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Mixtures including wastes from the mussel shell processing industry: retention of arsenic, chromium and mercury

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A B S T R A C T

Three mixtures containing ashes from the mussel shell calcination industry, sewage sludge, wood ash and/or mussel shell were studied. Such wastes are difficult to recycle individually, but performing adequate mixtures could aid to solve this problem. Two mixtures included different percentages of mussel shell calcination ashes, sewage sludge and mussel shell, while the third was composed by mussel shell calcination ashes, sewage sludge and wood ash. Adsorption was very high for some pollutants: 98–99% for Hg, and 90–96% for As, while it was not higher than 32% for Cr. The pH values in the mixtures showed a clear diminution in the alkalinity of the shell ashes. Further, a drastic reduction of the extreme electric conductivity of these ashes occurred. The carbon/nitrogen ratio in the mixtures clearly improved when compared with the individual wastes. The nutrient content was similar in the three mixtures. The heavy metals concentrations were low in all three mixtures. Calcite was the most prevalent crystalline compound (≥83%) and aragonite was greater than 3.7%. In view of these results, using such mixtures would facilitate the treatment and recycling of shell calcination ashes, as well as other wastes. The mixtures could be useful in degraded environments, such as mine dumps, due to their nutrient content and the adsorption potential for Hg and As.

1. Introduction

Mussel shells (*Mytilus galloprovincialis* Lamark) generated in the cannery industries are wastes with significant world production. In Galicia (Spain), more than 80,000 tonnes (Mg) of waste mussel shell are produced yearly (Peña-Rodríguez et al., 2010). Some factories treat this waste by calcination, with the aim of eliminating organic matter and finally obtaining an end product with commercial value. The calcination process creates a valuable material (calcined mussel shell) and new wastes. Some of these wastes are solid materials (namely calcination ashes), pasty materials (sewage sludge from the wastewater treatment plants in the same factories), liquid wastes (wastewaters) and exhaust gases.

Mussel shell calcination ashes are especially problematic wastes, which may attain a yearly production of 2000 Mg just in Galicia (Spain). Some relevant characteristics of this waste are: very high electric conductivity (EC), very alkaline pH, and physical and sensorial properties that makes it difficult to recycle the material. There is no current treatment for the productive reuse of this waste. Therefore, it is desirable to design treatment alternatives that are technically and scientifically founded to facilitate the reuse of these ashes.

Mussel shell calcination ashes have not been studied extensively. Pérez-Gregorio et al. (2010) examined the use of mussel shell ashes to retain polycyclic aromatic hydrocarbons, but they were discarded due to having polycyclic aromatic hydrocarbons by themselves.

In another study, Fernández-González et al. (2011) reported the polychlorinated biphenyls contents of this material.

There exist a significant body of literature on the use of other types of ashes, e. g., for recycling in cement. Reijnders (2005), reviewed disposal, uses and treatment of combustion ashes, indicating that there is substantial use of ashes from coal fired power plants in clinker production in the cement industry. Pan et al. (2008) studied the reuse of municipal solid waste incineration ash as a raw material for cement production, finding that, after

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Table 1
Materials included in the three mixtures studied (percentages, wet and dry basis; average values of 3 replicates; the coefficients of variation were <5% in all cases).

Mixture	% (w/w, wet basis)				% (w/w, dry basis)			
	Sewage sludge	Mussel ash	Wood ash	Mussel shell	Sewage sludge	Mussel ash	Wood ash	Mussel shell
M-32	58	39	0	3	45	51	0	4
M-58	60	30	0	10	47	40	0	13
M-78	60	35	5	0	47	48	5	0

performing various pretreatment processes, this production path can be a feasible alternative to disposal for the management of these ashes. Rajamma et al. (2009), studying new cement formulations incorporated with the biomass fly ashes sourced from a thermal power plant and from a co-generation power plant, found a good potential for the utilization in cement formulation.

Ballester et al. (2007) demonstrated the usefulness of mussel shell for the production of mortars, which could encourage future research on similar uses for ashes derived from the calcination of mussel shell.

Other alternatives to facilitate the productive recycling of these mussel shell ashes could be reusing this material on degraded environments, such as mine dumps, with the objective of favouring plant growth. But there are severe limitations to that, mainly due to the very high EC. If these ashes could be integrated into mixtures, especially with other wastes, whereby synergies removed undesirable qualities, the end products may be productively recycled, e. g., in mine dumps, productively recycling each component.

Some materials that could be used to form into mixtures could be sewage sludge, calcined mussel shell and wood ash. Such materials, having EC values lower than shell calcination ashes, would diminish the EC in the final mixture (high EC values meaning high soluble salts concentrations, it could damage plants and soils, so making interesting to achieve lower EC levels). Calcined mussel shell has proved to be adequate to improve soil condition and plant growth (Álvarez et al., 2012a, b), and wood ashes have been largely used and have shown low risk of water pollution, even in sloped areas (Núñez-Delgado et al., 2011).

Several studies support the benefit of mixtures of wastes showing better physical, chemical, organoleptic and agronomical characteristics than each residue alone. Pousada-Ferradás et al. (2011) studied mixtures including sewage sludge and wood ash, finding that the mixing process facilitated the treatment of each residue, and that the mixture could be used for agronomical recycling, especially in degraded environments. Dimitriou et al. (2006) tried sewage sludge and wood ash mixtures finding no heavy metal pollution in short rotation willow coppice.

Pousada-Ferradás et al. (2012) indicated that admixture of wood ash and sewage sludge achieved a stabilization of elements such as aluminium, iron, magnesium, nickel, cadmium, chromium and molybdenum, lowering their solubility compared with that in the ash or sludge alone, resulting in reduced risk of water pollution.

A concern in using waste mixtures is the existence of polycyclic aromatic hydrocarbons. Sueiro Blanco (2010) has shown that the mixing of several residues (including sewage sludge and wood ash) drastically reduced polycyclic aromatic hydrocarbons content.

By contrast, Pousada-Ferradás et al. (2011, 2012) observed that mixing sewage sludge and wood ash could not attain rapid and sufficient reductions in *E. coli* counts. This objective was achieved by adding highly alkaline materials to maintain a high pH value, especially higher than pH 12. Due to their pH values, mussel shell calcination ashes could be used to reach this objective.

As described, there have been a number of studies on mixtures of different wastes but none of them have included mussel shell calcination ashes (Dimitriou et al., 2006; Pousada-Ferradás et al., 2011, 2012; Sueiro Blanco, 2010). Recently we have carried out the first study characterizing different batches of mussel shell calcination ashes and a mixture including mussel shell ash, sewage sludge and wood ash (Seco-Reigosa et al., 2013), showing high arsenic and mercury retention potential. However, up to now there were not studies characterising and comparing the recycling potential of different mixtures including various percentages of valued (mussel shell) and waste materials (shell ashes and sewage sludge) from the mussel shell industry, and mixtures performed with waste materials from the mussel shell industry (shell ash and sewage sludge) and from the forest industry (wood ash).

In view of that all, the main objectives of this study are: a) characterizing (both chemically and instrumentally) three mixtures of wastes, two of them consisting of different percentages of mussel shell calcination ashes, sewage sludge and calcined mussel shell, and the third performed with mussel shell calcination ashes, sewage sludge and wood ash; b) assessing the suitability of these mixtures for recycling (especially in degraded environments), based on the results of the previous characterization, taking into account the nutrient contents and the pollutant retention potential of the mixtures derived from Hg, As and Cr adsorption/desorption trials.

2. Material and methods

2.1. Individual materials

Three different materials from Calizamar S.L. (Boiro, A Coruña Province, Spain) were used. This is the largest mussel shell treatment factory in Galicia (Spain), and it is also among the most important mussel shell facilities in the world. These three materials

Table 2
pH and EC time course evolution for the individual materials and the mixtures. Average values of three replicates, with coefficients of variation always <5%.

	pH				EC (dS m^{-1})			
	0 h	24 h	48 h	72 h	0 h	24 h	48 h	72 h
Mussel ash	12.96	12.58	12.82	12.84	18.35	18.85	18.08	18.31
Mussel shell	9.18	8.99	9.19	9.24	1.19	0.82	1.05	0.75
Sewage sludge	7.84	8.18	8.01	8.17	1.21	0.94	1.01	1.21
Wood ash	9.80	9.57	9.59	9.74	0.59	0.53	0.70	0.41
Mixture M-32	12.02	9.30	8.77	8.73	5.93	5.96	7.50	6.01
Mixture M-58	11.40	9.18	8.84	8.91	4.61	5.57	6.05	7.33
Mixture M-78	12.27	9.67	8.91	8.74	4.20	5.37	5.47	5.65

Table 3
C and N concentrations, and C/N ratio, in the individual materials and in the mixtures. Averages of three replicates, with standard deviation between brackets. The coefficients of variation were always <5%.

	%C	%N	C/N
Shell ash	13.63 (±0.06)	0.89 (±0.01)	15
Wood ash	41.07 (±0.76)	0.46 (±0.01)	89
Mussel shell	12.30 (±0.30)	0.20 (±0.01)	62
Sewage sludge	23.73 (±0.12)	3.45 (±0.02)	7
Mixture M-32	15.53 (±0.12)	1.31 (±0.03)	12
Mixture M-58	15.47 (±0.06)	1.22 (±0.01)	13
Mixture M-78	20.60 (±0.10)	1.34 (±0.02)	15

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