



Kinetics of Hg(II) adsorption and desorption in calcined mussel shells

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ABSTRACT

The potential use of calcined mussel shells to purify water contaminated with mercury was evaluated. The Hg(II) adsorption and desorption kinetics were studied in batch-type and stirred-flow chamber experiments. The adsorption/desorption experiments revealed some differences between the batches of shells used. The batch of shells that displayed the greatest capacity to adsorb Hg(II), via a highly irreversible reaction, also contained more Fe and Al than the other batches. The results of the stirred-flow chamber experiments indicated a high degree of irreversibility in the process of Hg(II) adsorption in the mussel shell, and that Hg(II) was rapidly retained. The results of these experiments also revealed that the efficiency of depuration differed depending on the length of time that the system was used: when the system was operated for 55 min, depurating 162 mL of inflowing water g⁻¹ mussel shell, a 90% reduction in the initial concentration of Hg(II) was obtained; use of the system for 90 min, depurating 265 mL water g⁻¹ mussel shell, produced a 75% reduction in the initial Hg(II), and use of the system for 162.5 min, depurating 487 mL of water g⁻¹ mussel shell, resulted in a 50% reduction in the initial Hg(II).

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1. Introduction

Galicia (NW Spain) is one of the main producers of mussels (*Mytilus galloprovincialis*) worldwide, along with China and Thailand. According to Caballero et al. [1], 224 919 tonnes of mussels were produced in Galicia in 1997, which represented 20% of the worldwide production. In 2005, mussel production in Galicia decreased to 205 256 tonnes, which corresponded to 11% of the worldwide production, 98% of the Spanish production, and almost 40% of European production [2]. It is estimated that some 120 000 tonnes of mussels are processed in canneries every year in Galicia, and that the remainder are sold fresh. The industry therefore generates large amounts of waste mussel shells. The shell accounts for around 32% of the total weight of mussels destined for consumption [2], and therefore in Galicia the amount of mussel shell waste generated per year will vary between 65 682 and 93 541 tonnes, depending on mussel production.

Treatment plants have been established in Galicia with the aim of recycling and utilizing waste mussel shells by transforming the material into a valuable final product.

Once the mussel shells have been transformed, the resulting material can be used for various purposes, such as water depura-

tion. In a study carried out in New Zealand, Currie et al. [3] showed that the use of calcined mussel shells eliminated around 90% of the phosphates in the water samples analysed, whereas the efficacy decreased to 40% when untreated mussel shells were used. However, information about the capacity of this material to retain heavy metals, specifically Hg(II), is scarce.

Mercury is a heavy metal that is emitted to the atmosphere from natural processes such as volcanic and geothermal activity and via erosion from soils, vegetation and surface waters [4]. However, total inputs of Hg(II) to the atmosphere have increased in the past two centuries as a result of emissions of mercury from anthropogenic activities such as mercury mining, fossil fuel combustion and waste incineration [5]. Despite substantial reductions in anthropogenic emissions of mercury, man-made sources still contribute significantly to global inputs of mercury.

Once in the atmosphere, natural or anthropogenic mercury can be widely dispersed and transported over long distances [6] before finally reaching soil surfaces and water bodies and accumulating there [7]. This process of atmospheric deposition, which partially accounts for the description of mercury as a global pollutant, also leads to increased concern about the environmental effects of mercury close to point sources of emission, as well as in areas that include so-called non-point sources of emission [8].

Thus, the mercury deposited in terrestrial ecosystems is considered one of the most dangerous pollutants for human beings and wildlife, especially as inorganic mercury can be converted to highly

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toxic methyl-Hg, which is a neurotoxin [9]. There is great concern about mercury pollution in many areas of the world, because of its high mobility in the environment and its ability to bioaccumulate in the food chain [10]. Means of immobilizing accumulated mercury are therefore required to minimize the potential toxicity of the metal.

In response to environmental problems caused by mercury, several studies have been carried out in recent years to investigate the retention of Hg(II) on different adsorbent materials, e.g. kaolin-humic acids [11], Fuller's earth and activated carbon [12], organosmectite composites [13], camel bone charcoal [14], silica gel [15], clays [16,17] and metal oxides and sulphides [18,19].

However, the capacity of material derived from waste mussel shells to adsorb Hg(II) has not previously been tested.

In the present study, the dynamics of Hg(II) adsorption and desorption by calcined mussel shells was investigated in batch-type adsorption-desorption experiments and stirred-flow chamber experiments, which enabled evaluation of the potential use of the material to purify water containing high levels of mercury.

2. Materials and methods

2.1. Samples and general analyses

Calcined mussel shell was obtained from a company that transforms waste mussel shells, in Galicia (Spain). The valorization process involved the following stages: reception and storage of mussel shells, washing and dripping, calcination, cooling, milling and sorting, final product storage, packing and shipment, as described by Barros et al. [2].

Samples of three different batches of calcined mussel shells were obtained in March, April and May 2008. Once in the laboratory, the samples were examined by scanning electron microscopy (JEOL JSM-6360LV) and X-ray diffraction analysis (Philips PW1710 diffractometer). The percentage moisture contents were calculated by the difference in weight before and after drying the samples at 105 °C to constant weight. The total contents of C, N and S in finely ground samples (ground in an agate mortar) were determined with a LECO CNS-2000 autoanalyser. The concentrations of inorganic carbon were determined with a LECO CC-100 digester, which measures the levels of CO₂ generated after acid digestion of the samples. Total analyses were carried out after microwave assisted digestion of 0.2 g of finely ground sample, with 6 mL of concentrated HCl, 2 mL of concentrated HNO₃ and 1 mL of ultra-pure water. Once the digestion process was completed, the metals (Na, K, Ca, Mg, Al, Fe, Mn, Zn and Cu) were quantified by ICP-OES, in a Perkin Elmer Optima 4300 DV spectrophotometer. In addition, X-ray fluorescence (USC in-house dispersion spectrophotometer) was used to quantify the Cr, Ni, As, Se and P.

A mercury analyser (MA-2000 Nippon Instruments) with a gold coated trap was used to determine the content of mercury in the samples, after thermal decomposition in a ceramic combustion tube; the mercury was detected in a double channel non-dispersive atomic fluorescence spectrometer by cold vapour atomic absorption (at a wavelength of 253.7 nm). All concentrations were expressed on an oven dry basis (105 °C).

2.2. Adsorption experiments

For the mercury adsorption studies, 10 mL of a 0.01 M solution of NaNO₃ and a known concentration of Hg(II) (as Hg(NO₃)₂), i.e. between 15 and 90 μM Hg), were added to 200 mg of calcined mussel shell. The samples were shaken for 1 h, then centrifuged at 4000 rpm for 10 min. The amount of Hg(II) adsorbed was calculated as the difference between the amount added and that measured

after 24 h contact. The Hg(II) in the supernatant was measured by formation of cold vapour and atomic absorption spectrophotometry. The adsorption was also quantified at different pH values, after addition of different concentrations of HNO₃ (0.001, 0.002, 0.005, 0.007 and 0.010 M) to the initial 105 μM solution of Hg(II). All of the experiments were carried out in triplicate.

Freundlich (Eq. (1)) and Langmuir (Eq. (2)) isotherms were used to describe the adsorption behavior of Hg(II). These equations are expressed as follows:

$$X = K_f C^{1/n} \quad (1)$$

$$X = \frac{K_L X_m C}{1 + K_L C} \quad (2)$$

where X is the amount of solute retained per unit weight of adsorbent ($\mu\text{mol kg}^{-1}$); C is the equilibrium concentration of the solute remaining in the solution (μM); K_f and $1/n$ are the Freundlich coefficients in Eq. (1); K_L ($\text{L } \mu\text{mol}^{-1}$) is a constant related to the energy of adsorption, and X_m ($\mu\text{mol kg}^{-1}$) is the maximum adsorption capacity of the sample.

2.3. Desorption experiments

At the end of the adsorption period (1 h), 10 mL of Hg(II)-free 0.01 M NaNO₃ solution were added to the samples. The samples were then shaken for 1 h and the supernatant removed for analysis by centrifugation at 4000 rpm for 10 min. The process (suspension, equilibration, centrifugation, separation) was repeated 4 more times (final volume of extract 50 mL). The mercury and pH were measured in the supernatant. The amount of interstitial Hg(II) was calculated by the difference in weight. The process was carried out for two initial concentrations of Hg(II) (15 and 105 μM solutions). Desorption was also measured at different concentrations of HNO₃ added (0.001, 0.002, 0.005, 0.007 and 0.010 M) to the initial 105 μM solution of Hg(II). Mercury desorption data are expressed as percentages of previously adsorbed Hg(II).

2.4. Stirred-flow chamber (SFC) experiments

Experiments to determine Hg(II) retention and release were carried out in a stirred-flow chamber. A diagram of the experimental system, which consists of the jars containing the required solutions, a peristaltic pump, a stirred-flow chamber and a fraction collector, is shown in Fig. 1.

The experimental procedure consisted of placing 200 mg of calcined mussel shell in the stirred-flow chamber and passing a 0.01 M solution of NaNO₃ containing a known concentration of Hg(II) (42 μM solution) through the chamber. The flow rate was 0.6 mL min⁻¹, and 5 mL volumes were collected in glass tubes (maintaining the flow for approximately 2.5 min per tube). The total adsorption period was 200 min, after which desorption was carried out with a 0.01 M solution of Hg(II)-free NaNO₃ at the same flow rate and time. The Hg(II) in the samples was measured by atomic absorption spectrometry by formation of cold vapour.

3. Results and discussion

3.1. General characteristics

Scanning electron microscopy (SEM) revealed that the calcined mussel shells mainly consisted of large prismatic particles, with a small fraction of submicron particles (Fig. 2a and b), as previously reported [20]. The observed structure is consistent with that previously reported for mussel shells [3].

X-ray diffraction (XRD) analyses revealed the presence of both calcite and aragonite, as well as dolomite. Currie et al. [3] found

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