Kinetic and morphology study of alginate-vineyard pruning waste biocomposite vs. non modified vineyard pruning waste for dye removal

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ARTICLE INFO

Article history:
Received 31 January 2015
Revised 27 May 2015
Accepted 28 May 2015
Available online 28 September 2015

Keywords:
Immobilized alginate-vineyard
Dyes
Kinetic studies
Roughness
Spherical shape

ABSTRACT

In this work a comparative bioadsorption study between a biocomposite consisting of hydrolysed vineyard pruning waste entrapped in calcium alginate spheres and non entrapped vineyard residue was carried out. Results have demonstrated that the biocomposite based on lignocellulose-calcium alginate spheres removed 77.3% of dyes, while non entrapped lignocellulose eliminated only removed 27.8% of colour compounds. The experimental data were fitted to several kinetic models (pseudo-first order, pseudo-second order, Chien–Clayton model, intraparticle diffusion model and Bangham model); being pseudo-second order the kinetic model that better described the adsorption of the two biocomposites. In addition, a morphological study (roughness and shape) of alginate-vineyard biocomposite was established under extreme conditions, observing significant differences between hydrated and dehydrated alginate-vineyard biocomposite. The techniques used to carry out this morphological study consisted of scanning electron microscopy (SEM), profilometry and 3D surface analysis.

Introduction

Nowadays environmental requirements are becoming of great importance, since there is an increased interest in the industrial use of renewable resources such as lignocellulosic residues for the formulation of eco-friendly adsorbents (Kim et al., 2014; Alves et al., 2013; Deng et al., 2011; Perez-Ameneiro et al., 2014a). Thus, significant efforts are now being made in the research and development of polysaccharide derivatives as the basic materials for new applications. In particular, the increasing costs of conventional adsorbents certainly make lignocellulosic-based materials, composed by natural polymers, one of the most attractive bioadsorbents for wastewater treatment (Sharma and Rajesh, 2014; Kumar et al., 2014). Different studies have demonstrated that lignocellulosic-based polymers have exceptional removal capabilities for certain pollutants such as dyes and metal ions as compared to other low-cost adsorbents and commercial activated carbons (Batzias et al., 2009; Rosas-Castor et al., 2014; Sidiras et al., 2013; Velazquez-Jimenez et al., 2013). Thus, cellulose-based biocomposites, has been widely used in wastewater purification due to its good biocompatibility, and excellent handling, which can be easily formulated into spheres, membranes and hollow fibres. Cellulose is composed of β-1,4 linked glucopyranose units, with polymer chains associated by

http://dx.doi.org/10.1016/j.jes.2015.05.032
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hydrogen bonds forming bundles of fibrils, also called microfibrillar aggregates, where highly ordered crystalline regions alternate with disordered amorphous domains. Therefore, peat and grape marc compost, entrapped in calcium alginate hydrogels, have been proposed for their dye-binding capability from wastewater (Vecino et al., 2013; Perez-Ameneiro et al., 2014b). Nevertheless, peat and composted grape marc have other uses like soil amendments that can prevent their use as biosorbsents in comparison with the lignocellulosic fraction of vineyard pruning waste. Moreover it was observed that the lignocellulosic fraction of vineyard pruning waste, encapsulated in calcium alginate beads, has excellent properties for the removal of micronutrients from wastewater (Vecino et al., 2014); although it would be important to evaluate the capacity of this lignocellulosic residue to remove other contaminants like dyes and study the adsorption mechanism under different kinetic models. In addition it would be interesting to know if the immobilization of this lignocellulosic residue in calcium alginate spheres increases the biosorption capacity of vineyard pruning waste in comparison with the raw hydrolysed vineyard pruning waste.

This work deals with a comparative study between the directly utilization of the lignocellulosic fraction of vineyard pruning waste against the utilization of an alginate-vineyard biocomposite spheres, for the removal of dye compounds from an agro-industrial effluent. Different kinetic models (pseudo-first order, pseudo-second order, Chien–Clayton model, intraparticle diffusion model and Bangham model) were used to explain the adsorption of dyes onto the two biosorbents. Moreover, 3D surface visualizations and profilometry analysis of hydrated and dehydrated calcium alginate spheres, containing vineyard pruning waste, were included in this study.

1. Materials and methods

1.1. Preparation of the lignocellulosic fraction of vineyard pruning waste

Lignocellulosic residue was collected from a local wine-producer (Galicia, North-West Spain). Vineyard pruning waste was dried and milled (<1 mm), homogenized in a single batch and hydrolysed with H2SO4 following the methodology proposed by Bustos et al. (2004). After hydrolysis a solid fraction composed by cellulose and lignin was dried and sieved up to a particle size of 0.5 mm and submitted to a quantitative hydrolysis in order to determine the cellulose and lignin concentration in the biosorbent (Vecino et al., 2014). Thus the percentage of cellulose in the adsorbent was calculated on the basis of glucose in the liquid phase, which was analysed by high performance liquid chromatography (HPLC) equipped with diode array detection (DAD) and refractive index detection (RID) (Agilent Technologies 1200 Series, Germany). Separation was performed using a Rezex RHM-Monosaccharide H+ (8%) column (Phenomenex, USA) with the column oven kept at 65°C. The mobile phase consisted in Milli-Q water plus 0.005 N of H2SO4, the injection volume was 20 μL and the flow rate was 0.4 mL/min.

Otherwise, the solid residue that remains after quantitative hydrolysis, was considered as the Klason lignin.

1.2. Development of the alginate-vineyard biocomposite spheres

Alginate-vineyard biocomposite spheres were prepared by mixing 1.25% of cellulose residue with 2.2% of sodium alginate, in order to form an emulsion that was introduced drop-wise in a crosslinking solution of calcium chloride 0.475 mol/L (Vecino et al., 2014).

For comparative purposes, during the kinetic adsorption study, hydrolysed vineyard pruning waste was also used without encapsulation.

1.3. Morphology characterization of lignocellulosic powder and alginate-vineyard biocomposite

1.3.1. Scanning electron microscope (SEM) images

Previously to obtain SEM images, the alginate-vineyard biocomposite 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 hr at 4°C. Following, the alginate-vineyard biocomposite was introduced in 1% OsO4 in cacodylate 0.1 mol/L buffer during 1 hr at 4°C. Dehydration was carried out with 30% of ethanol during 15 min and then ethanol using a different graded series (50%–2× 15 min; 70%–2× 15 min; 80%–2× 15 min; 90%–2× 15 min and 100%–3× 15 min) and amylacetate:ethanol in an ordered series (1:3–2× 15 min; 2:2–2× 15 min; 3:1–2× 15 min and amylacetate 100%–3× 15 min) in order to replace the ethanol for a liquid miscible with liquid CO2. The biocomposite was dried at the chamber critical point, cut in liquid N2, covered with gold and observed using SEM (Jeol JSM-6700F FEG) operating at an acceleration voltage of 5.0 kV for secondary-electron imaging (SEI/LEI).

The lignocellulosic powder undergoes non dehydration process. The powder was covered with gold and observed by SEM.

1.3.2. 3D surface roughness analysis

3D images of alginate-vineyard biocomposite were obtained with an Infinite Focus-SL Alicona GmbH (Graz, Austria) using an objective lense 10×, lateral resolution of 2 μm and vertical resolution of 500 nm. This system allows intuitive and quick measurement of micro structured surfaces, due to the high resolution and high density of number of points measured (4 millions of points); it is possible to calculate the diameter and the surface roughness within the same 3D measurement of the alginate-vineyard biocomposites. Post-processing Measure Suite software provides the tools to filter out the 3D measurement into waviness and roughness components by using a cut-off frequency filter of 80 μm.

In addition, an optical profilometer Zeta-20™ (Zeta Instruments, CA) was used in order to obtain a 3D surface visualization and roughness parameters (Ra, Rq, Rz, Rp, Rv) using Z scan range of μm and controlled by Zeta 3D software.

The roughness and radius of calcium alginate spheres containing the lignocellulosic adsorbent were studied during 22 min of hydration followed by a period of 75 min of dehydration at 19.5°C and 73 min of rehydration.

1.4. Commercial dye

Amaranth is a commercial dye (85%, Acros organics, USA) that was used as standard to obtain the amount of dye compounds.
contained in the winery effluent. Eq. (1) shows the linear relationship between the colour index (CI) of dye compounds contained in the winery effluent and the concentration of amaranth dye. CI of winery effluents was quantified by measuring the absorbance at 620, 520 and 420 nm (Eq. (2)). Therefore, the amount of colour compounds in wastewater was measured as equivalents of amaranth dye.

\[ C_i = 19.4663 \times CI - 0.2238 \]  
\[ \text{Cl} = A_{520} + A_{420} + A_{620} \]  

1.5. Dye compounds from winery industry

Agro-industrial effluent with the presence of dyes compounds was obtained from a local winery industry in Galicia, North-West of Spain, and kept at 4°C before use.

1.6. Bioadsorption of dyes: kinetic experiments

In order to establish the bioadsorption kinetics, batch adsorption experiments were carried out in 250 mL Erlenmeyer flasks placed in an orbital shaker at 150 rpm and 25°C. The solid/liquid ratio used was 1:1 (V/V). Samples were obtained at 5, 10, 20, 30, 40, 50, 60, 90 and 120 min for analysis of dye compounds and filtered through a 0.45 μm pore size membrane (PTFE Hydrophilic, Advantec, Japan) before analysing them by a double-beam spectrophotometer (Jasco V-650, Spain).

The adsorption capacity for the alginate-vineyard biocomposite and lignocellulosic powder was calculated at each time, \( q_t \) (mg/g), following the Eq. (3):

\[ q_t = \frac{(C_0 - C_t)V}{W} \]  

where, \( C_0 \) and \( C_t \) (mg/L) are the concentrations of dye compounds in the winery wastewater before and after treatment respectively, \( V \) is the volume of the winery wastewater used during batch experiments (L) and \( W \) (g) is the mass of lignocellulosic residue.

The percentage of dye removed (R) from wastewater was calculated following Eq. (4).

\[ R\% = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \]  

where, \( C_0 \) and \( C_t \) are initial and final dye contents.

The kinetic bioadsorption of dyes onto the bioadsorbents was studied using different kinetic models: pseudo-first order (Lagergren, 1898), pseudo-second order (Ho and McKay, 1999), Chien–Clayton model (Chien and Clayton, 1980), intraparticle diffusion (Weber and Morris, 1963) and Bangham model (Aharoni and Ungarish, 1977).

2. Results and discussion

2.1. Chemical characterization of lignocellulosic powder and alginate-vineyard biocomposite

The bioadsorbent obtained after quantitative hydrolysis with sulphuric acid of vineyard pruning waste, was composed by 39.0% cellulose and 40.1% lignin, being these percentages similar to those reported by Moldes et al. (2007).

2.1.1. Scanning electron microscopy (SEM) study

Fig. 1 shows high-resolution images of non-encapsulated hydrolysed vineyard pruned waste (Fig. 1a, b, c), the external surface of the biocomposite, consisting of calcium alginate hydrogel (Fig. 1d, e, f) and internal surface of vineyard pruning waste contained in the calcium alginate spheres (Fig. 1g, h, i) at different magnifications, respectively. Images revealed high amount of irregular and interconnected pores in the surface of vineyard pruning waste. These pores may be the areas where interaction sites are available to dye adsorption.

2.1.2. 3D surface roughness analysis

Surface roughness, often shortened to roughness, is a measure of the texture of a surface. Roughness values can either be calculated on a profile (line) or on a surface (area). The most common profile roughness parameters consist of \( R_a \), \( R_q \), \( R_z \), \( R_p \) and \( R_v \) (UNE ISO 4287:1999/A1:2010; UNE ISO 4288:1998; UNE ISO, 11562:1998) whereas area roughness parameters comprise \( S_a \), \( S_q \), \( S_z \), \( S_p \) and \( S_v \) (UNE ISO, 25178-2:2013).

\( S_a \) and \( S_q \) parameters represent a general measure of the texture comprising the surface of the alginate-vineyard biocomposite, which may be used to indicate significant deviations in the biocomposite characteristics. Moreover, \( S_p \), \( S_v \), and \( S_z \) parameters evaluated from the absolute highest and lowest points found on the surface. \( S_p \), the maximum peak height, is the height of the highest point, \( S_v \), the maximum valley depth, is the depth of the lowest point (expressed as a negative number) and \( S_z \) the maximum height of the surface, is calculated from \( S_z = S_p - S_v \). Table 1 shows the \( S_a \), \( S_q \), \( S_z \), \( S_p \) and \( S_v \) values of calcium alginate biocomposite spheres, based on vineyard pruning waste, before and after dehydration process. Moreover, radius and surface roughness parameters were measured to track the hydration and dehydration process. These parameters are very robust and representative of the hydration and dehydration process, as they are measured over a significant area of the alginate-vineyard biocomposites. Fig. 2a and b shows the variation in the radius and \( S_a \) respectively of alginate-vineyard biocomposite spheres after a cycle of hydration and dehydration process. As it can be observed in Fig. 2a and b calcium alginate spheres containing vineyard pruning waste recovered its original shape and size. It was observed that the manipulation during the rehydration process did not have a strong influence on the radius and surface roughness parameters. On the other hand, Fig. 3 shows 3D images of the alginate-vineyard biocomposite evaluated in this work, before (Fig. 3a) and after (Fig. 3b) dehydration processes based on a profile roughness. In this case it was observed that the profile roughness of dehydrated alginate-vineyard biocomposite was five times higher than not dehydrated biocomposite.

In addition, 3D roughness parameters based on the values of \( R_a \), \( R_q \), \( R_z \), \( R_p \) and \( R_v \) values were obtained in this work; where \( R_a \) is defined as the roughness average, \( R_q \) as the root-mean-square roughness, \( R_z \) as the average maximum profile height, \( R_p \) as the maximum profile peak height and \( R_v \) is the maximum profile valley depth (Mummery, 1993; Korkut et al., 2008). Table 1 includes the differences found in these parameters before and after dehydration of the lignocellulosic
biocomposite and Fig. 4a and b shows 3D surface images employed to obtain these parameters. The strong increase in roughness after dehydrating the biocomposite is obvious. In addition, Fig. 4c shows the surface texture of the alginate-vineyard biocomposite spheres before and after dehydration process.

### Table 1 – Different roughness parameters based on ISO standards.

<table>
<thead>
<tr>
<th>Parameters based on ISO standards</th>
<th>Parameters</th>
<th>Alginate-vineyard biocomposite</th>
<th>Dehydrated alginate-vineyard biocomposite</th>
</tr>
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<tbody>
<tr>
<td>Radius (mm)</td>
<td>2.06</td>
<td>1.68</td>
<td></td>
</tr>
<tr>
<td>Area (mm²)</td>
<td>12.94</td>
<td>7.10</td>
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<tr>
<td>$P_a$ (μm)</td>
<td>4.05</td>
<td>10.53</td>
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</tr>
<tr>
<td>$P_q$ (μm)</td>
<td>5.64</td>
<td>14.84</td>
<td></td>
</tr>
<tr>
<td>$P_z$ (μm)</td>
<td>23.41</td>
<td>63.49</td>
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<td>Roughness parameters based on ISO 4287/4288/11562</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$S_a$ (μm)</td>
<td>5.60</td>
<td>11.46</td>
<td></td>
</tr>
<tr>
<td>$S_q$ (μm)</td>
<td>8.31</td>
<td>16.26</td>
<td></td>
</tr>
<tr>
<td>$S_z$ (μm)</td>
<td>166.15</td>
<td>302.92</td>
<td></td>
</tr>
<tr>
<td>$S_p$ (μm)</td>
<td>102.13</td>
<td>125.10</td>
<td></td>
</tr>
<tr>
<td>$S_v$ (μm)</td>
<td>64.02</td>
<td>177.81</td>
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<tr>
<td>Roughness parameters based on ISO 4287/4288</td>
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</tr>
<tr>
<td>$R_a$ (μm)</td>
<td>0.13</td>
<td>0.79</td>
<td></td>
</tr>
<tr>
<td>$R_q$ (μm)</td>
<td>0.17</td>
<td>1.09</td>
<td></td>
</tr>
<tr>
<td>$R_z$ (μm)</td>
<td>0.67</td>
<td>4.53</td>
<td></td>
</tr>
<tr>
<td>$R_p$ (μm)</td>
<td>0.65</td>
<td>1.99</td>
<td></td>
</tr>
<tr>
<td>$R_v$ (μm)</td>
<td>0.33</td>
<td>6.67</td>
<td></td>
</tr>
</tbody>
</table>
Furthermore, based on the normative of the Spanish Association for Standardisation and Certification (UNE ISO, 1101:2013), Fig. 5 shows the spherical shape in 3D images of alginate-vineyard biocomposite, at initial state (Fig. 5a) and after dehydration (Fig. 5b) used to calculate the radius by fitting the alginate-vineyard biocomposites surface to a sphere.

Important differences were observed between hydrated and dehydrated biocomposite. Table 1 includes the radius and area of alginate-vineyard biocomposite spheres, corresponding with these images.

In addition, some researchers (Mattsson et al., 2008) have reported that the roughness parameters preferred in micrometry are the P-parameters ($P_a$, $P_q$ and $P_z$) based on primary profile data introduced in ISO standards 4287 (UNE ISO 4287:1999/A1:2010) and 4288 (UNE ISO 4288:1998); where $P_a$ is defined as the arithmetic mean deviation of the assessed profile, $P_q$ is the root mean square deviation of the assessed profile (equivalent to the standard deviation of the surface structure) and $P_z$ is the maximum height of profile. Table 1 shows the difference between $P_a$, $P_q$ and $P_z$ values before and after dehydration process of the alginate-vineyard biocomposite. It can be observed that after dehydration the roughness of the lignocellulosic biocomposite was highly increased.

2.2. Adsorption of dye compounds on vineyard pruning waste bioadsorbents: a kinetic study

It has been demonstrated that hydrolysed vineyard pruning waste, entrapped in calcium alginate beads, has exceptional capabilities for the removal of anionic and cationic micronutrients, as well carbon and nitrogen in an industrial wastewater (Vecino et al., 2014), however there are not comparative studies about this entrapped and non entrapped vineyard pruning waste adsorbent for the removal of dye compounds. Furthermore, kinetic studies were carried out to know the dye adsorption mechanism onto both adsorbents, entrapped and non entrapped hydrolysed vineyard pruning waste.

Fig. 6 shows the kinetic profile of dye removal obtained during the adsorption of dye compounds onto the bioadsorbents based in vineyard pruning waste. The dye compounds in the raw wastewater gave a CI of 1.81, which corresponds, with 35.6 mg/L of dye compounds measured as equivalents of amaranth dye.

When vineyard pruning waste was encapsulated in calcium alginate spheres, the lignocellulosic adsorbent increased its adsorption capacity in comparison with the utilization of non immobilized vineyard pruning waste for the same concentration.

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**Fig. 2** – Variation of the radius (a) and area roughness ($S_a$) (b) of alginate-vineyard biocomposite after a cycle of hydration-dehydration.

**Fig. 3** – Waviness and roughness images used to calculate surface roughness ($P_a$, $P_q$, $P_z$; $S_a$, $S_q$, $S_z$, $S_p$, $S_v$) of the alginate-vineyard biocomposite (a) before and (b) after dehydration process.
of lignocellulosic residue (1.25 g). Non-encapsulated vineyard pruning waste only eliminated 27.8% of dye compounds, whereas alginate-vineyard biocomposite removed 77.3%; these data correspond with a reduction of CI of 1.31 and 0.41 respectively. Only when the amount of vineyard pruning waste increased up to 7.56 g, which is the dry weight of the alginate-vineyard biocomposite spheres, the same percentage of dyes removal was obtained (77.7%).

The bioadsorption of dye compounds onto alginate-vineyard biocomposite were conveniently represented by kinetic models, which are helpful to predict the behaviour of these bioadsorbents.

Eq. (5) represents the linear form of the pseudo-first order model (Lagergren, 1898):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

where, $q_e$ (mg/g) and $q_t$ (mg/g) are the concentration of adsorbed dyes at equilibrium and at a defined time $t$, respectively, and $k_1$ (1/min) is the rate constant of pseudo-first order adsorption.

The kinetic coefficients obtained in this case showed that there is a clear difference between non-encapsulated hydrolysed vineyard pruning waste and the alginate-vineyard biocomposite formulated (Table 2). Thus, non-encapsulated vineyard pruning waste gave a theoretical capacity of 0.48 mg/g, whereas entrapped vineyard pruning waste in calcium alginate spheres increases the capacity until 1.23 mg/g. Fig. 7a shows the correlation between the experimental data and the theoretical data when these were described by using pseudo-first order kinetic model. Non-encapsulated vineyard pruning waste was used at two different concentrations (1.25 g and 7.65 g), observing that only when the concentration of vineyard pruning waste increased up to 7.65 g similar capacity with encapsulate vineyard pruning waste can be obtained.

Moreover, sorption kinetics were also described using a pseudo-second order model following Eq. (6) (Ho and McKay, 1999):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

where, $k_2$ (g/mg min) is the equilibrium rate constant of pseudo-second order adsorption. In this case, Eq. (6) 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 not need to know any parameter beforehand.

Table 2 includes the kinetic parameters obtained after modelling the experimental data following pseudo-second order kinetic model and Fig. 7b shows the variation of the experimental data when they were adjusted to this pseudo-second order kinetic model, observing that there are a close agreement between the experimental and theoretical capacities predicted by the model. The best capacities predicted by the model were achieved using alginate-vineyard biocomposite.

Furthermore, adsorption kinetics can also be adjusted to the Elovich equation (Elovich and Larionov, 1962a, 1962b), which, although firstly was used to explain the adsorption kinetics of gases on solids, it has been successfully applied for the adsorption of solutes from a liquid solution (Eq. (7)).

$$\frac{dq}{dt} = \alpha \exp(-\beta q_t)$$

(7)

Chien and Clayton (1980) proposed the simplification of Eq. (7) by assuming $\alpha \beta t \gg 1$, and considering the boundary conditions $q_t = 0$ for $t = 0$ and $q_t = q_e$ at $t = t$. In the Chien–Clayton expression (Eq. (8)), $\alpha$ (min mg/g) is the initial sorption rate, and $\beta$ (g/mg) is related to the extent of surface coverage and activation energy for chemisorption.

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

(8)

Regarding the kinetic parameters obtained after applying the Chien–Clayton kinetic model (Table 2), it was observed that $\alpha$ value predicted by this model to the encapsulated vineyard pruning waste was higher (1.74) than that obtained using 1.25 g of vineyard pruning waste without entrapping; however when the concentration of non-encapsulated vineyard pruning waste was increased to 7.65 g higher initial sorption rates were obtained deduced by the higher $\alpha$ values achieved (3.01); although the adsorption capacity was lower than using vineyard pruning waste encapsulated in calcium alginate spheres (Fig. 7c).

Moreover, 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 such as surface adsorption, ion exchange, complexation, complexation–chelation or microprecipitation; experimental data have been fitted to the intraparticle diffusion model (Weber and Morris, 1963) following Eq. (9).

$$q_t = k_P t^{0.5} + C$$

(9)

where $k_P$ is the intraparticle diffusion rate constant (mg/(g·min)) 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 (see Fig. 7d). 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. In this case, the 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. These results are similar to those achieved by some authors using lignocellulosic residues. Thus, Perez-Ameneiro et al. (2014b) found that, the intercept was between 0.325 and 0.172 using a lignocellulosic biocomposite based on composted grape marc.

Finally, following Eq. (10) experimental data were fitted to Bangham model (Aharoni and Ungarish, 1977):

$$
\log \left[ \log \left( \frac{C_0}{C_0 - q_t m} \right) \right] = \log \left( \frac{k_0 m}{Z 303 V} \right) + \alpha \log t
$$

where, $C_0$ (mg/L) is initial concentration of adsorbent in solution, $V$ (L) is the volume of solution, $m$ (g/L) is the weight of adsorbent used per litre of solution, $q_t$ (mg/g) the amount of adsorbent retained at time $t$, and $\alpha$ and $k_0$ are constants. As such, $\log (\log (C_0 / (C_0 - q_t m)))$ values were plotted against log $t$ in Fig. 7e. The linearity of these plots confirms the applicability of the Bangham equation and indicates that diffusion of dyes into pores of the adsorbent controls the adsorption process (Aharoni et al., 1979) although according to the intraparticle diffusion model other processes are involved in the elimination of dyes from wastewater.

For all the kinetic studies, good correlation coefficients ($r^2$) were obtained with values between 0.899 and 0.999 (see Table 2), although the best $r^2$ were obtained using the pseudo-second order kinetic model. Thus, pseudo-second order was the model that better explained the behaviour of the bioadsorption process.

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Kinetic parameters</th>
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<th>Lignocellulosic residue (7.65 g)</th>
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<td>Pseudo-first order</td>
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<td>$r^2$</td>
<td>0.998</td>
<td>0.999</td>
<td>0.999</td>
</tr>
<tr>
<td>Chien–Clayton model</td>
<td>$\alpha$</td>
<td>1.737</td>
<td>0.631</td>
<td>3.015</td>
</tr>
<tr>
<td></td>
<td>$\beta$</td>
<td>3.291</td>
<td>7.733</td>
<td>25.167</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.997</td>
<td>0.959</td>
<td>0.994</td>
</tr>
<tr>
<td>Intraparticle diffusion model</td>
<td>$k_p$</td>
<td>0.107</td>
<td>0.043</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>$C$</td>
<td>0.912</td>
<td>0.380</td>
<td>0.223</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.938</td>
<td>0.826</td>
<td>0.911</td>
</tr>
<tr>
<td>Bangham model</td>
<td>$\alpha$</td>
<td>0.335</td>
<td>0.254</td>
<td>0.237</td>
</tr>
<tr>
<td></td>
<td>$k_0$</td>
<td>0.006</td>
<td>0.005</td>
<td>0.002</td>
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<tr>
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<td>$r^2$</td>
<td>0.998</td>
<td>0.916</td>
<td>0.994</td>
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</table>

Table 2 – Comparison of kinetic parameters for pseudo-first order, pseudo-second order, Chien–Clayton, intraparticle diffusion and Bangham kinetic models.

Fig. 7 – Kinetic plots for the adsorption of dye compounds onto the studied biocomposites applying different kinetic models. (a) Pseudo-first order; (b) pseudo-second order; (c) Chien–Clayton model; (d) intraparticle diffusion model; (e) Bangham model.
and that the intraparticle diffusion is not the only controlling step. Several authors like Huayue et al. (2014) prepared a novel magnetic calcium alginate/maghemite hydrogel beads or Genlin et al. (2014) fabricated an adsorbent consisting of carboxymethyl cellulose-acrylic acid observing that the adsorption of copper (II) and dyes respectively, also follows a pseudo-second order kinetic adsorption mechanism.

### 3. Conclusions

In comparison with classical adsorbents such as activated carbons, alumina or silica gels, vineyard pruning waste entrapped in calcium alginate spheres appear as an eco-friendly, biodegradable and manageable alternative for the efficient removal of dye compounds from industrial wastewater. Among all kinetic models evaluated pseudo-second is the model providing the best fit. Evaluation of alginate-vineyard biocomposite roughness, by different methods, revealed that biocomposite was very sensitive to dehydration providing an increase in roughness, although once rehydrated; the biocomposite recovered its shape and original roughness what suggests that this biocomposite is very malleable and it can serve as a potential adsorbent for the effective treatment of industrial effluents in treatment plants.

### Acknowledgments

Authors wish to thank to the Spanish Ministry of Economy and Competitiveness (this work was funded by FEDER funds under the project CTM2012-31873). Xanel Vecino gratefully acknowledges the University of Vigo for her predoctoral contract and we are also grateful to P. Martinez for his technical assistance (ScienTec Iberica).

### References


Perez-Ameneiro, M., Vecino, X., Vega, L., Devesa-Rey, R., Cruz, J.M., Moldes, A.B., 2014b. Elimination of micronutrients from winery...
wastewater using entrapped grape marc in alginate beads. 


