



## 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<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup> 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 CO<sub>2</sub> 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 HNO<sub>3</sub> 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 NaNO<sub>3</sub> and a known concentration of Hg(II) (as Hg(NO<sub>3</sub>)<sub>2</sub>), 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 HNO<sub>3</sub> (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 ( $\mu\text{M}$ );  $K_f$  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 NaNO<sub>3</sub> 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 HNO<sub>3</sub> 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 NaNO<sub>3</sub> containing a known concentration of Hg(II) (42 μM solution) through the chamber. The flow rate was 0.6 mL min<sup>-1</sup>, 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 NaNO<sub>3</sub> 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

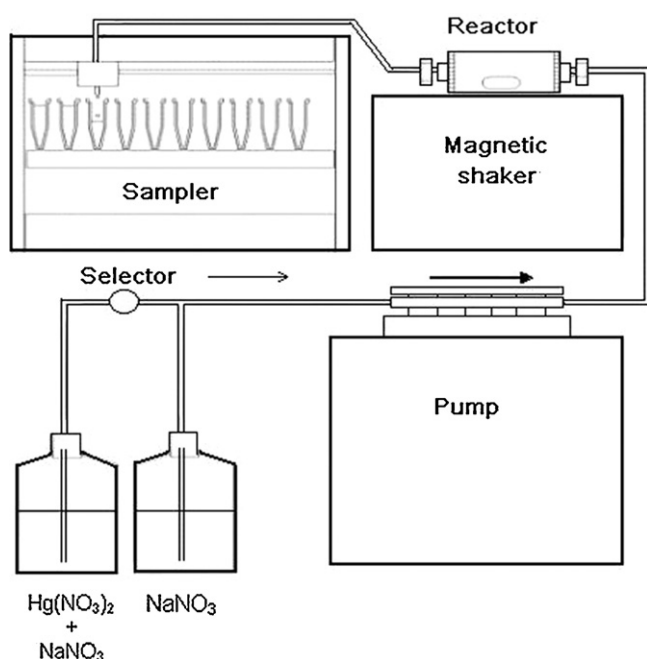


Fig. 1. Diagram of the system used in the stirred-flow chamber experiments.

that the crystalline component of raw mussel shell samples was aragonite, that heat treatment at 650, 750 and 800 °C resulted in the formation of calcium oxide, and that calcite was also detected after heat treatment (calcite is not present in raw mussel shells).

The percentage moisture content of batches 1 and 2 of mussel shell was 1% and that of batch 3 was 5%; this was the first indication of differences between batch 3 and the other batches.

The initial concentrations of Hg(II) in the batches of calcined mussel shells, expressed in  $\mu\text{g kg}^{-1}$ , and the corresponding standards deviations, were: 14.752 ( $\pm 2.351$ ), in batch 1, 14.239 ( $\pm 1.146$ ) in batch 2, and 7.649 ( $\pm 0.804$ ) in batch 3. The results show a clear difference between batch 3 and the other two batches. It was therefore expected that the characteristics and qualities of the different batches of calcined mussel shell would display a certain degree of variability.

The initial levels of Hg(II) were not high in any of the batches of shells. We used the values reported by Brown et al. [21] as reference values (i.e. between  $<5$  and  $31 \mu\text{g kg}^{-1}$  for uncontaminated samples, and between 23 and  $4637 \mu\text{g kg}^{-1}$  for areas affected by contamination). It must be taken into account that these levels of Hg(II) were reached in mussel shells throughout the biological cycle, and were not due to retention processes taking place in the inert shell after death of the bivalve.

The concentrations of Cr, Ni, As or Se were below the detection limit of X ray fluorescence.

The general characteristics of the samples of mussel shell are shown in Table 1.

### 3.2. Batch experiments: adsorption and desorption

Freundlich and Langmuir parameters for Hg(II) adsorption obtained from the fits of  $X$  and  $C$  data to Eq. (1) and Eq. (2) are shown in Table 2. The equilibrium pH of the sample was fairly stable (mean value,  $7.8 \pm 0.1$  ( $n = 72$ )), and there were no significant differences between samples or between concentrations of Hg(II). The distribution of mercury species was calculated by use of MINTEQA2 software [22]. Under the experimental conditions (pH 7.8) and at two different concentrations (15 and  $105 \mu\text{M}$ ), 100% of the mercury corresponded to the  $\text{Hg}(\text{OH})_2$  species, which is the most stable

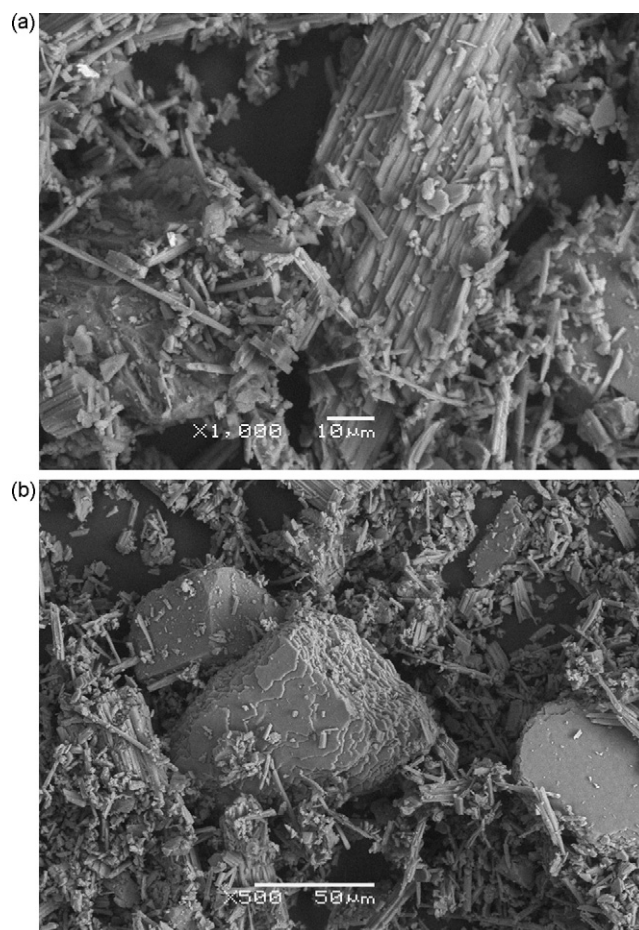


Fig. 2. (a) SEM micrograph of mussel shell samples ( $\times 1000$ ). (b) SEM micrograph of mussel shell samples ( $\times 500$ ).

species in the pH range of natural waters (5–9) [23]. Another factor that may affect speciation of mercury is the dissolved organic matter, which was found, by absorbance measurement at 400 nm [24], to be very low (between  $1.0$  and  $2.8 \text{ mg L}^{-1}$ ). Speciation of mercury, at  $2.8 \text{ mg L}^{-1}$  dissolved organic matter and  $105 \mu\text{M}$  mercury indicated that the predominant fraction (96%) continued to be  $\text{Hg}(\text{OH})_2$ , with the remainder (4%) bound to the dissolved organic matter.

The fits of the adsorption data to the Langmuir and Freundlich models were satisfactory. The  $R^2$  values indicated that the Langmuir equation provided a better fit (0.889–0.949) than the Freundlich equation (0.835–0.886), despite the theoretical limitations of the former [25]. The Freundlich equation works well when applied to solid heterogeneous surfaces. It is an empirical equation in which the  $K_f$  can be considered as the amount adsorbed when  $C$  is equal to 1. Similar  $K_f$  values were obtained for samples of mussel shell from batches 1 and 2 (1036 and 1078 respectively, Table 2), and the value for batch 3 was much higher (2089, Table 2). This clearly indicates another important difference between the shells in batch 3 and those in the other batches, and provides further evidence of the variability expected in this type of material.

The exponential parameter  $n$  may be interpreted as “adsorption intensity” or the degree of dependence of the adsorption process on the concentration of Hg(II). In this case the values of  $n$  were very similar for all three batches of mussel shell, with a mean value of 0.3 (Table 2).

The adsorption maxima ( $X_m$ ) calculated from the fits to the Langmuir equation for the 3 batches of shells analysed ranged between 2974 and  $4340 \mu\text{mol kg}^{-1}$ , with the highest value corre-

**Table 1**

General characteristics of the batches of calcined mussel used in the study. Total C, S, N and inorganic C are in % whereas metal and P values are expressed in mg kg<sup>-1</sup>.

Shell batch	C <sub>total</sub>	S	N	C <sub>inorganic</sub>	Na	K	Ca	Mg	Al	Fe	Mn	Zn	Cu	P
1	12.2	0.21	0.08	11.7	3860	158	430905	1502	60	69	4	3	2	528
2	12.2	0.21	0.08	11.6	3877	153	401035	1420	66	82	4	3	2	942
3	12.8	0.21	0.26	11.2	5326	503	399439	1968	374	602	14	17	4	890

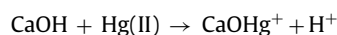
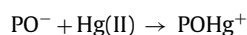
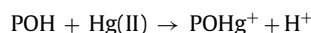
**Table 2**

Parameters obtained from the fits to Freundlich and Langmuir equations. Adsorbed (μmol kg<sup>-1</sup>), equilibrium (μmol L<sup>-1</sup>).

Shell batch	Langmuir equation			Freundlich equation		
	K <sub>L</sub>	X <sub>m</sub>	R <sup>2</sup>	K <sub>F</sub>	n	R <sup>2</sup>
1	0.3 ± 0.1	3145 ± 191	0.926	1036 ± 157	0.31 ± 0.05	0.886
2	0.4 ± 0.1	2974 ± 191	0.889	1076 ± 158	0.30 ± 0.05	0.883
3	0.9 ± 0.2	4340 ± 240	0.949	2089 ± 203	0.30 ± 0.06	0.835

sponding to batch 3. These values contrast with those obtained for silico–aluminous ashes (3.2 mg g<sup>-1</sup>) and sulpho–calcic ashes (4.9 mg g<sup>-1</sup>) [26].

The general mechanism of adsorption may be similar to that proposed by Hassan et al. [14]. Analysis of the calcined mussel shells indicated that calcium and phosphorus are important components (Table 1), and that the following reactions may occur in the presence of Hg(II):



The different results obtained may be due to the higher concentrations of Fe and Al in batch 3 than in batches 1 and 2 (Table 1), as high levels of these metals would provide a greater number of Hg(II) binding sites. The role of Fe oxides in adsorbing Hg(II) has long been recognised [18], and one metal binding mechanism occurs via the OH<sup>-</sup> of oxyhydroxides [27].

Adsorption decreased by less than 10% in the 3 batches of mussel shell after addition of acid (between 0.001 and 0.01 M HNO<sub>3</sub>), which is consistent with the low variation in pH obtained as a result of the buffering effect of the calcium carbonate in the samples.

The percentages of Hg(II) desorption were low, indicating that the process of adsorption of Hg(II) by mussel shell is fairly irreversible. The percentages of desorption for two initial concentrations of Hg(II) (15 and 105 μM) are shown in Table 3. The percentages increased as the initial concentration of Hg(II) increased, from 9% to 19–24% in the samples in batches 1 and 2, and from 0% to 4% in batch 3. In other words, the batch 3 samples did not only have a greater capacity to adsorb Hg(II), but the degree of irreversibility of adsorption was also higher, possibly because of the higher contents of Fe and Al in this batch of shells. Kim et al. [28] studied the mechanism of adsorption of Hg(II) by Fe and Al oxyhydroxides and concluded that the predominant mode of Hg(II)

adsorption in these phases is via the formation of complexes with a mono- or bidentate internal sphere, resulting in formation of strong bonds and almost irreversible adsorption of Hg(II).

The percentages of desorption tended to decrease as acid was added to the samples (Fig. 3). The batch 3 samples were again observed to differ from the others as the percentages of desorption did not vary significantly as the amount of acid increased, which again may be related to the presence of more Fe and Al oxyhydroxides. The decrease in the percentages of desorption was related to a slight decrease in pH (Fig. 3) and to an increase in the amount of Ca released (Table 4). In batches 1 and 2, there was a potentially negative relationship between the percentage desorption of Hg(II) and the Ca released (Fig. 4).

### 3.3. Stirred-flow chamber experiments

Only batch 1 mussel shells, which displayed the lowest capacity to adsorb Hg(II) and highest rate of desorption of Hg(II) of the three batches studied, were used in these experiments. In other words, the least favourable batch was evaluated.

The results of the Hg(II) adsorption/desorption experiments in the stirred-flow chamber are shown in Fig. 5. It was found that the mussel shell was capable of retaining 9.81 mmol kg<sup>-1</sup> of Hg(II), for an initial input to the reactor of 0.04 mmol L<sup>-1</sup>. In the desorption experiment carried out immediately after adsorption, 5.34 mmol kg<sup>-1</sup> were released (54% of that previously retained). With this information, and taking into account that the processes

**Table 4**

Release of Ca during the process of desorption of Hg(II) for different inputs of acid. The coefficients of variation for triplicate tests were lower than 10%.

Shell batch	HNO <sub>3</sub> added (M)	pH	Ca released (mg kg <sup>-1</sup> )
1	0	8.4	1.7
	0.001	8.0	2.1
	0.002	7.9	3.3
	0.005	7.9	5.7
	0.007	7.9	7.4
	0.01	7.8	10.8
2	0	8.0	1.6
	0.001	7.8	2.0
	0.002	7.8	3.1
	0.005	8.0	5.5
	0.007	7.9	7.5
	0.01	7.8	10.0
3	0	8.0	1.4
	0.001	7.9	2.1
	0.002	7.8	2.6
	0.005	7.9	5.4
	0.007	7.8	7.3
	0.01	7.8	9.8

**Table 3**

Percentage desorption of Hg(II) at different initial concentrations of Hg(II) (15 and 105 μM solutions) and for an initial pH of 8.

Shell batch	[Hg(II)] (μM)	Mean	Standard deviation
1	15	9	0.9
	105	24	1.1
2	15	9	1.0
	105	19	0.4
3	15	0.0	0.0
	105	4	0.9

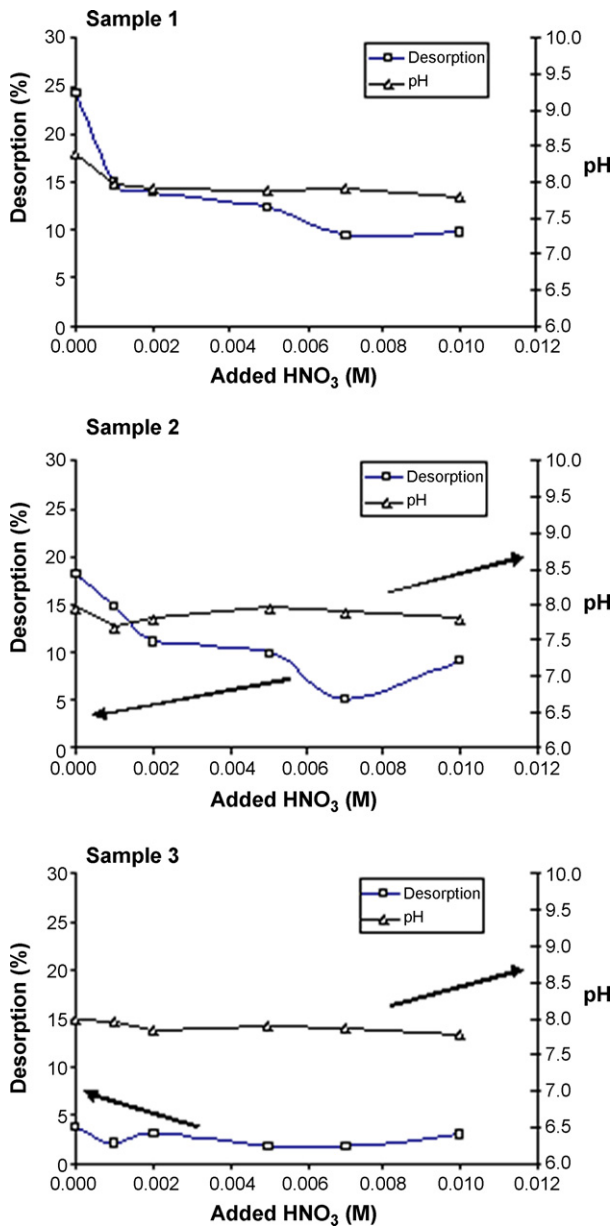


Fig. 3. Variation in pH and the percentage desorption on the basis of the amount of acid added during the desorption process.

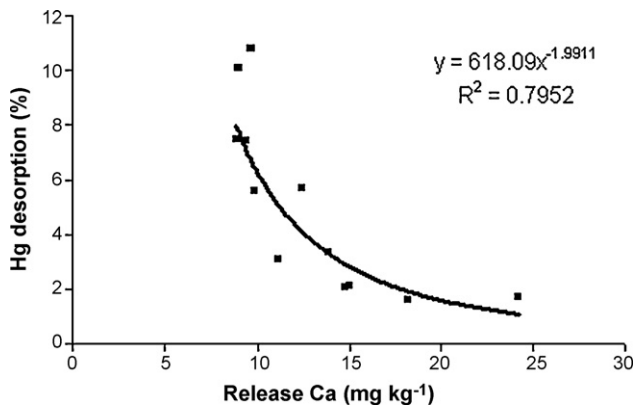


Fig. 4. Relation between the percentage of Hg(II) desorbed and Ca released after addition of acid (the shells in batch 3 were not included as the percentage desorption was very low and did not vary after addition of acid).

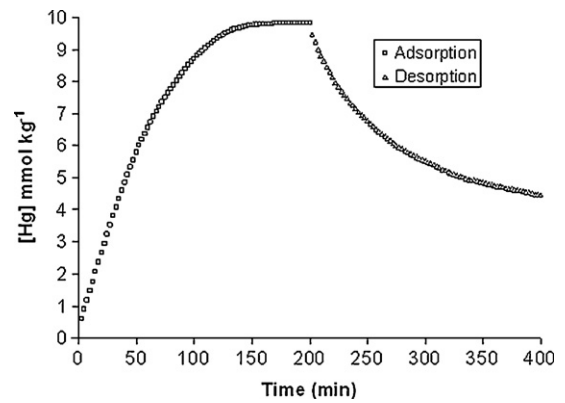


Fig. 5. Changes in adsorption and posterior desorption of Hg(II) over time in the stirred-flow chamber experiment.

involved in Hg(II) release are much more efficient in stirred-flow chamber experiments than in batch experiments [29], we can deduce that the adsorption of Hg(II) by mussel shell is a highly irreversible reaction.

Retention of Hg(II) occurred rapidly in the reactor; 50% of the total Hg(II) finally adsorbed was retained within 40 min, more than 90% of the maximum adsorption occurred within 102.5 min, and 100% was adsorbed after 175 min. The rapid retention in the first minutes of the experiment indicates that two types of reaction occur during the process of adsorption: rapid adsorption in the first moments, followed by slower reactions. The latter are characterized by stronger bonds, due to mechanisms such as precipitation and/or secondary adsorption at sites with larger activation energies [30]. Rapid adsorption processes are generally limited by diffusion, which is usually considered as the limiting factor in metal sorption [31]. A plot of relative adsorption ( $q/q_{\max}$ ) against the time parameter ( $t^{1/2}$ ) is shown in Fig. 6; the linear relationship obtained is characteristic of diffusion-dominated processes. From the initial moment until 44% of the maximum adsorbance was reached, Hg(II) adsorption was limited by the amount of Hg(II) that entered the reactor. From this moment (35 min), retention of Hg(II) was produced by rapid adsorption reactions, i.e. those reactions limited by diffusion of Hg(II). This occurred until 61% of the maximum retention occurred (52.5 min), after which the slow adsorption reactions began to predominate.

The reduction in the initial concentration of Hg(II) is of interest with regard to the use of calcined mussel shells to decontaminate waters with high concentrations of Hg(II). In the stirred-flow chamber, the percentage reduction in the concentration of Hg(II) in the

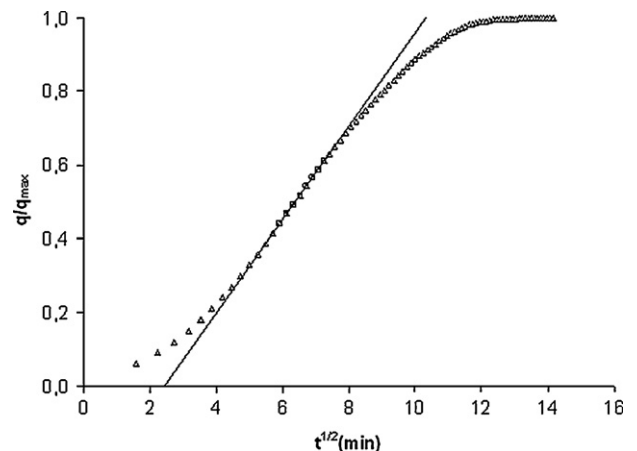
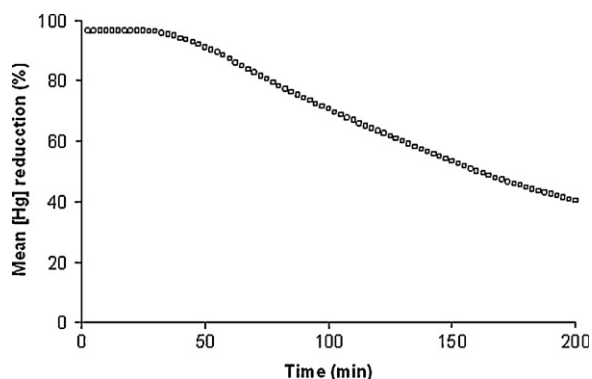


Fig. 6. Changes in the relative adsorption ( $q/q_{\max}$ ) over time.



**Fig. 7.** Percentage reduction in the initial concentrations of Hg(II) over time (the final concentration of Hg(II) was measured in the output from the reactor used in the stirred-flow chamber experiment).

reactor output differed in relation to the processing time (Fig. 7). It was found that use of the reactor (flow chamber) for 55 min, depurating 162 mL of inflowing water per gram of mussel shell, resulted in a reduction of 90% of the initial concentration of Hg(II). Use of the reactor for 90 min, thus depurating 265 mL g<sup>-1</sup> reduced the efficacy to 75% reduction in Hg(II), and use of the reactor for 162.5 min, thus depurating 487 mL of water per gram of mussel shell resulted in a 50% reduction in the initial concentration of Hg(II).

#### 4. Conclusions

In view of the results of the batch adsorption/desorption experiments we can conclude that the batch 3 shells had a greater capacity to adsorb Hg(II) and also that the adsorption reaction was highly irreversible.

Taking into account the results of the stirred-flow chamber experiments, and the fact that release of Hg(II) was much more efficient in the flow chamber than in batch experiments, we can conclude that adsorption of Hg(II) by the mussel shells was generally rapid and highly irreversible.

As regards the potential use of mussel shell to purify water contaminated with mercury, under the experimental conditions in the stirred-flow chamber, use of the system for 55 min, thus depurating 162 mL of inflowing water per gram of mussel shell resulted in a 90% reduction in the initial concentration of Hg(II), use of the system for 90 min, depurating 265 mL g<sup>-1</sup>, resulted in a 75% reduction in Hg(II), and use of the system for 162.5 min, depurating 487 mL water per gram of mussel shell resulted in a 50% reduction in Hg(II). We can therefore conclude that this system may be useful for purifying water, and deserves further research.

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