Fixed-bed adsorption of Tricaine Methanesulfonate onto pyrolysed paper mill sludge

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Abstract

The removal of Tricaine Methanesulfonate from water in a fixed-bed column packed with pyrolysed paper mill sludge was evaluated for application in Recirculating Aquaculture Systems. Breakthrough adsorption curves were determined for this pharmaceutical, under different operating conditions. In a laboratory-scale approach, with synthetic effluent, a bed adsorption capacity of 125 mg g^{-1} was obtained under a flux of $56 \text{ L min}^{-1}\text{m}^{-2}$, with 400 mg L^{-1} of MS-222 with 4.5 cm bed depth. The performance of the continuous adsorption in a column packed with biological paper mill sludge-based carbon, using real aquaculture wastewater as matrix, was not significantly affected. Then, scale-up was carried out and the bed depth service time model was applied and provided good predictions. Finally, the thermal regeneration of the exhausted adsorbent was assessed, which revealed satisfactory results for one cycle reusability after saturation; however, considering the nature of its precursor, the use of new adsorbent could be more profitable than its regeneration, functioning also as an additional option for the management of such wastes.

Keywords

Fish anaesthetic; water recycling; packed column reactor; scale-up; thermal regeneration.

1. Introduction

Therapeutic organic chemicals are usually employed in intensive aquaculture systems to treat diseases and to control growth, reproduction and stress. Tricaine - Methanesulfonate (MS-222), commercially named Tricaine-S, has been widely used as fish anaesthetic to reduce fish stress during handling and confinement operations. This pharmaceutical is administered by solubilisation in the tank's water, which, therefore, becomes contaminated. The recommended doses of this anaesthetic are significantly different among species and depend on the desired anaesthesia level. Accordingly, MS-222 concentration can vary from 20 mg L⁻¹ (*Cyprinus carpio* and *Sparus aurata*) to 480 mg L⁻¹ (*Hippoglossus hippoglossus*) for deep anaesthesia (Ross and Ross, 2008; Topic Popovic et al., 2012).

The implementation of Recirculating Aquaculture Systems (RASs) in intensive aquaculture systems involves cleansing of water for reuse through fish culture tanks so as to reduce the need for water and minimize the discharge of nutrients and organic pollutants into the environment (Martins et al., 2010). A typical RAS consists of primary treatment (sedimentation and/or filtration to remove mostly suspended solid waste), biological treatment (to convert the ammonia and nitrite into nitrate through nitrification in aerobic biological filters) and tertiary treatment processes such as oxygenation, ozonation and UV irradiation aimed at removing organic matter, mainly nitrogen-containing compounds, and disinfection (Martins et al., 2010; Miller and Semmens, 2002; Summerfelt et al., 2009). Carbon filters, mostly fixed-bed activated carbon columns, may be also used in addition to biological filters as a polishing stage to remove persistent nonbiodegradable organic materials, such as pharmaceuticals (Lawson, 1995). However, the main drawback of activated carbons is their high price (Robinson et al., 2001). Alternatively, the utilization of low-cost adsorbents for the

removal of aquaculture medicines has been proposed by a few authors: Gupta et al. (2004), Mittal et al. (2005), Akar et al. (2013) and Sartape et al. (2014), who studied the batch adsorption of the fungicide malachite green onto bottom ash, de-oiled soya, spent tea leaves and wood apple shells, respectively. Also under batch operation conditions, Ferreira et al. (2015) evaluated the removal of MS-222 from water by adsorption onto biochars from different wastes and promising results were obtained with the paper mill sludge-based adsorbent. However, continuous fixed-bed systems hold some advantages over batch-type adsorbers for water treatment (McKay, 1995) and are frequently used in the aquaculture industry as auxiliary filters to support biofiltration in RASs (Helfrich and Libey, 2011; Lawson, 1995).

In this context, the aim of this study was the evaluation of the fixed-bed adsorption of MS-222 from water, using a paper mill sludge-based adsorbent. For this purpose, the influence of important design parameters (feed flow rate, influent concentration and bed depth) was analysed and different mathematical models were fitted to the experimental data. In view of application in RASs, an experiment using a real effluent from aquaculture was performed and results compared with those using a synthetic effluent. Also, both scale-up and regeneration of the saturated adsorbent were assessed in this work.

2. Materials and Methods

2.1. Preparation of the adsorbent material

Biological paper mill sludge (BS) was provided by a local mill that employs the kraft elemental chlorine free pulp production process. Adsorbents based on biological sludge were produced by pyrolysis following the procedure described by Calisto et al. (2014). Briefly, BS was dried in an oven at 105 °C for 24 h and then grinded with a

mortar grinder and transferred into porcelain crucibles. Afterwards, BS was pyrolysed at 800 °C for 150 min (heating ramp of 10 °C min⁻¹), under N₂ saturated atmosphere, using a muffle (Nüve furnace MF 106). The resultant biochar was washed with HCl 1.2 M (37%, Panreac) and then with distilled water until neutral pH, as described by Ferreira et al. (2016). After washing, biological sludge-based carbon (BSC) was dried in an oven for 24 h at 105 °C. Finally, BSC was sieved and particle size between 0.18 and 0.5 mm was used in this study. Physical and chemical characterization of the starting materials and respective pyrolysed and acidic washed materials can be found elsewhere (Calisto et al., 2014; Ferreira et al., 2016).

2.2. Fixed-bed column adsorption experiments

Fixed-bed column experiments were conducted in a 1 cm diameter and 13 cm length glass column (CHROMAFLEX®). A thermostatic recirculating bath (ThermoScientific HAAKE A10) maintained the temperature constant, at 18 °C, by circulating water through an acrylic jacket surrounding the column body. A flow adapter, with a 20 µm porosity HDPE bed support, was attached to the top of the column. The column was packed with BSC (1.0, 2.0 and 2.5 g) resulting in different bed depths, Z (4.5, 9.0 and 13.0 cm, respectively). As represented in Figure 1, synthetic influent solutions, C_i (100, 250 and 400 mg L⁻¹ of MS-222 (>97%, TCI Europe) in ultra-pure water, buffered with NaHCO₃ 10⁻² M to pH 7.0-7.5, according to the required for farmed fish, as mentioned in section 1) were pumped up flow by a peristaltic pump (Gilson Minipuls 3) with different fluxes, F (15, 27, 56 L min⁻¹m⁻²). Effluent samples were collected by a programmable fractions collector (Gilson FC 203B Fraction Collector), filtered through 0.22 µm Simplepure PVDF filters, and analysed for the concentration of MS-222 by Micellar Electrokinetic Chromatography (MEKC), as

described in section 2.3. MS-222 physico-chemical properties are presented in Table S1.

In order to recreate the real conditions, a fixed-bed experiment was performed using an effluent from a national fish producer as aqueous matrix ($F=56 \text{ L min}^{-1}\text{m}^{-2}$, $C_i=250 \text{ mg L}^{-1}$ and $Z=4.5 \text{ cm}$). This aquaculture farm produces fishes in intensive system and has a RAS implemented that consists of sedimentation tanks followed by moving bed biofilters, ozonation and oxygenation processes and allows reutilizing approximately 95% of water on a system flow basis. The collected aquaculture wastewater used in adsorption experiments contained $27 \pm 3 \text{ mg L}^{-1}$ of dissolved organic carbon (DOC), $46 \pm 2 \text{ mg L}^{-1}$ of inorganic carbon (IC), 20-21‰ of salinity and pH 7-7.5.

A scale-up experiment was performed using the same experimental setup, with a 2.5 cm diameter and 50 cm length glass column (13/219 POBEL). This column was packed with 55 g of BSC (corresponding to a bed depth of 35 cm) and a solution of MS-222 (250 mg L^{-1}) was passed through the column at a flux of $24 \text{ L min}^{-1}\text{m}^{-2}$.

2.2.1. Fixed-bed column data analysis

In order to evaluate the adsorption of MS-222 in a BSC packed column under different operating conditions, breakthrough curves were obtained by expressing C/C_i as a function of operation time (t , in min) or volume (V , in mL), where C and C_i (mg L^{-1}) are the effluent and influent concentration, respectively. From a practical point of view, the breakthrough point allows determine the volume of effluent treated (V_b). Usually, this point is settled according to the target quality of the final effluent; however, in the case of MS-222 there is not yet a maximum limit established of discharge into the environment. So, the breakthrough point was considered as the point where effluent

concentration reaches about 10% of the influent concentration ($C/C_i \approx 0.1$). The time corresponding to this point is the breakthrough time (t_b). When the effluent concentration reaches 95% of the influent concentration, it is considered the saturation point (corresponding to a saturation time (t_s)). The total mass of solute adsorbed by the adsorbent at the saturation time, q_s (mg g⁻¹), can be calculated using the following expression:

$$q_s = \frac{Q}{1000} \frac{C_i A}{m} = \frac{Q}{1000m} \int_{t=0}^{t=t_s} \left(1 - \frac{C}{C_i}\right) dt \quad (1)$$

where Q (mL min⁻¹) is the flow rate; A (min) is the area above the breakthrough curve and m (g) is the dry weight of adsorbent in the column.

2.2.2. Mathematical models

Several simple mathematical models have been proposed to predict the dynamic behaviour of fixed-bed columns and estimate the kinetic coefficients. The models developed by Thomas (Thomas, 1944), Clark (Clark, 1987), Yoon-Nelson (Yoon and Nelson, 1984) and Dose-Response (Yan et al., 2001) were fitted to the experimental breakthrough curves using GraphPad Prism 5 software.

For the scale-up, the bed depth service time (BDST) model (Hutchins, 1973), which establishes a relationship between the bed depth, Z (cm), and the operation time, was used on the basis of previously obtained results.

A short description of each of the above models is presented below.

Thomas Model

Thomas model (Thomas, 1944) is one of the most generally used in column performance theory, based on the assumption of adsorption-desorption with no axial dispersion and no mass transfer and following second-order reversible reaction kinetic.

The maximum adsorption capacity of the adsorbent, q_{Th} (mg g⁻¹), and the adsorption rate constant, k_{Th} (mL min⁻¹ mg⁻¹), could be calculated by fitting this model, as follows:

$$\frac{C}{C_i} = \frac{1}{1 + e^{\left(\left(\frac{k_{Th}}{Q}\right)(m q_{Th} - C_i V)\right)}} = \frac{1}{1 + e^{\left(\frac{k_{Th} m q_{Th}}{Q} - k_{Th} C_i t\right)}} \quad (2)$$

Clark Model

Clark (1987) used the mass-transfer coefficient in combination with the Freundlich isotherm to define a new relation for the breakthrough curve, as follows:

$$\frac{C}{C_i} = \frac{1}{1 + A e^{-k_C t}} \quad \text{with} \quad A = \left(\frac{C_i^{n_F - 1}}{C_b^{n_F - 1}} - 1 \right) e^{k_C t_b} \quad (3)$$

where n_F is the Freundlich constant (previous studies determined $n_F = 8 \pm 1$, $r^2 = 0.9851$ (Ferreira et al., 2016)); k_C (min⁻¹) is the adsorption rate constant and C_b (mg L⁻¹) the solute concentration at breakthrough time.

Yoon-Nelson Model

Yoon-Nelson model (Yoon and Nelson, 1984) is based on the assumption that the rate of decrease in the probability of adsorption for each solute molecule is proportional to the probability of solute adsorption and the probability of solute breakthrough on the adsorbent. Equation (4) represents this model:

$$\frac{C}{C_i} = \frac{e^{(k_{YN} t - k_{YN} t_{50\%})}}{1 + e^{(k_{YN} t - k_{YN} t_{50\%})}} \quad (4)$$

where k_{YN} (min⁻¹) is the adsorption rate constant and $t_{50\%}$ (min) the time required for retaining 50 % of the initial solute concentration ($C/C_i = 0.5$).

Dose-Response Model

The Dose-Response model (Yan et al., 2001), commonly used in pharmacology to describe different types of processes, is currently being applied to describe fixed-bed biosorption. This model basically diminishes the error resulting from the use of the Thomas model, particularly at the lowest and highest times of the breakthrough curve. The mathematical expression of the model is represented as below:

$$\frac{C}{C_i} = \frac{C_s}{C_i} - \frac{\frac{C_s}{C_i}}{1 + \left(\frac{v}{V_{50\%}}\right)^\alpha} = \frac{C_s}{C_i} - \frac{\frac{C_s}{C_i}}{1 + \left(\frac{t}{t_{50\%}}\right)^\alpha} \quad (5)$$

where C_s is the solute concentration at t_s and α is the constant of the Dose-Response model.

Bed Depth Service Time (BDST) Model

The BDST model (Hutchins, 1973), assumes that the adsorption rate is controlled by the surface reaction between the solute and the unused capacity of the adsorbent according to:

$$t = \frac{N_0}{C_i v} Z - \frac{1}{k_{BDST} C_i} \ln\left(\frac{C_i}{C} - 1\right) \quad (6)$$

where N_0 (mg L⁻¹) is the dynamic bed adsorption capacity; v (cm min⁻¹) is the linear fluid velocity, which is defined as the ratio between the volumetric flow, Q_v (cm³ min⁻¹), and the cross-sectional area of the bed, S_c (cm²); and k_{BDST} (L mg⁻¹ min⁻¹) is the adsorption rate constant. N_0 and k_{BDST} can be determined from the slope and intercept of the plot of t vs. Z . A simplified form of the BDST model is expressed by equation (7):

$$t = aZ - b \quad (7)$$

with:

$$a = \frac{N_0}{C_i v} \quad (8)$$

$$b = \frac{1}{k_{BDST} C_i} \ln\left(\frac{C_i}{C} - 1\right) \quad (9)$$

By varying the column bed depth (Z), a and b have the same values; however, applying equation (6), a new operation time is obtained. If there is a change in the initial solute concentration C_i to a new value C_i' , the new values of a and b can be, respectively, obtained from the slope and the intercept according to the relations proposed by Hutchins (1973):

$$a' = a \frac{C_i}{C_i'} \quad (10)$$

$$b' = b \frac{C_i \ln\left(\frac{C_i'}{C} - 1\right)}{C_i' \ln\left(\frac{C_i}{C} - 1\right)} \quad (11)$$

Also, when the linear flow rate is changed from v to v' , the new value of the slope (a) is obtained by:

$$a' = a \frac{v}{v'} \quad (12)$$

However, the intercept (b) remains unchanged because it depends on the inlet solute concentration C_i .

2.3. BSC regeneration experiments

The saturated BSC from one of the fixed-bed experiments ($Z=13.0$ cm, $C_i=250$ mg L⁻¹, $F=56$ L min⁻¹m⁻²) was removed from the column and dried in an oven at 105 °C overnight. Then, under N₂ saturated atmosphere, BSC was subjected to a heating rate of 10 °C min⁻¹ up to 600 °C, which was kept during 90 min. The final temperature of 600 °C was chosen to guarantee thermal degradation of MS-222, as can be seen by the results of thermogravimetric analysis (TGA) performed to MS-222 presented in Figure S1. After regeneration, the fixed-bed experiment was repeated under identical operation conditions ($Z=13$ cm, $C_i= 250$ mg L⁻¹, $F=56$ L min⁻¹m⁻²), and the whole process (saturation-regeneration) was repeated up to three cycles.

Specific surface area (S_{BET}) and total micropore volume (W_0) were determined by N₂ adsorption isotherms. These analyses were acquired at 77 K using a Micromeritics Instrument, Gemini VII 2380. The samples were previously outgassed at 120 °C for 12 h.

2.4. *Determination of the MS-222 concentration in water by MEKC*

MEKC analyses were performed using a Beckman P/ACE MDQ (Fullerton, CA, USA) instrument, equipped with a UV-Vis detection system, for quantification of MS-222 in the aqueous phase. A dynamically coated silica capillary of 40 cm of length (30 cm to the detection window) and 75 µm of internal diameter was used as described by Calisto et al. (2011). For capillary coating, sodium hydroxide 1 M and 0.5 % (w/v) of hexadimethrine bromide (polybrene, ≥ 95%, Sigma Aldrich) in 0.5 M sodium chloride (≥ 99.5%, Fluka) were used. Time of injection of aqueous samples and standard solutions were 4 s at 0.5 psi and the electrophoretic separation was performed in direct polarity mode with a positive power supply of 22 kV, at 30 °C. Detection of MS-222 was monitored at 220 nm. The separation buffer consisted of 20 mM of sodium tetraborate (Borax, Riedel-de Haën) and 30 mM of sodium dodecylsulphate (SDS, 99 %, for electrophoresis, Sigma Aldrich), pH 9.2. 3-ethoxy-4-hydroxybenzaldehyd (Ethylvanilin, 99 %, Sigma Aldrich) was used as internal standard, spiked in all samples and standard solutions at a final concentration of 33.4 mg L⁻¹. Capillary washing between runs consisted of 1 min of ultra-pure water obtained from a Milli-Q Millipore system (Milli-Q plus 185) followed by 2 min of separation buffer. Samples were filtered through 0.22 µm Simplepure PVDF filters prior to analysis. Samples and standard solutions were analysed in triplicate.

3. Results and Discussion

A complete physicochemical characterization of the adsorbent herein used, before and after pyrolysed and acidic washed, may be found elsewhere (Calisto et al., 2014; Ferreira et al., 2016). Briefly, Fourier transform infra-red spectroscopy (FTIR) analysis of the BS presented typical bands of cellulose, hemicelluloses and carbonates in its composition. Elemental composition showed high contents of elemental C and O (39% and 23%, dry basis, respectively) and < 6% of N, H and S elements. After pyrolysis, the aliphatic groups disappeared, due to the cellulose and hemicelluloses thermal decomposition, and some aromatic groups remained; however the ash content of pyrolysed BS was high (about 50%) and, consequently, S_{BET} and total micropore volume were low ($11 \text{ m}^2 \text{ g}^{-1}$ and $0.0014 \text{ cm}^3 \text{ g}^{-1}$, respectively) (Calisto et al., 2014). After washing with 1.2 M HCl, the physical properties of BSC were improved, *i.e.*, S_{BET} increased significantly ($258 \text{ m}^2 \text{ g}^{-1}$) as well as total micropore volume ($0.039 \text{ cm}^3 \text{ g}^{-1}$); however, these values are still far from commercial activated carbons (with S_{BET} commonly ranging from 600 to 2000 $\text{m}^2 \text{ g}^{-1}$). Concerning the pH of BSC surface, Boehm titration and PZC results indicated that BSC is a material with high quantity of basic groups (4.2 mmol g^{-1}) and, at the working pH (7-7.5), BSC has a positive surface charge (PZC 10.4) (Ferreira et al., 2016).

In a previous study, kinetic and equilibrium adsorption experiments in batch mode were performed for the same adsorbate-adsorbent system. In the same conditions of the present work, the maximum adsorption capacity of BSC in batch equilibrium was $83 \pm 2 \text{ mg g}^{-1}$ (estimated by Langmuir model, $r^2=0.99$) and the Freundlich constant, n , was 8 ± 1 (estimated by Freundlich model, $r^2=0.98$) (Ferreira et al., 2016).

3.1. *Effect of the flow rate, influent concentration and bed depth*

Breakthrough curves at different fluxes are presented in Figure 2 a.) (keeping $C_i=250 \text{ mg L}^{-1}$ and $Z=4.5 \text{ cm}$). The results show that the saturation time (t_s) decreases with the increase of the flux, and, consequently, reduces the volume of treated effluent until breakthrough point, mainly between 15 and $27 \text{ L min}^{-1}\text{m}^{-2}$, as can be seen in Table 1. This fact is due to the decrease of the contact time between the MS-222 molecules and the BSC particles at higher fluxes when compared with $15 \text{ L min}^{-1} \text{ m}^{-2}$. However, between flux 27 and $56 \text{ L min}^{-1} \text{ m}^{-2}$, the volume treated until the breakthrough point is almost the same, varying only 5%. Therefore, under the operation conditions here considered, the use of $56 \text{ L min}^{-1} \text{ m}^{-2}$ of flux may be more advantageous (same volume treated in less time). Concerning the total adsorption capacity of the bed, there are no differences between the different fluxes tested (differences under 2%). Comparing these values with the ones obtained in batch system (83 mg g^{-1}) (Ferreira et al., 2016), BSC might have a slightly better performance in continuous system.

The effect of the variation of MS-222 influent concentration, while keeping the other parameters constant ($F=56 \text{ L min}^{-1} \text{ m}^{-2}$; $Z=4.5 \text{ cm}$), is shown in Figure 2 b.). The first point that stands out is the shape of the breakthrough curves: for lower values of influent concentration, the adsorption occurs slowly, so the curve is less steep; for increased influent concentrations, the steepness of the slope increases, attaining bed saturation in less time. This increase in adsorption rate of MS-222 onto BSC for higher influent concentrations is associated with the relative concentration gradients, *i.e.*, higher concentration gradient at high influent concentration of MS-222 provides higher driving force for the transfer process to overcome the mass transfer resistance. In this case, the mass transfer zone is small and the adsorption process is mostly controlled by intraparticle diffusion, as several authors reported (Canteli et al., 2014; Salman et al.,

2011; Tan et al., 2008). From Table 1, it can be seen that higher influent concentrations reduce both the volume treated and the saturation time, while total adsorption capacity increases.

The breakthrough curves obtained for MS-222 adsorption onto different bed depths of BSC ($Z=4.5$; 9.0 and 13.0 cm) are illustrated in Figure 2 c.), at constant flux and influent concentration ($F=56$ L min⁻¹ m⁻²; $C_i=250$ mg L⁻¹). The results show that both breakthrough and saturation times increased as bed depth increased, and consequently the volume of treated effluent increased significantly (Table 1). The increase in the breakthrough time is related to the larger mass of adsorbent and to the longer distance it takes the mass transfer zone to move from the entrance to the exit of the bed when its depth is increased. On the other hand, the bed adsorption capacity varies only 4% for the different depths investigated.

3.2. Breakthrough curves data modelling

To describe the column breakthrough curves obtained at different fluxes, influent concentrations and bed depths, the models presented in section 2.2.2 were used. The experimental and theoretical breakthrough curves are shown in Figure 2 and the model parameters obtained from the corresponding fittings are presented in Table 2. Among the considered models, the one by Clark was the less appropriate to describe the experimental data, with coefficients of determination, r^2 , below 0.99 and predicted breakthrough times with a deviation larger than 18% from experimental data. Then, the Thomas and the Yoon-Nelson models better fitted the experimental data and are apparently coincident (Figure 2), both with similar coefficients of determination (Table 2). Both models predict the adsorption rate constant and, in general, they follow the same trend, *i.e.*, adsorption rate increased with increasing flux and decreased with

increasing bed depth. The discordance between the models is for the variation of influent concentration, for which according to the Thomas model the adsorption rate was not significantly affected, while according to the Yoon-Nelson model the adsorption rate increased with the increase of influent concentration, as already observed by experimental data, in section 3.1. Thomas model allows calculating the maximum adsorption capacity of the bed, q_{Th} , and the fitted values (Table 2) are in accordance with q_s shown in Tables 1, with less than 5% of deviation. Yoon-Nelson model predicts the time necessary to reach 50% of the influent concentration, $t_{50\%}$, and the fitted values are close to the experimental ones (Table 2), with less than 2% of deviation. So, the breakthrough curves predicted by either the Thomas or the Yoon-Nelson models showed reasonably good agreement with the experimental results, with some deviations at the beginning and at the end of the curves.

For all the conditions examined, the Dose-Response model was the most adequate to describe the experimental data, with the highest coefficients of determination, all above 0.996 (Table 2). From Figure 2, it is easily observed that the use of this model minimizes the errors presented by the other models considered in this work. The normalized concentration at saturation time (C_s/C_i) and $t_{50\%}$ were predicted by Dose-Response model (Table 2) with less than 2 and 1% of deviation from the experimental values (Table 1), respectively. This model has been widely applied for modelling continuous fixed-bed adsorption of inorganic pollutants, such as heavy metals (Calero et al., 2009; Singh et al., 2012), as well as for organic pollutants, such as pharmaceuticals (Katsigiannis et al., 2015).

3.3. *Aquaculture Wastewater*

The continuous experiment using aquaculture wastewater was carried out in order to evaluate the performance of a column packed with BSC for the removal of MS-222 in a real situation of salinity and, essentially, organic and inorganic matter. Breakthrough curves using synthetic and real matrices are presented in Figure 3 for the same conditions of flux, influent concentration and bed depth ($F=56 \text{ L min}^{-1} \text{ m}^{-2}$; $C_i=250 \text{ mg L}^{-1}$; $Z=4.5 \text{ cm}$). Both results are quite similar, although the wastewater breakthrough curve is less steeped in the beginning, increasing slightly the slope at the end of the curve and, consequently, attaining the bed saturation earlier (as can be seen in Table 1). However, Table 1 also shows that other experimental parameters do not diverge significantly: time and volume at breakthrough point have differences of 13% between matrices, while bed adsorption capacities differ only 6%.

The experimental and theoretical breakthrough curves using aquaculture wastewater as matrix are shown in Figure S2 and, for comparison purposes, the model parameters obtained from the corresponding fittings to both matrices are presented in Table S2. All models fit the experimental wastewater breakthrough curve, with r^2 higher than 0.99. Comparing the predicted parameters of both matrices, the adsorption rate parameters are slightly lower for the real matrix, which is a consequence of the lower steepness in the beginning of the curve, possibly caused by an initial competition between the organic and/or inorganic matter and MS-222 molecules for the adsorption sites onto BSC. However, as mentioned above, the bed adsorption capacity experimentally obtained was not significantly affected by the presence of organic and inorganic matter. Moreover, regarding the predicted q_{Th} , t_b and $t_{50\%}$ parameters, there are no differences between both synthetic and real matrices, with variations under 2% (see Table S2). Thus, it may be assumed that the presence of organic and inorganic matter in

solution does not affect the performance of the MS-222 continuous adsorption in a BSC packed column.

3.4. Scale-up

Figure 4 shows the iso-concentration lines for MS-222 retained in the fixed-bed at 10, 50 and 90% of breakthrough points for the three bed depths considered, as presented in Figure 2 c.). Table 3 gives the slopes and intercepts of the fitted lines, which correspond to a and b respectively, according to Equation (7). Also, Table 3 depicts BDST model parameters, N_0 and k_{BDST} , which were calculated from Equations (8) and (9). It may be observed that N_0 increased with increasing of breakthrough point, as for the increase of the slope, and the k_{BDST} decreased with increasing breakthrough point. However, the line for 50% of breakthrough does not pass through the origin, $b \neq 0$, which has been related by some authors with the existence of more than one rate-limiting step (Cortés-Martínez et al., 2008; El Qada et al., 2006). In fact, previous studies of adsorption kinetics of MS-222 onto BSC and other two adsorbents revealed the presence of two steps: for initial conditions, adsorption was controlled by intraparticle diffusion and then, when the molecules reach the intraparticle sites, the external diffusion becomes the rate limiting step (Ferreira et al., 2016).

For the scale-up experiment, both the internal diameter and bed depth of the fixed-bed column were increased up to 2.5 cm and 35 cm, respectively, and the flux used was $24 \text{ L min}^{-1} \text{ m}^{-2}$. Under these conditions, $v = 2.4 \text{ cm min}^{-1}$ and a new BDST model parameter, a_{new} was calculated recurring to Equation (12). Meanwhile, the intercept, b_{new} remained the same as for the unchanged initial concentration (C_i). Predicted and experimental breakthrough curves are represented in Figure 5 while Table 4 depicts the experimental and calculated times from BDST model for the breakthrough

points considered (10, 50 and 90%). As can be observed in Figure 5, the BDST model satisfactorily predicted experimental scale-up results, with a maximum deviation of 11% , which occurred for $C/C_i=0.7$. Thus, one can conclude that BDST model provides good prediction of breakthrough curves at different conditions.

3.5. *Regeneration studies*

Breakthrough curves after thermal regeneration of exhausted BSC are presented in Figure 6 for three consecutive cycles. It is clearly observed in Table 5 that t_b and, consequently, the volume of effluent treated at breakthrough, V_b , decreased 11, 34 and 48% at the first, second and third cycles, respectively. This may be related to the decrease of adsorption capacity of the regenerated BSC and/or to the loss of BSC during the thermal regeneration process, due to oxidation and attrition, which resulted in the loss of about 20% of weight. However, the time of saturation, t_s , and the bed adsorption capacity, q_s were slightly higher for the first regeneration cycle. For this first cycle of BSC saturation-regeneration, N₂ adsorption isotherms were performed and the results are presented in Table S3. It can be observed an obvious decrease of S_{BET} after BSC saturation with MS-222, while the total micropore volume analysis was inconclusive. During the BSC regeneration, may occur the thermal desorption of the adsorbed MS-222 molecules, together with some MS-222 degradation and, consequently, the S_{BET} increase significantly, without, however, attaining the original surface area. Therefore, BSC regeneration and reusability for the adsorption of MS-222 could be considered for one cycle, after which its performance decreases significantly. Notwithstanding, regeneration costs must be carefully addressed in view of the economic efficiency of the whole adsorption process. In this sense, considering the nature of the BSC precursor (waste produced at very large scale all over the world by pulp and paper mills) and its

production process (without applying any chemical or physical activation procedure), obtaining new BSC could be more profitable than its regeneration. In fact, low-cost adsorbents, such as those from waste products, are typically not regenerated but the exhausted materials are disposed of by landfill or incineration (Worch, 2012).

4. Conclusions

Continuous adsorption experiments of MS-222 onto BSC revealed that decreasing influent flux and concentration resulted in larger volume of effluent treated at breakthrough time; additionally, the highest volume treated (968 mL) was obtained for the highest bed depth (13 cm). Furthermore, a maximum bed adsorption capacity of 125 mg g^{-1} was obtained under a flux of $56 \text{ L min}^{-1} \text{ m}^{-2}$, with 400 mg L^{-1} of MS-222 in 4.5 cm bed depth. It was demonstrated that, in general, fixed-bed column data can be adequately described by the Dose-Response model with less than 2% of deviation from the experimental values. Also, the performance of the continuous adsorption in a BSC packed column using real aquaculture wastewater as matrix was not affected significantly in the presence of organic (high DOC content) and inorganic matter, which is a great advantage for the possible application of BSC as adsorbent in RASs.

On the other hand, the application of BDST model resulted in an excellent prediction of scale-up experiments, with an error of less than 11% compared with experimental data. The thermal regeneration process carried out with the exhausted BSC provided good results for its reusability only for one cycle ($q_s=124 \text{ mg g}^{-1}$); its performance decreased significantly in the subsequent cycles ($q_s=80 \text{ mg g}^{-1}$ in the third cycle). Considering the nature of its precursor, the use of new BSC could be more profitable than its regeneration, functioning also as an additional option for the management of such wastes.

In conclusion, the fixed-bed adsorption using BSC may be considered an inexpensive and environmentally friendly process which can be applied in the treatment of aquaculture wastewaters containing MS-222.

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References

- Akar, E., Altinişik, A., Seki, Y., 2013. Using of activated carbon produced from spent tea leaves for the removal of malachite green from aqueous solution. *Ecological Engineering* 52, 19-27.
- Calero, M., Hernáinz, F., Blázquez, G., Tenorio, G., Martín-Lara, M.A., 2009. Study of Cr (III) biosorption in a fixed-bed column. *Journal of Hazardous Materials* 171, 886-893.

- Calisto, V., Domingues, M.R.M., Erny, G.L., Esteves, V.I., 2011. Direct photodegradation of carbamazepine followed by micellar electrokinetic chromatography and mass spectrometry. *Water Research* 45, 1095-1104.
- Calisto, V., Ferreira, C.I.A., Santos, S.M., Gil, M.V., Otero, M., Esteves, V.I., 2014. Production of adsorbents by pyrolysis of paper mill sludge and application on the removal of citalopram from water. *Bioresource Technology* 166, 335-344.
- Canteli, A.M.D., Carpiné, D., Scheer, A.d.P., Mafra, M.R., Igarashi-Mafra, L., 2014. Fixed-bed column adsorption of the coffee aroma compound benzaldehyde from aqueous solution onto granular activated carbon from coconut husk. *LWT - Food Science and Technology* 59, 1025-1032.
- Clark, R.M., 1987. Evaluating the cost and performance of field-scale granular activated carbon systems. *Environmental Science & Technology* 21, 573-580.
- Cortés-Martínez, R., Solache-Ríos, M., Martínez-Miranda, V., Alfaro-Cuevas, R., 2008. Removal of Cadmium By Natural and Surfactant-Modified Mexican Zeolitic Rocks in Fixed Bed Columns. *Water, Air, and Soil Pollution* 196, 199-210.
- El Qada, E.N., Allen, S.J., Walker, G.M., 2006. Adsorption of Basic Dyes onto Activated Carbon Using Microcolumns. *Industrial & Engineering Chemistry Research* 45, 6044-6049.
- Ferreira, C.I.A., Calisto, V., Otero, M., Nadais, H., Esteves, V.I., 2016. Comparative adsorption evaluation of biochars from paper mill sludge with commercial activated carbon for the removal of fish anaesthetics from water in Recirculating Aquaculture Systems. *Aquacultural Engineering* 74, 76-83.
- Ferreira, C.I.A., Calisto, V., Santos, S.M., Cuerda-Correa, E.M., Otero, M., Nadais, H., Esteves, V.I., 2015. Application of pyrolysed agricultural biowastes as adsorbents for

fish anaesthetic (MS-222) removal from water. *Journal of Analytical and Applied Pyrolysis* 112, 313-324.

Gupta, V.K., Mittal, A., Krishnan, L., Gajbe, V., 2004. Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash. *Separation and Purification Technology* 40, 87-96.

Helfrich, L.A., Libey, G., 2011. *Fish Farming in Recirculating Aquaculture Systems*. Department of Fisheries and Wildlife Sciences; Virginia Tech.

Hutchins, R.A., 1973. New method simplifies design of activated carbon systems - Water bed-depth service time analysis. *Chemical Engineering Journal* 20, 133-138.

Katsigiannis, A., Noutsopoulos, C., Mantziaras, J., Gioldasi, M., 2015. Removal of emerging pollutants through Granular Activated Carbon. *Chemical Engineering Journal* 280, 49-57.

Lawson, T.B., 1995. *Fundamentals of aquacultural engineering*, 1st ed. Chapman & Hall, New York, USA.

Martins, C.I.M., Eding, E.H., Verdegem, M.C.J., Heinsbroek, L.T.N., Schneider, O., Blancheton, J.P., d'Orbcastel, E.R., Verreth, J.A.J., 2010. New developments in recirculating aquaculture systems in Europe: A perspective on environmental sustainability. *Aquacultural Engineering* 43, 83-93.

McKay, G., 1995. *Use of Adsorbents for the Removal of Pollutants from Wastewater*, 1st ed. CRC Press, New York, USA.

Miller, D., Semmens, K., 2002. *Waste Management in Aquaculture*. Aquaculture Information Series AQ02-1.

Mittal, A., Krishnan, L., Gupta, V.K., 2005. Removal and recovery of malachite green from wastewater using an agricultural waste material, de-oiled soya. *Separation and Purification Technology* 43, 125-133.

- Robinson, T., McMullan, G., Marchant, R., Nigam, P., 2001. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology* 77, 247-255.
- Ross, L.G., Ross, B., 2008. *Anaesthetic and Sedative Techniques for Aquatic Animals*, 3rd ed. Blackwell Publishing Ltd, Oxford, UK.
- Salman, J.M., Njoku, V.O., Hameed, B.H., 2011. Batch and fixed-bed adsorption of 2,4-dichlorophenoxyacetic acid onto oil palm frond activated carbon. *Chemical Engineering Journal* 174, 33-40.
- Sartape, A.S., Mandhare, A.M., Jadhav, V.V., Raut, P.D., Anuse, M.A., Kolekar, S.S., 2014. Removal of malachite green dye from aqueous solution with adsorption technique using *Limonia acidissima* (wood apple) shell as low cost adsorbent. *Arabian Journal of Chemistry* <http://dx.doi.org/10.1016/j.arabjc.2013.12.019>.
- Singh, A., Kumar, D., Gaur, J.P., 2012. Continuous metal removal from solution and industrial effluents using *Spirogyra* biomass-packed column reactor. *Water Research* 46, 779-788.
- Summerfelt, S.T., Sharrer, M.J., Tsukuda, S.M., Gearheart, M., 2009. Process requirements for achieving full-flow disinfection of recirculating water using ozonation and UV irradiation. *Aquacultural Engineering* 40, 17-27.
- Tan, I.A.W., Ahmad, A.L., Hameed, B.H., 2008. Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies. *Desalination* 225, 13-28.
- Thomas, H.C., 1944. Heterogeneous Ion Exchange in a Flowing System. *Journal of the American Chemical Society* 66, 1664-1666.

Topic Popovic, N., Strunjak-Perovic, I., Coz-Rakovac, R., Barisic, J., Jadan, M., Persin Berakovic, A., Sauerborn Klobucar, R., 2012. Tricaine methane-sulfonate (MS-222) application in fish anaesthesia. *Journal of Applied Ichthyology* 28, 553-564.

Worch, E., 2012. *Adsorption Technology in Water Treatment, Fundamentals, Processes, and Modeling*, 1st ed. Walter de Gruyter GmbH & Co. KG, Berlin, Germany.

Yan, G., Viraraghavan, T., Chen, M., 2001. A New Model for Heavy Metal Removal in a Biosorption Column. *Adsorption Science & Technology* 19, 25-43.

Yoon, Y.H., Nelson, J.H., 1984. Application of Gas Adsorption Kinetics I. A Theoretical Model for Respirator Cartridge Service Life. *American Industrial Hygiene Association Journal* 45, 509-516.

— Thomas Model   --- Clark Model
 --- Yoon-Nelson Model   — Dose-response Model

Figure Captions

Figure 1 - Schematic diagram of the experimental setup for fixed-bed column experiments.

Figure 2 - Breakthrough curves for MS-222 adsorption onto BSC at different **a.)** flux; **b.)** influent concentration, and **c.)** bed depth. The experimental data were fitted to Thomas, Clark, Yoon-Nelson and Dose-Response models.

Figure 3 - Breakthrough curves for adsorption of MS-222 in ultra-pure water and aquaculture wastewater onto BSC.

Figure 4 - Iso-concentration lines for breakthrough points of 10, 50 and 90% and for bed depths of 4.5, 9 and 13 cm ($C_i=250 \text{ mg L}^{-1}$; $F=56 \text{ L min}^{-1} \text{ m}^{-2}$; $v=5.6 \text{ cm min}^{-1}$).

Figure 5 - BDST model predicted and experimental breakthrough curves of scale-up experiment ($C_i=250 \text{ mg L}^{-1}$; $Z=35 \text{ cm}$; $F=24 \text{ L min}^{-1} \text{ m}^{-2}$; $v=2.4 \text{ cm min}^{-1}$).

Figure 6 - Breakthrough curves for saturation of BSC with MS-222 and subsequent cycles of regeneration-adsorption ($F=56 \text{ L min}^{-1} \text{ m}^{-2}$; $C_i=250 \text{ mg L}^{-1}$; $Z=13 \text{ cm}$).

Tables

Table 1 - Column data from breakthrough curves for the fixed-bed adsorption of MS-222 (solutions in ultra-pure water) onto BSC at different fluxes (F); influent concentrations (C_i); bed depths (Z); and also using aquaculture wastewater as matrix

	t_b (min)	V_b (ml)	$t_{50\%}$ (min)	t_s (min)	q_s (mg g ⁻¹)
F (L min⁻¹ m⁻²)					
15	365	438	400	515	104
27	165	347	188	290	102
56	80	352	99	155	102
C_i (mg L⁻¹)					
100	170	748	205	310	87
250	80	352	99	155	102
400	57	251	66	93	125
Z (cm)					
4.5	80	352	99	155	102
9	130	572	175	285	98
13	223	968	245	345	102
Aquaculture Wastewater^a	70	308	100	125	108

^a Conditions: $F=56$ L min⁻¹m⁻²; $C_i=250$ mg L⁻¹; $Z=4.5$ cm

Table 2 - Thomas, Clark, Yoon-Nelson and Dose-Response model parameters at different flux, influent concentration and bed depth

Parameters	F (L min ⁻¹ m ⁻²)				C_i (mg L ⁻¹)				Z (cm)			
	15	27	56		100	250	400		4.5	9	13	
Thomas	k_{Th} (mL min ⁻¹ mg ⁻¹)	0.167±0.007	0.22±0.01	0.40±0.02	0.49±0.01	0.40±0.02	0.40±0.02		0.40±0.02	0.185±0.005	0.28±0.01	
	q_{Th} (mg g ⁻¹)	102.8±0.3	99.0±0.6	107.5±0.5	85.6±0.3	107.5±0.5	124.0±0.6		107.5±0.5	96.4±0.4	106.2±0.3	
	r^2	0.99	0.99	1.00	0.99	1.00	0.99		1.00	1.00	0.99	
Clark	k_C (min ⁻¹)	0.1246±0.0007	0.203±0.002	0.362±0.003	0.155±0.001	0.362±0.003	0.618±0.004		0.362±0.003	0.169±0.001	0.249±0.001	
	t_b (min)	435	207	108	227	108	72		108	194	260	
	r^2	0.96	0.97	0.99	0.98	0.99	0.98		0.99	0.98	0.98	
Yoon-Nelson	k_{YN} (min ⁻¹)	0.038±0.001	0.053±0.003	0.099±0.004	0.046±0.001	0.099±0.004	0.170±0.008		0.099±0.004	0.046±0.001	0.067±0.003	
	$t_{50\%}$ (min)	408±1	193±1	99.3±0.5	207.8±0.7	99.3±0.5	67.1±0.3		99.3±0.5	176.0±0.6	247.6±0.7	
	r^2	0.99	0.99	1.00	0.99	1.00	0.99		1.00	1.00	0.99	
Dose-Response	C_s/C_i	0.944±0.008	0.950±0.006	0.962±0.002	0.971±0.002	0.962±0.002	0.967±0.003		0.962±0.002	0.970±0.003	0.956±0.004	
	$t_{50\%}$ (min)	402.3±0.9	188.6±0.7	97.7±0.2	204.7±0.3	97.7±0.2	66.2±0.1		97.7±0.2	172.6±0.3	245.1±0.4	
	a	17.8±0.6	11.5±0.4	10.8±0.2	10.4±0.1	10.8±0.2	12.3±0.3		10.8±0.2	8.5±0.1	18.4±0.5	
	r^2	1.00	1.00	1.00	1.00	1.00	1.00		1.00	1.00	1.00	

Table 3 - Predicted parameters for the BDST model at $F=56 \text{ L min}^{-1} \text{ m}^{-2}$

C/C_i	$a \text{ (min cm}^{-1}\text{)}$	$b \text{ (min)}$	$N_0 \text{ (mg mL}^{-1}\text{)}$	$k_{BDST} \text{ (mL mg}^{-1} \text{ min}^{-1}\text{)}$	r^2
0.10	16.7	2.89	22.9	3.10	0.9588
0.50	17.1	-22.7	23.4	0	0.9998
0.90	20.6	-35.1	28.4	0.255	0.9962

Table 4 - Predicted breakthrough times based on the BDST model parameters for scale-up column at $v=2.4 \text{ cm min}^{-1}$

C/C_i	$a' \text{ (min cm}^{-1}\text{)}$	$b' \text{ (min)}$	$t_{cal} \text{ (h)}$	$t_{exp} \text{ (h)}$	Error (%)
0.10	38.1	2.89	22.2	21.3	4
0.50	39.1	-22.7	23.2	25.7	10
0.90	47.3	-35.1	28.2	29.7	5

Table 5 - Column data obtained from BSC saturation and subsequent regeneration-adsorption cycles ($F=56 \text{ L min}^{-1} \text{ m}^{-2}$; $C_i=250 \text{ mg L}^{-1}$; $Z=13 \text{ cm}$)

	$t_b \text{ (min)}$	$V_b \text{ (ml)}$	$t_{50\%} \text{ (min)}$	$t_s \text{ (min)}$	$q_s \text{ (mg g}^{-1}\text{)}$
BSC saturation	223	968	245	345	102
Cycle 1	195	858	250	360	124
Cycle 2	145	638	195	355	100
Cycle 3	115	506	150	230	80

Supplementary Material

Fixed-bed adsorption of Tricaine Methanesulfonate onto pyrolysed paper mill sludge

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Thermogravimetric analysis (TGA) procedure

Thermal analysis of MS-222 was carried out by thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTGA). Non-isothermal TG analysis was performed using a TAG analyser (Shimadzu TGA-50 instrument). The analysis was carried out under a $20 \text{ cm}^3 \text{ min}^{-1}$ N_2 flow at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ from room temperature to $950 \text{ }^\circ\text{C}$. Approximately 20 mg of sample was used. The weight loss (TG) and derivative curves (DTG) of MS-222 was represented as a function of temperature, to allow the known of MS-222 degradation temperatures.

Figure S1 - TG and DTG curves of MS-222.

Table S1 - Physico-chemical properties of MS-222

MS-222	
Structure	
CAS	886-86-2
M_w (g mol ⁻¹)	261.29
S_w (g L ⁻¹)	100
pKa	3.6 ^a
ACD/logD (pH 7.4)	1.54

Source: ChemIDplus, U.S. National Library of Medicine.

M_w – Molecular weight

S_w – Water solubility (20 °C)

pKa – Acid dissociation constant (25 °C)

ACD/log D - octanol-water distribution constant from ACD/Labs Software

^a Value from Dubé and Epel (1986).

Figure S2 - Breakthrough curves for MS-222 adsorption onto BSC in a real aquaculture wastewater matrix.

Table S2 – Thomas, Clark, Yoon-Nelson and Dose-Response model parameters for different matrices

Model	Parameters	Ultra-pure water	Aquaculture wastewater
		$F=56 \text{ L min}^{-1} \text{ m}^{-2}$; $C_i=250 \text{ mg L}^{-1}$; $Z=4.5 \text{ cm}$	
Thomas	$k_{Th} (\text{mL min}^{-1} \text{ mg}^{-1})$	0.40 ± 0.02	0.30 ± 0.01
	$q_{Th} (\text{mg g}^{-1})$	107.5 ± 0.5	109.1 ± 0.6
	r^2	1.00	1.00
Clark	$k_C (\text{min}^{-1})$	0.362 ± 0.003	0.25 ± 0.01
	$t_b (\text{min})$	108	110
	r^2	0.99	0.99
Yoon-Nelson	$k_{YN} (\text{min}^{-1})$	0.099 ± 0.004	0.078 ± 0.003
	$t_{50\%} (\text{min})$	99.3 ± 0.5	97.0 ± 0.5
	r^2	1.00	1.00
Dose-Response	C_s/C_i	0.962 ± 0.002	1.07 ± 0.02
	$t_{50\%} (\text{min})$	97.7 ± 0.2	98 ± 1
	a	10.8 ± 0.2	6.7 ± 0.4
	r^2	1.00	0.99

Table S3 – N₂ isotherms of BSC before and after saturation and after regeneration

Sample	BSC ^a	BSC saturated (cycle 1)	BSC regenerated (cycle 1)
$S_{BET} (\text{m}^2 \text{ g}^{-1})$	258	98.6	195
$W_0 (\text{cm}^3 \text{ g}^{-1})$	0.039	-	0.023

^aValues from Ferreira et al. (2016).

S_{BET} – specific surface area; W_0 - total micropore volume

References

Dubé, F., Epel, D., 1986. The relation between intracellular pH and rate of protein synthesis in sea urchin eggs and the existence of a pH-independent event triggered by ammonia. *Experimental Cell Research* 162, 191-204.

Ferreira, C.I.A., Calisto, V., Otero, M., Nadais, H., Esteves, V.I., 2016. Comparative adsorption evaluation of biochars from paper mill sludge with commercial activated carbon for the removal of fish anaesthetics from water in Recirculating Aquaculture Systems. *Aquacultural Engineering* 74, 76-83.

Highlights

- MS-222 adsorption in a column packed with biological paper mill sludge-based carbon;
- A total adsorption capacity of 125 mg g⁻¹ was obtained, in a lab-scale;
- No competitive effect was observed in adsorption using real aquaculture wastewater;
- Bed depth service time model provided good predictions to scale-up;
- Biochar production acts as wastes management adding economical value.