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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

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ABSTRACT

Tricaine methanesulfonate (MS-222), benzocaine and 2-phenoxyethanol (2-PE) are widely used in intensive aquaculture systems to control stress during handling and confinement operations. This work aimed to study the adsorptive removal of these anaesthetics from water, comparing two waste-based adsorbents produced by pyrolysis of paper mill sludge with a commercial activated carbon. The use of commercial activated carbon resulted in maximum adsorption capacities of 631, 435 and 289 mg g^{-1} for MS-222, benzocaine and 2-PE, respectively (obtained by the fitting of Langmuir-Freundlich model), which are between 4 and 8 times higher than those determined for the alternative adsorbents. Even so, the obtained results point to the promissory utilization of these waste-based adsorbents in Recirculating Aquaculture Systems, as an integrated way of managing such residues and treatment of aquaculture waters contaminated with anaesthetics.

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1. Introduction

World food fish aquaculture production has grown in the last decade, expanding at an average annual rate of 6.2% in the period 2000–2012. The implementation of systems for the indoor rearing (intensive aquaculture system) of many species of fish have also contributed to this impressive development. Holding of fish under indoor controlled conditions, nutrient cycles, bacterial action and water quality have been important to rear fish in intensive aquaculture systems (FAO, 2014). Organic chemical therapeutants are often used in intensive aquaculture systems to manage the animals, treat diseases and control growth, reproduction and stress. Anaesthetics are administered to farmed fish to control stress during handling and confinement operations, such as netting, weighing, sorting, vaccination, transport and slaughter (Ashley, 2007; Harikrishnan et al., 2011; Zahl et al., 2012). The most widely fish anaesthetics used in intensive aquaculture systems are tricaine methanesulfonate (MS-222), commercially named by Tricaine-S, benzocaine and 2-phenoxyethanol (2-PE) (Costello et al., 2001; EFSA, 2008; FDA, 2011; Ross and Ross, 2008). The recommended doses of each anaesthetic are significantly different among species and depend on the desired anaesthesia level: MS-222 concentration varies from 20 mg L^{-1} to 480 mg L^{-1} (for *Hippoglossus hippoglossus* and *Cyprinus carpio*, respectively); benzocaine varies between 25 mg L^{-1} and 200 mg L^{-1} (for *Salmo solar* and *Prochilodus lineatus*, respectively); 2-phenoxyethanol varies from 0.1 cm^3 L^{-1} to 1.2 cm^3 L^{-1} (for *Oncorhynchus nerka* and *Cyprinus carpio*, respectively) (Ross and Ross, 2008; Topic Popovic et al., 2012). MS-222 is acidic in solution and could be irritant to fish (Palmer and Mensinger, 2004) and to prevent this effect, the anaesthetic solutions should be buffered using sodium bicarbonate or Tris-buffer at pH 7.0–7.5 (Ross and Ross, 2008). These pharmaceuticals are administrated by inhalation, *i.e.*, solubilized in the tank's water, which, therefore, becomes contaminated.

The water quality is one of the most critical factors for the success of the fish culture in aquaculture activity. The implementation of Recirculating Aquaculture Systems (RASs) in intensive fish culture systems allows cleaning the water for reuse through fish culture tanks, maintaining the water quality. RASs also provide the opportunity to reduce water consumption and, at the

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same time, to decrease the discharge of waste, specially organic pollutants, into the environment (Martins et al., 2010). A typical RAS consists of primary decantation (primary treatment), nitrification (biological treatment), oxygenation, ozonation and, more recently, UV irradiation aiming at the removal of organic matter, mainly nitrogen-containing compounds, and disinfection (Lepine et al., 2015; Martins et al., 2010; Summerfelt et al., 2009; Wik et al., 2009). The use of carbon filters has been purposed in addition to biological filters as a polishing stage to remove persistent nonbiodegradable organic materials where the veterinary pharmaceuticals are included (Lawson, 1995; Oladoja et al., 2015). In this sense, the adsorptive removal of chemical therapeutants used in aquaculture from water has been scarcely studied and mostly using activated carbon as adsorbent: Aitcheson et al. (2000) efficiently removed malachite green, formaldehyde, chloramine-T and oxytetracycline from their single and multicomponent solutions by adsorption onto an activated carbon in batch system (Aitcheson et al., 2000, 2001); also, Marking et al. (1990) tested the large scale continuous removal of malachite green (ectoparasiticide and fungicide) from hatchery effluent using an activated carbon filter and obtained about 69 mg g^{-1} of adsorption capacity. Concerning the fish anaesthetics, Dawson et al. (1976) tested the adsorption of MS-222, benzocaine and other fish toxicants onto activated carbon and the maximum adsorption capacity obtained was up to 64 mg g^{-1} (Dawson et al., 1976). Despite their high efficiency, the main drawback of activated carbons is their high price (Rakić et al., 2013), which is highly related to the raw material costs and the activation route (Stavropoulos and Zabaniotou, 2009). Alternatively, the authors of this work produced adsorbents just by the pyrolysis of agricultural biowastes and without any activation step, and successfully used them for the adsorptive removal of MS-222 from water with adsorption capacities up to 34 mg g^{-1} (Ferreira et al., 2015).

The present work aimed to study the utilization of adsorbents produced from industrial residues whose management is challenging (primary and biological paper mill sludge), for removal of three different fish anaesthetics, MS-222, benzocaine and 2-PE, from water. Also, the comparison of the adsorptive performance of these alternative materials with that of a commercial powder activated carbon (PAC) was aimed.

2. Materials and methods

2.1. Adsorbent materials

Two adsorbents based on paper mill sludge were produced following the procedure described by Calisto et al. (2014). Briefly, primary and biological paper mill sludge, PS and BS respectively, were pyrolysed at 800 °C for 150 min (heating ramp of 10 °C min^{-1}), under N_2 saturated atmosphere, using a muffle (Nüve furnace MF 106), corresponding to PS800-150 and BS800-150. Both biochars were washed with HCl 1.2 M followed by distilled water until neutral pH, for removal of ashes and other inorganic matter. After washing, pyrolysed and washed PS and BS were dried in an oven for 24 h at 105 °C, originating PS800-150-HCl and BS800-150-HCl, respectively (diameter: <0.18 mm).

The commercial powder activated carbon PULSORB (PAC), provided by Chemviron Carbon, was used as reference carbon for comparison proposes (diameter: 0.05 mm).

2.2. Materials characterization

The acquisition of the data of elemental analysis involving the determination of the sample content in C, H, N and S was performed in a LECO TruSpec CHNS Micro analyzer, using sulfamethazine as calibration standard. The oxygen content was calculated by difference.

The quantification of functional groups present on the adsorbents surface (biochars and PAC) was performed by the Boehmí's method (Boehm, 1994). Accordingly, each adsorbent was added to 0.05 M NaOH (99.3%, José Manuel Gomes dos Santos, Portugal), 0.05 M $NaHCO_3$ (>99.5%, Fluka), 0.05 M Na_2CO_3 (>99.5%, Panreac) or 0.05 M HCl (37%, Panreac) solutions into polypropylene tubes at a final concentration of 10 g L^{-1}, under N_2 atmosphere. The mixture was stirred in an overhead shaker (Heidolph, Reax 2) at 200 rpm, inside a thermostatic incubator at 25 °C for 24 h. Subsequently, the supernatants were filtered and 15 mL of each one were titrated with 0.1 M HCl or 0.1 M NaOH solutions in order to quantify the total acid and basic functional groups, respectively. In addition, the different acidic groups on the adsorbents surface were determined as follows: the amount of carboxyl groups was estimated by neutralization with $NaHCO_3$ solution; the amount of lactones was obtained from the difference between the neutralization with Na_2CO_3 solution and that determined for the $NaHCO_3$ solution; and the amount of phenols was estimated from the difference between the neutralization with NaOH solution and that determined for the Na_2CO_3 solution. Note that NaOH and HCl solutions were standardized with $C_8H_5KO_4$ (99.8%, Panreac) and Na_2CO_3 solutions, respectively, for the determination of their exact concentration.

The point of zero charge (PZC) of each adsorbent was obtained according to the procedure described by Souza et al. (2014). Accordingly, the highest dosage of PS800-150-HCl, BS800-150-HCl and PAC used in the adsorption experiments (6, 5 and 1.5 g L^{-1}, respectively) was shaken with 0.1 M NaCl (>99.5%, Panreac) solutions in polypropylene tubes at different initial pH (pH_i) ranging from 2 to 11. The pH was adjusted using 1 M and 0.1 M of NaOH or HCl solutions. After equilibration for 24 h, the final pH was measured (pH_f). The PZC value (pH_{PZC}) corresponds to the pH at which pH_i and pH_f coincided, which was determined by plotting the ΔpH *vs.* pH_i (the PZC corresponds to pH value where the curve crosses the *x*-axis).

The N_2 adsorption isotherms were acquired at 77 K using a Micromeritics Instrument, Gemini VII 2380. The samples were previously outgassed at 120 °C for 12 h.

2.3. Fish anaesthetics

Adsorption tests were performed for three fish anaesthetics: Tricaine methanesulfonate (>97%, TCI Europe)—MS-222; Ethyl 4-Aminobenzoate (>99%, TCI Europe)—Benzocaine, and 2-Phenoxyethanol (>98.5%, TCI Europe)—2-PE. All anaesthetic solutions were buffered using $NaHCO_3$ to pH 7–7.5, according to the recommended by Ross and Ross (2008). The anaesthetics physicochemical properties relevant to this work are summarized in Table 1.

2.4. Determination of the anaesthetics concentration in water by micellar electrokinetic chromatography (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 anaesthetics in the aqueous phase. A dynamically coated silica capillary was used as described by Calisto et al. (2011). For capillary coating, hexadimethrine bromide (polybrene, ≥95%, Sigma Aldrich), sodium chloride and sodium hydroxide 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 for 2.8 min, at 30 °C. Detection of benzocaine, MS-222 and 2-PE were monitored at 200, 220 and 230 nm, respectively. The separation buffer consisted on 20 mM of sodium tetraborate (Borax, Riedel-de Haën) and 30 mM of sodium dodecylsulphate

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