept – C – equals zero, then the intraparticle diffusion is the only controlling step. However, if C does not pass through the origin, it indicates that there are other processes involved in the rate of adsorption.

Table 4 include the kinetic parameters obtained for the different models used in this work and Fig. 3 shows how experimental results adjust to the theoretical data predicted by pseudo-first order (Fig. 3a), pseudo-second order (Fig. 3b), Chien–Clayton (Fig. 3c) and intraparticle diffusion (Fig. 3d) models. Kinetic studies were carried out for different initial concentrations of pigments in the effluent from winery industry (24.7, 16.5, 11.3 and 8.8 mg/L). In all the cases, good agreement was observed between the experimental and theoretical data predicted by equations for the different kinetic models used; with values of correlation coefficients (R^2) from 0.935 to 0.999 (see Table 4). However, although the regression coefficients are indicative of the suitability of all the models proposed to describe the kinetics of the process, the theoretical q_e values for pseudo-second order model are more in concordance with those obtained experimentally, than the theoretical q_e values obtained using the pseudo-first order kinetic model. Hence, it can be speculated that the adsorption process follows a pseudo-second order kinetic model.

Regarding the kinetic parameters obtained after applying the Chien–Clayton kinetic model, it can be observed that α values predicted by this model (4.99–6.66 mg/g min) are higher than those obtained by Nethaji and Sivasamy (2011), whose values were between 0.56 and 1.24 mg/g min. These authors used activated carbon from palm flower, instead of grape marc, to remove dyes from water. Since α parameter determines the initial sorption rate, it can be speculated that the adsorption process is more favorable using calcium alginate–grape marc biopolymer than using activated carbon from palm flower.

In addition, Table 4 shows the kinetic parameters for the intraparticle diffusion model indicating that the adsorption process is partially controlled by intraparticle diffusion, because when all the experimental data are taken into account the correlation coefficients are between 0.927 and 0.967; whereas if only the first 6 experimental results are used in the adjustment of the data, better correlation coefficients are obtained (0.987–0.992). In Fig. 3d only the points corresponding to the linear part of the curve were included. Moreover intraparticle diffusion model gave C values higher than 0, which indicates that there are other processes, apart from the intraparticle diffusion, involved in the rate of adsorption.

4. Conclusions

From the data showed in this study it can be concluded that the heterogeneous biopolymer composed by biodegraded grape marc and calcium alginate formulated in this work can be a potential adsorbent for the treatment of color wastewater. Among the independent variables tested, the concentration of pigment and the pH had the most significant effect on the adsorption process, whereas temperature had a negligible effect. Moreover, after analyzing the kinetic parameters obtained, it was observed that the adsorption process follows a pseudo-second order kinetic model, existing a high concordance between the experimental and theoretical adsorption capacity.

Acknowledgments

We are grateful to the Xunta de Galicia (project GPC, ref. CN2012/277). Vecino X gratefully acknowledges the University of Vigo for her predoctoral contract.

References

Annadurai, G., Juang, R. S., & Lee, D. J. (2002). Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. *Journal of Hazardous Materials*, *92*, 263–274.

Arvanitoyannis, I. S., Ladas, D., & Mavromatis, A. (2006). Potential uses and applications of treated wine waste: A review. *International Journal of Food Science and Technology*, *41*, 475–478.

Atkinson, R. J., Hingston, F. J., Posner, A. M., & Quirk, J. P. (1970). Elovich equation for the kinetics of isotopic exchange reactions at solid–liquid interfaces. *Nature*, *226*, 148–149.

Berns, R. S. (2000). *Billmeyer and Saltzman's principles of color technology* (3rd ed.). New York: John Wiley & Sons.

Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S., & Escaleira, L. A. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta*, *76*, 965–977.

Box, G. E. P., & Behnken, D. W. (1960). Simplex-sum designs – A class of 2nd order rotatable designs derivable of those of 1st order. *Annals of Mathematical Statistics*, *31*, 838–864.

Chien, S. H., & Clayton, W. R. (1980). Application of Elovich equation to the kinetics of phosphate release and sorption in soils. *Soil Science Society of America Journal*, *44*, 265–268.

Devesa-Rey, R., Bustos, G., Cruz, J. M., & Moldes, A. B. (2011). Optimization of entrapped activated carbon conditions to remove coloured compounds from winery wastewaters. *Bioresource Technology*, *102*, 6437–6442.

Elovich, S. Y., & Larionov, O. G. (1962a). Theory of adsorption from nonelectrolyte solutions on solid adsorbents – 1. Simplified analysis of the equation of the adsorption isotherm from solutions. *Bulletin of the Academy of Sciences of the USSR Division of Chemical Science*, *11*, 191–197.

Elovich, S. Y., & Larionov, O. G. (1962b). Theory of adsorption from nonelectrolyte solutions on solid adsorbents – 2. Experimental verification of the equation for the adsorption isotherm from solutions. *Bulletin of the Academy of Sciences of the USSR Division of Chemical Science*, *11*, 198–203.

Ho, Y. S., & McKay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochemistry*, *34*, 451–465.

Kumar, M., Tamilarasan, R., & Sivakumar, V. (2013). Adsorption of Victoria blue by carbon/Ba/alginate beads: Kinetics, thermodynamics and isotherm studies. *Carbohydrate Polymers*, *98*, 505–513.

Lagergren, S. (1898). About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens Handlingar*, *24*, 1–39.

Moldes, A. B., Vázquez, M., Domínguez, J. M., Díaz-Fierros, F., & Barral, M. T. (2007). Evaluation of mesophilic biodegraded grape marc as soil fertilizer. *Applied Biochemistry and Biotechnology*, *141*, 27–36.

Nethaji, S., & Sivasamy, A. (2011). Adsorptive removal of an acid dye by lignocellulosic waste biomass activated carbon: Equilibrium and kinetic studies. *Chemosphere*, *82*, 1367–1372.

Paradelo, R., Moldes, A. B., & Barral, M. T. (2009). Treatment of red wine vinasses with non-conventional substrates for removing coloured compounds. *Water Science and Technology*, *59*, 1585–1592.

Sanghi, R., & Verma, P. (2013). Decolorisation of aqueous dye solutions by low-cost adsorbents: A review. *Coloration Technology*, *129*, 85–108.

Vázquez, D., Lage, M. A., Parajó, J. C., & Vázquez, G. (1992). Fractionation of eucalyptus wood in acetic acid media. *Bioresource Technology*, *40*, 131–136.

Vecino, X., Devesa-Rey, R., Cruz, J. M., & Moldes, A. B. (2013). Entrapped peat in alginate beads as green adsorbent for elimination of dye compounds from vinasses. *Water, Air, & Soil Pollution*, *224*, 1–9.

Vecino, X., Devesa-Rey, R., Moldes, A. B., & Cruz, J. M. (2012). Optimization of batch operating conditions for the decolourization of vinasses using surface response methodology. *Microchemical Journal*, *102*, 83–90.

Völz, H. G. (2001). *Industrial color testing* (2nd ed.). New York: Wiley-VCH.

Weber, W. J., & Morris, J. C. (1962). *Advances in water pollution research: removal of biologically resistant pollutant from waste water by adsorption. Proceedings of the First International Conference on Water Pollution Symposium* (2) Oxford: Pergamon Press.