Chemosphere 111 (2014) 24–31

Contents lists available at ScienceDirect

Chemosphere

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

Formulation of an alginate-vineyard pruning waste composite as a new eco-friendly adsorbent to remove micronutrients from agroindustrial effluents

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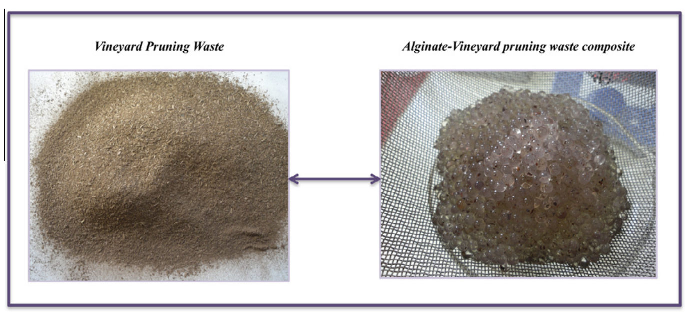
HIGHLIGHTS

- Winery wastewater micronutrients.
- Alginate-vineyard pruning waste composite as adsorbent.
- Eutrophication reduction.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 June 2013
Received in revised form 14 February 2014
Accepted 1 March 2014

Handling Editor: X. Cao

Keywords:
Alginate-vineyard pruning waste composite
Eco-friendly adsorbent
Agroindustrial wastewater
Micronutrients
Adsorption

ABSTRACT

The cellulosic fraction of vineyard pruning waste (free of hemicellulosic sugars) was entrapped in calcium alginate beads and evaluated as an eco-friendly adsorbent for the removal of different nutrients and micronutrients (Mg, P, Zn, K, N–NH_4, SO_4, TN, TC and PO_4) from an agroindustrial effluent (winery wastewater). Batch adsorption studies were performed by varying the amounts of cellulosic adsorbent (0.5–2%), sodium alginate (1–5%) and calcium chloride (0.05–0.9 M) included in the biocomposite. The optimal formulation of the adsorbent composite varied depending on the target contaminant. Thus, for the adsorption of cationic contaminants (Mg, Zn, K, N–NH_4 and TN), the best mixture comprised 5% sodium alginate, 0.05 M calcium chloride and 0.5% cellulosic vineyard pruning waste, whereas for removal of anionic compounds (P, SO_4 and PO_4), the optimal mixture comprised 1% sodium alginate, 0.9 M calcium chloride and 0.5% cellulosic vineyard pruning waste. To remove TC from the winery wastewater, the optimal mixture comprised 3% of sodium alginate, 0.475 M calcium chloride and 0.5% cellulosic vineyard pruning waste.

1. Introduction

The over-enrichment of water with micronutrients (such as P, N–NH_4, PO_4, K and Mg) has emerged as one of the main causes of poor water quality (Garg and Garg, 2002). Effluents from wine- and food-related industries contain micronutrients that can cause serious environmental problems due to the eutrophication of rivers and lakes. To prevent such problems, the development of safe effective treatments, such as eco-friendly adsorbents, is a current challenge for chemical engineers.

Lignocellulosic waste biomass is gaining attention worldwide as a renewable, widely available, cheap and environmental friendly source of carbon for biotechnological processes (Bustos et al.,

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http://dx.doi.org/10.1016/j.chemosphere.2014.03.004
0045-6535/

2005; Moldes et al., 2007; Portilla-Rivera et al., 2009; Vecino et al., 2012a) and for making adsorbent materials (Nethaji and Sivasamy, 2011).

Previous studies have shown that many types of lignocellulosic waste, such as vineyard pruning waste, can be hydrolyzed to extract hemicellulosic sugars, which can be fermented easily and cheaply to produce valuable substances, such as lactic acid and biosurfactants. However, the cellulosic fraction of the lignocellulosic material remains as a by-product of this process (Bustos et al., 2005; Moldes et al., 2007; Portilla-Rivera et al., 2009; Vecino et al., 2012a). The implementation of such processes on an industrial scale must be cost competitive with chemical synthesis, and this can generally only be achieved when several valuable products can be obtained from the same residue (Devesa-Rey et al., 2011b). Thus, the use of the hydrolyzed cellulosic fraction of vineyard pruning waste as an eco-friendly adsorbent is of potential interest for increasing the cost-effectiveness of the biotechnological production of biosurfactants or lactic acid based on the utilization of hemicellulosic sugars from lignocellulosic residues.

Some crude lignocellulosic residues have been tested as adsorbents; for example, Villaescusa et al. (2004) and Yuan-Shen et al. (2004) evaluated the application of grape stalk waste and wine processing waste to remove heavy metals from water, and Paradelo et al. (2009) evaluated the capacity of grape marc compost to remove dye compounds from winery effluents.

Devesa-Rey et al. (2011a) and Vecino et al. (2012b) proposed the immobilization of activated carbon in alginate beads to produce a more commercially viable and manageable adsorbent. The adsorbent was tested for its effectiveness in removing dye compounds from winery effluents, and it was found to reduce the color index of effluents from winery industry by almost 100%.

In the present study, vineyard pruning waste was hydrolyzed with sulfuric acid to yield a solid fraction, comprising cellulose and lignin, which was entrapped in calcium alginate beads to produce a commercially viable and manageable adsorbent. The formulation of this biocomposite was optimized on the basis of its capacity to remove nutrients and micronutrients (Mg, P, Zn, K, $N–NH_4$, SO_4, TN, TC and PO_4) from a winery effluent.

2. Materials and methods

2.1. Preparation of the eco-adsorbent

Vineyard pruning waste was collected from local wine-producers in Galicia (NW Spain). The lignocellulosic biomass was dried and milled (<1 mm), homogenized in a single batch (to avoid compositional differences) and stored until use. Based on previous works (Bustos et al., 2004), samples of the ground vineyard pruning waste were hydrolyzed under constant conditions (3% H_2SO_4, 15 min, 130 °C, liquid/solid ratio 8:1 g/g), and the solid fraction, mainly comprising cellulose and lignin, was washed with water and air-dried.

2.2. Characterization of the lignocellulosic fraction of vineyard pruning waste

The composition of the vineyard pruning waste was determined by quantitative hydrolysis (Cruz et al., 2007). The waste was first hydrolyzed with 72% sulfuric acid, at 30 °C for 1 h, and then diluted with water (to 4% sulfuric acid) and heated at 121 °C for 1 h. The solid residue remaining after hydrolysis was considered to be Klason lignin; the hydrolysates, which contain the monomeric sugars of vineyard pruning waste (mainly glucose and xylose) were analyzed by HPLC, on an Interaction ION-300 column (Alltech, Breda, The Netherlands) mobile phase, H_2SO_4 0.01 M; flow rate, 0.4 mL min^{-1}; IR and UV detection. The percentage of cellulose and hemicelluloses in the solid fraction was calculated on the basis of the contents of monomeric sugars, glucose and xylose in the hydrolysates.

The waste was then decomposed (by thermocatalysis), and the contents of C, N, H and S were determined in a Fisons-EA-1108 CHNS-O element analyser (Thermo Scientific).

2.3. Characterization of the agroindustrial effluent

Effluent was collected from local wineries. The micronutrients analyzed in this agroindustrial wastewater were: Mg, P, Zn, K, $N–NH_4$, SO_4, TN, TC and PO_4.

Samples before determination of Mg, K, P and Zn were acidified and heated by microwave digestion. The digested samples were quantified by inductively coupled plasma-optical emission spectrometry (ICP-OES, Perkin Elmer, Norwalk, USA, Optima 4300 DV). The instrumental operating parameters applied for the determination of Mg (285.213 nm), P (213.617 nm), Zn (206.200 nm) and K (766.490 nm) by ICP-OES were as followed: radial mode; 1300 W; the nebulizer was cross-flow and the spray chamber was scott-type. The gas flow for plasma, auxiliary gas and nebulizer were 15, 0.2 and 1.4 L min^{-1} respectively.

Total Carbon (TC) and Total Nitrogen (TN) were digested by thermocatalysis (Multi N/C 3100, Analytik Jena, Jena, Germany) and analyzed by non-dispersive IR detection and chemiluminescence detection respectively.

The PO_4 and SO_4 contents were analyzed by ion chromatography (709 IC Pump, 732 IC Conductivity Detector, 733 IC Separation Center and Metrosep A Supp 5 as column, Metrohm, Herisau, Switzerland), and the $N–NH_4$ was determined by the colorimetric method-Berthelot‘s reaction (Glick, 1969), using a segmented continuous flow autoanalyser (Bran + Luebbe AA3 autoanalyser). The green complex from the reaction was measured at 660 nm.

2.4. Formulation of the eco-friendly adsorbent

Different formulations of alginate-vineyard pruning waste composite were prepared by mixing hydrolyzed biomass from vineyard

Table 1
Independent and dependent variables used in this study.

Variable	Nomenclature	Units	Range of variation
(a) Independent variables			
Vineyard pruning waste	V	%	0.5–2
Sodium alginate	A	%	1–5
Calcium chloride	C	M	0.05–0.900
Variable	**Nomenclature**	**Definition**	**Range of variation**
(b) Dimensionless, coded independent variables			
Vineyard pruning waste	x_1	(V-1.25)/0.75	(−1, 1)
Sodium alginate	x_2	(A-3)/2	(−1, 1)
Calcium chloride	x_3	(C-0.475)/0.425	(−1, 1)
Variable	**Nomenclature**	**Units**	
(c) Dependent variables			
qE_{Mg}	y_1	mg g^{-1}	
qE_P	y_2	mg g^{-1}	
qE_{Zn}	y_3	mg g^{-1}	
qE_K	y_4	mg g^{-1}	
qE_{N-NH4}	y_5	mg g^{-1}	
qE_{SO4}	y_6	mg g^{-1}	
qE_{TN}	y_7	mg g^{-1}	
qE_{TC}	y_8	g g^{-1}	
qE_{PO4}	y_9	mg g^{-1}	