



## Bench-scale tests on ultrasound-assisted acid washing and thermal desorption of mercury from dredging sludge and other solid matrices

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### ABSTRACT

A series of ultrasonic assisted acid washing and thermal desorption tests were performed on sludge and other solid matrices with the aim to assay these removal technologies and to determine if the application of low frequency ultrasound was effective to enhance mercury removal. Unpolluted dredging sludge, 820 K calcinated dredging sludge, silica and alumina were characterized, polluted with a known concentration of mercury and treated both by acid washing and thermal desorption with and without low frequency ultrasound application. The acid washing was carried out by a 4% HNO<sub>3</sub> acid solution and the thermal desorption was performed in a 370–620 K range.

X-ray semi-quantitative analysis of dredging sludge before and after acid washing and granulometric curves of the matrices after the ultrasonic treatment were considered in order to evidence chemical or physical changes during these treatments. Total residual mercury measurements were carried out before and after sonication. Results showed not measurable acid washing extraction from polluted dredging sludge, a little (3%) extraction from 820 K heat-treated sludge and a significant (10–20%) extraction from alumina and silica within 120 min of treatment. The ultrasound application gave generally poor improvement of the mercury removal. On the contrary thermal desorption of mercury was somewhat effective for alumina, silica and heat-treated dredging sludge samples in which mercury removal was 30–40% at 370 K and 90–99% at 570 K. Likewise ultrasound application did not improve desorption. Instead, the thermal treatment of dredging sludge had a negligible amount of mercury desorption at 370 K but it reached 95% at 570 K. The application of ultrasound improved the thermal extraction of 25% in the 470–520 K range of temperature.

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### 1. Introduction

Among the heavy metals introduced into the environment mercury is certainly one of the major contaminants due to its extreme toxicity at low levels and its tendency to bioaccumulate within food chains. Geochemical and environmental studies have shown that elemental and ionic mercury can be converted by biological processes into highly toxic organo-mercury compounds such as methyl mercury which is the most common organic form of mercury found in polluted environment and the most hazardous one for its ecological and human health effects [1,2]. Hence treatment and removal of mercury from sediments are necessary in order to control its methylation and bioaccumulation. In the nineties, a significant mercury pollution was discovered in the Grado–Marano lagoon in North-East Italy during dredging procedures of some canals. Located in the Northern part of the Adriatic Sea, the Grado and Marano's

Lagoon takes up a depression limited by the Tagliamento and by the Isonzo (Soča) river mouths. The access to harbors and the navigation through the internal canals are periodically obstructed by sediments polluted mainly by contaminants such as heavy metals and organic halogens. Therefore it is necessary to dredge the lagoon regularly.

Atmospheric deposition, mining residues and industrial discharges are just some of the possible causes of the presence of mercury in the aquatic systems. Marano and Grado lagoons have experienced significant historic mercury contamination from mining (Idria Mercury mines of Slovenia) and industrial point sources (chloro-alkali plant in the region since 1950) [3]. The high content of mercuric species observed in this region prompted numerous studies on the natural and industrial mercury source of this pollution [4–8].

The study started from the need to find an environmentally friendly method to extract mercury from dredged sediments of the Grado–Marano lagoon (North-East Italy) with the hope to relocate the treated material back into the aquatic system. Management decisions like relocation into the aquatic system or placement on river embankments are key options to consider, but in any case costs

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for pre-treatment and removal of pollution excesses should remain acceptable.

A first selection of some useful methods to attain the environmental recovery of this polluted area was performed in a waste management plan and some treatment techniques were analyzed.

Among these, the acid washing and the thermal desorption were selected as practicable techniques to treat various mercury polluted solid matrices and thus a number of tests to assay the performance of these methods on natural dredging sludge and other matrices were planned. On the basis of some recent results reporting the improvement of mercury extraction in solid matrices by the use of low frequency ultrasound [9,10], sonication was considered as potential support to the above mentioned specific dredging sludge treatments. The final goal was to compare performances in total mercury removal on different natural and synthetic matrices.

It is generally recognized that ultrasound is a great help in the pre-treatment of solid samples in analytical chemistry as it facilitates and accelerates operations such as the extraction of organic and inorganic compounds from solid matrices. In fact very high effective temperatures (which increase solubility and diffusivity) and pressures (which improves penetration and transport) are created during cavitation and sonolysis at the interface between an aqueous or organic solution and solids, as a consequence high extractive power is brought to the mixture. Some interesting investigations have been conducted concerning the effects of ultrasonic treatment in desorption and removal of different compounds or chemical contaminants: heavy metals from dredge sediments [11,12], diesel from simulated soil [13], organic components from marine sediments [14] and also mercury and methylmercury from different matrices [15,16,10]. Moreover, it is well known that a solid slurry can be physically modified by the low frequency sonication, but there are few reports which verify whether traditional extractive treatments of metals in dredging sludge can be improved by an ultrasonic pre-treatment without losing the general characteristics of such solid matrix in the perspective of its recovery and re-deposition as sediment.

The final goal of this preliminary research was to assess some bench-scale tests in order to support a scale up design and to propose a treatment with minor environmental impact.

## 2. Materials and methods

### 2.1. Origin and characterization of the untreated solid matrices

The sediments from the Grado Marano lagoon have a fine grain size distribution mostly characterized by silt (63.5%), clay (22.5%) and sand (14%). The mineralogical quality of the sediment is predominantly typified by dolomite, quartz and calcite, however slight presence of plagioclases, muscovite, pirite and halite was also evidenced. The total organic content, as volatile solids, was about 5% of the total weight of the dry dredging sludge. The dredging sludge samples of this study were drawn at a humidity around 50% from a hopper dredger.

Unfortunately, for a long time, samples from the contaminated area were not available (area has been impounded), so unpolluted dredging material was collected from lagoon, dried and successively polluted. The concentration of mercury in the unpolluted sludge was 0.5 ppm.

A general pollution procedure was used for all matrices studied (see following) in which 50 g of the solid matrix was mixed for 24 h with 350 ml of a 0.75 mM aqueous solution of  $\text{HgCl}_2$  in a 1 l reactor, then the slurry mixture was centrifuged, separated and characterized for the tests. After this pollution procedure the natural dredged material resulted polluted with 200 ppm of mercury with an average humidity of 50%. This sample, which in the following text will be referred as dredging sludge, represents a simulation of the natural

**Table 1**

Surface areas and approximate organic humic content of the solid matrices.

	Surface area ( $\text{m}^2/\text{g}$ )	Humic material ( $\text{mg}/\text{g}$ )
Alumina	161	0
Silica	2	0
Heat-treated sludge	8	0.05
Dredging sludge	19	0.92

polluted sample from which it differs for the type of the pollution and its aging. We assume that its composition is very close to the one of the polluted sites because they are coming from the same area.

The second solid matrix selected for the experiments was obtained by burning the same dredging sludge, in a muffle at 820 K and successively polluting it with the general procedure described above. In this calcinated sample, which in the following text will be referred as heat-treated dredging sludge, the organic content was eliminated by burning. Some residual humic acids content was found (Table 1). The calcination caused at the same time a reduction of the calcium magnesium carbonate (dolomite) respect to the original dredging sludge (Table 2).

Mercury removal from alumina and silica was also studied. The objective of these experiments was to evaluate the role of these two inorganic matrices with different chemical nature, surface area (Table 1) and grain size (Fig. 2), in the mercury release. It is worth to note that silica represented approximately 75% of the composition of the dredging sludge. The two inorganic matrices were polluted by the same standard procedure described above. Also in this case the final pollution was of 200 ppm of mercury.

### 2.2. Experimental set-up and analysis

In all experimental sessions of this study residual total mercury measurements were carried out before and after treatment processes together with time development/temperature variation of mercury extraction/desorption. Subsequently the percentage of extraction/desorption was calculated. For the assay of total mercury content the atomic adsorption analytical method was applied by the LECO<sup>®</sup> AMA 254 instrument. In Fig. 1 the experimental devices used in the treatments is presented.

A grain size characterization of the slurries was performed by a Horiba LA-950 Laser scattering particle size distribution analyzer in order to control the granulometric changes when the sonication pre-treatment was applied (Fig. 2), and an X-ray semi-quantitative analysis was carried out to describe the main inorganic changes during the extraction/desorption (Table 2). Structural features of the samples were investigated by X-ray diffraction. Spectra were recorded on a Philips X'Pert diffractometer (equipped with a real

**Table 2**

X-ray semi-quantitative analysis of natural dredging sludge and heat-treated dredging sludge (approximate by weight percent composition).

	290 K	After acid washing (290 K)	After thermal desorption (620 K)
Dredging sludge			
Quartz	73	81	73
Calcite	7	0	7
Dolomite	11	11	12
Albite	8	8	8
Halite	1	0	0
Heat-treated dredging sludge			
Quartz	76	84	76
Calcite	9	0	9
Dolomite	0	0	0
Albite	14	16	15
Halite	1	0	0

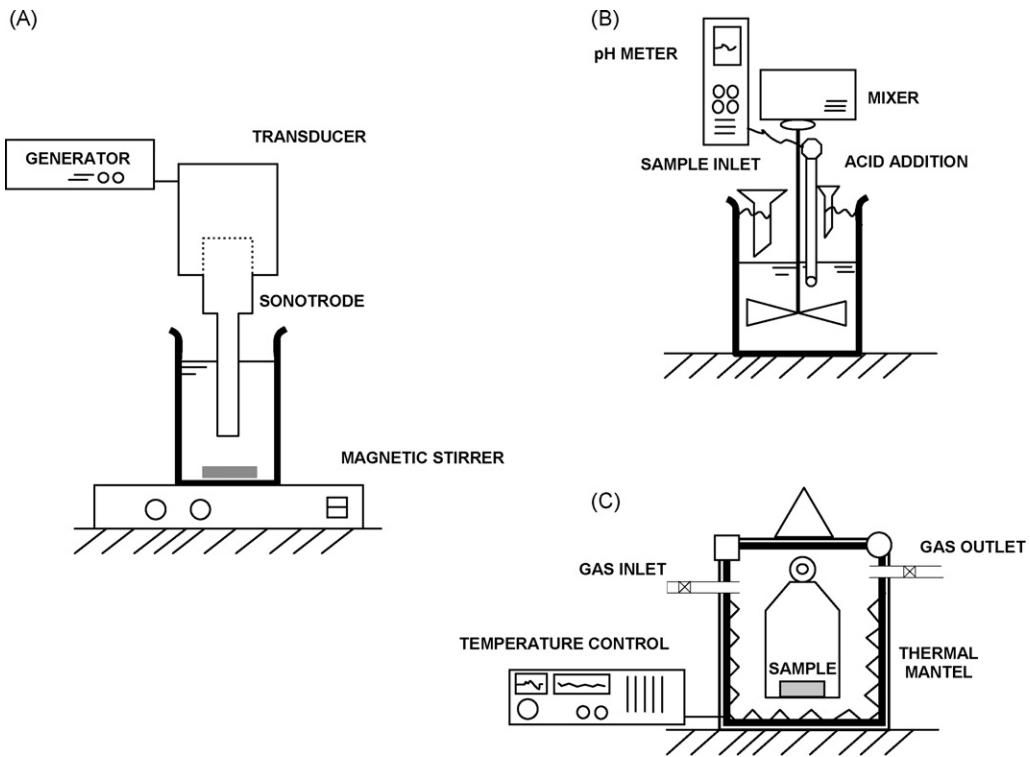


Fig. 1. Schematic drawing of the batch equipment used for the experimental tests: a = ultrasonic device; b = acid washing system; and c = thermal desorption system.

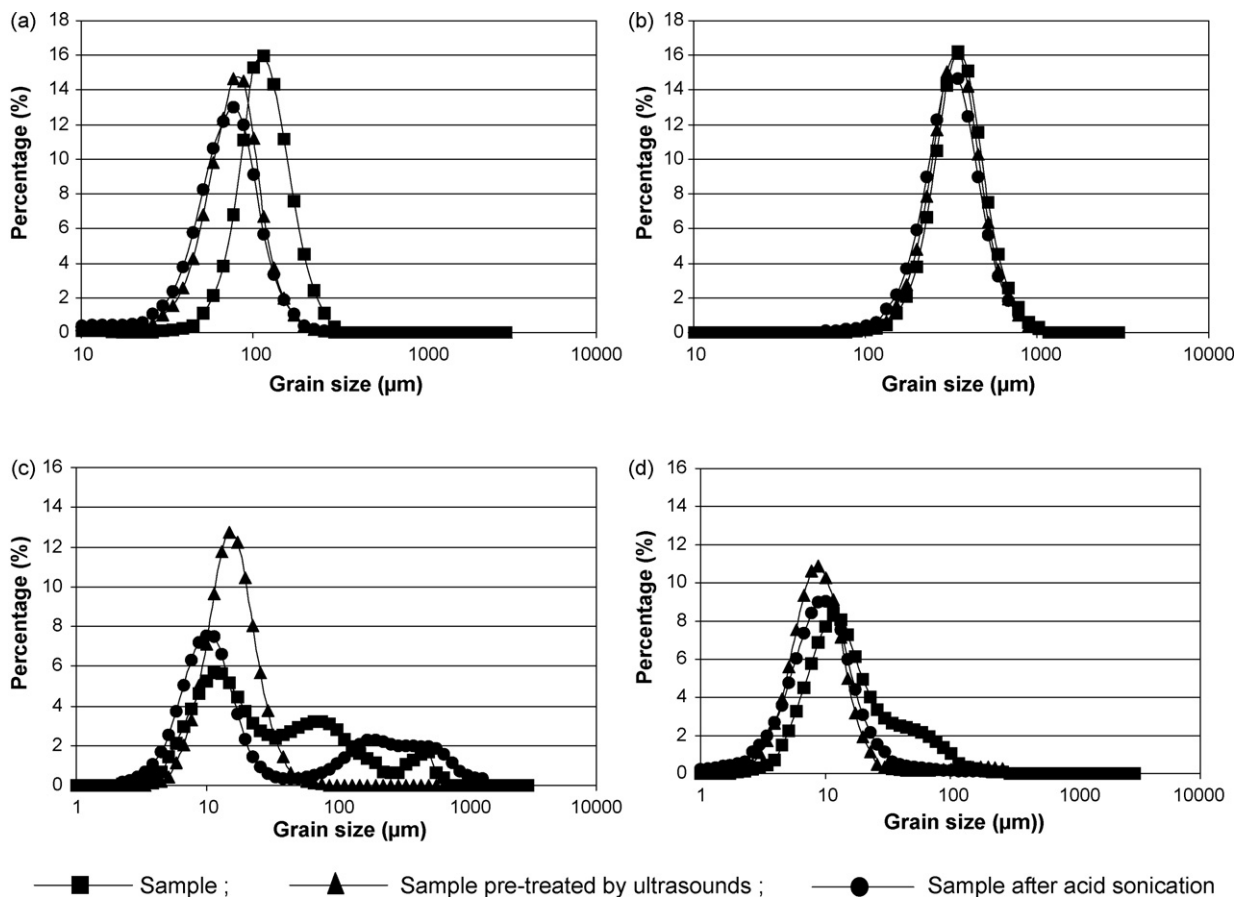


Fig. 2. Grain size distribution of the solid matrices: (a) alumina; (b) silica; (c) heat-treated dredging sludge; and (d) dredging sludge.

time multiple strip detector) operated at 40 kV and 40 mA using Ni-filtered Cu-K $\alpha$  radiation. The Philips X'Pert HighScore software was used for phase identification obtaining a semi-quantitative analysis of XRPD data. The RIR constant (obtained from the ICDD data base) is related to the ratio between intensity peaks for the known amount of corundum compared to the intensity peaks of the unknown amount of a selected mineral phase of the powder. This technique is an "estimation" of the "weight percent" concentrations useful to provide excellent "relative" amounts for similar type samples with an estimated error of +5% or more.

In Table 1 the surface areas of the solid matrices are reported. This measurement was performed according to the B.E.T. method by nitrogen adsorption at 77 K, using a Tristar 3000 gas adsorption analyzer.

In Table 1 the organic humic content in the matrices is given. This measurement was carried out treating the samples by basified and acidified sequences following conventional methods [17].

### 2.3. Ultrasonic treatment

All the solid matrices were processed by the same ultrasonic treatment before the mercury acid extraction and thermal desorption. A Dr Hielscher GmbH - UIP 250 model device with BS24d22 sonotrode was used for the ultrasonic processing, during each test a setting by the KI method [18] was carried out to verify the sonication performances. This method was useful to verify whether the cavitation energy induced in the liquid by the sonotrode remained constant during the sonication processes. The total cavitation energy in the slurries was estimated about 200 kJ/l.

The sonotrode (diameter of 22 mm and a length of 10 cm) was immersed up to 5 cm in a cylindrical glass reactor with a volume of 150 ml, the ultrasonic device ran in a batch mode with a 20 kHz frequency, 250 W power and 20% frequency in all the experimental tests. The time selected for the ultrasonic pre-treatment of all solid matrices was 10 min. This treatment time was selected on the basis of some preliminary experiments which showed that longer sonication times resulted in similar or even worse extraction performances, in particular for acid washing. This negative effect of long time sonication on Hg(II) desorption was also observed by other authors [10].

### 2.4. Acid washing and thermal extractions

For the acid washing experiments 200 ml of the samples (solid matrix with 90% water) was loaded in a 800 ml batch reactor continuously stirred. A solution of HNO<sub>3</sub> (Fluka reagent, 65 vol.%) was gradually added until pH 4 (controlled by a pHmeter) was reached. This pH was chosen in order to have an acid treatment with low impact in a possible scale up. After the chosen washing time the sample was centrifuged and dried at 90 °C for 15 h. Its residual humidity was measured by means of a moisture analyzer. Samples were withdrawn at different times in order to determine extraction vs time curves. In these experiments two conditions of sonication were considered, one in which sonication was performed during acid extraction (acid sonication) and the other where ultrasound was applied as pre-treatment.

Thermal desorption was achieved in a batch mode and in air flow, the sample was loaded into the reactor, then the temperature was risen to the set value at the established slope-time rating. The sample was first heated iso-thermally for 5 min at 320 K, then it was heated to the final temperature by a thermal slope of 10 K min<sup>-1</sup> and finally temperature was maintained constant at the final value for 5 min. Once the thermal cycle was finished, the system was cooled and the sample withdrawn for the analysis without other treatments. The mercury content was measured in samples collected at 370, 420, 470, 520, 570 and 620 K, all matrices were

investigated with and without sonication pre-treatment. Additionally a 290 K temperature sample was also analyzed as a control.

## 3. Results and discussion

### 3.1. Matrices modification

The composition of dredging sludge and heat-treated dredging sludge is reported in Table 2. The halite dissolved out when the two matrices were mixed with the mercury solution in the general pollution procedure. When dredging sludge was burned to 820 K dolomite disappeared (this phenomena is evident over 620 K). At the same time calcination causes a decrease of the surface area of the solid matrix (from 19 m<sup>2</sup>/g in dredging sludge to 8 m<sup>2</sup>/g in the heat-treated dredging sludge). When the acid washing was applied to dredging sludge and heat-treated dredging sludge calcite solvated out of the slurries.

As previously observed, slightly acidic conditions were selected in order to limit the treatment impact. Fig. 3 shows the efficacy of tested washing remediation at pH 4, in terms of percentage of mercury removal from the solid in different conditions. It can be noticed that acid washing, with or without ultrasound treatment, does not improve the release of mercury from both dredging sludge and heat-treated dredging sludge while it affects their chemical nature removing the carbonates by an acid–base reaction.

The same extraction conditions allow removal of about 15–20% of mercury from inorganic material such as alumina and silica, but the efficiency is dropping to about 2–3% for heat-treated dredging sludge and to about 0–0.5% for dredging sludge. This result suggests that mercury is mainly bound to the organic components of the matrix as the ability to remove mercury is decreasing going from a totally inorganic matrices to samples with an increased amount of organic matter [19,20].

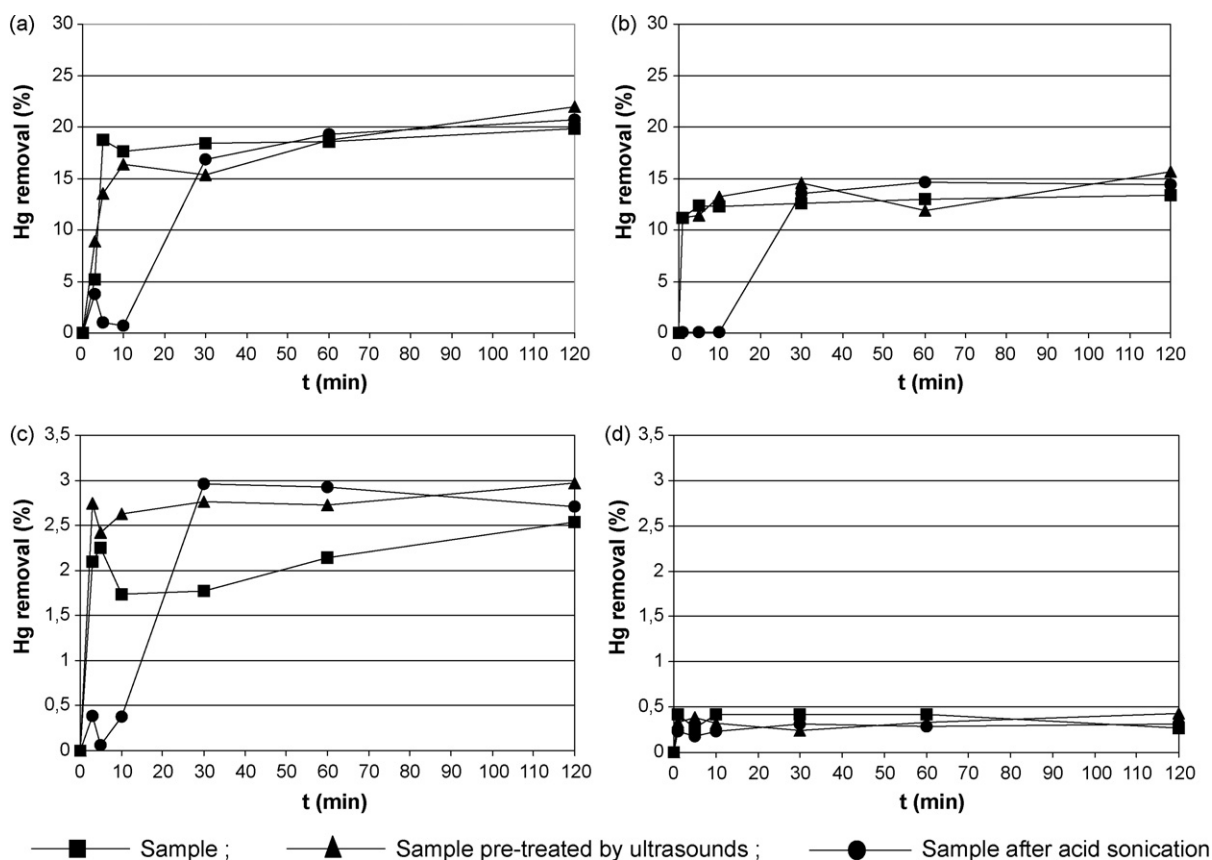
On the other hand surface area effects on the efficacy of the extraction of mercury cannot be ruled out. Furthermore, when a maximum temperature of 620 K was applied in thermal treatment, no evident changes in inorganic components were observed between the heat-treated dredging sludge and dredging sludge (Table 2). On this basis we can hypothesize that the thermal treatment maintains substantially the chemical character of the matrices while affecting their organic content as observed elsewhere [21–25].

In Fig. 2 the granulometric curves of the untreated solid matrices, the matrices pre-treated with a 10 min ultrasound application and the matrices treated with ultrasounds during acid extraction are reported. During acid washing tests some changes of the grain size distribution of the matrices were noticed. In particular, the ultrasound application caused in both, dredging sludge and heat-treated dredging sludge, a substantial decrease of the particle size with a distribution centered at about 10  $\mu$ m. During the acidic treatment with the simultaneous ultrasonic application, the granulometric curve appeared more narrow. This fact should be connected with partial reaction of carbonate granules by acid treatment. Moreover, sonication caused a small grain size diminution of alumina slurry but did not affect the grain size of silica.

### 3.2. Acid washing

The solid matrices considered in these acid washing experiments had different performances regarding the total mercury extraction, but the ultrasonic application provided a general little improvement in various extraction trials and for the different matrices.

In Fig. 3 the percentages of mercury extraction by acid washing, at different extraction times and for both ultrasound pre-treatment



**Fig. 3.** Percentage of mercury removal from solid matrices by acid washing at different extraction times. (a) alumina; (b) silica; (c) heat-treated dredging sludge; and (d) dredging sludge.

and ultrasound application during acid extraction (acid sonication), are reported.

In all experiments, when the first 10 min of sonication was applied together with acid washing, the extraction of mercury appears to be inhibited with respect to sole acid washing or acid washing pre-treated by ultrasound. This fact could be connected to the wavering of the acid extraction equilibrium caused by the sonication and cavitation phenomena and to possible transformation occurring in the matrix during the treatment [10].

The ultrasonic pre-treatment did not result in a significant enhancement of acid extraction from the matrices considered. Mercury removal potential has to be considered similar to not sonicated samples.

The acid washing trials on alumina slurry without the application of ultrasound showed a maximum extraction percentage of about 20% which was reached quickly during the first 3–10 min and maintained for all 120 min of extraction. As previously observed the ultrasound application did not improve markedly the mercury removal. The silica slurry demonstrated similar extraction performances, in the first 10 min the acid washing without the sonication reached its maximum percentage corresponding to about 15%. Then the ultrasound treatment did not enhance the mercury extraction. It seems easier to remove mercury from alumina than from silica.

The tests on heat-treated dredging sludge samples demonstrated mercury was barely extracted by acid washing reaching removal of about 2–3%, however the ultrasonic treatment seemed to have a positive effect during first 60 min of acid extraction. In this case many factors such as the nature of inorganic components, buffer conditions and resulting grain size distribution could significantly influence in mercury extraction. Nevertheless for the purposes of this preliminary study this effect was not very significant.

The percentage of mercury extraction from dredging sludge samples was negligible.

The alumina and silica represented two pure matrices from which it is possible to remove significantly mercury. This indicated the possibility to extract mercury by designed acid washing from inorganic media with different surface areas (Table 1) and chemical nature, but ultrasound application had little effect on extraction performance (Fig. 3).

It can be noted that heat-treated dredging sludge, which contains mainly inorganic components, exhibited an evident extraction of mercury compared to dredging sludge which contains a measurable amount of organics (Table 1). In fact, in the heat-treated dredging sludge a somewhat mercury extraction corresponded to a little humic content. This significant behavior should be connected to the ligand role of the organic humic material that bound effectively the mercury to the matrices. It is well known that the ability of humic substances to form stable complexes with polyvalent cations facilitates the segregation of metals in soil and sludge [25–27].

### 3.3. Thermal desorption

In Fig. 4 the results of the thermal mercury desorption are depicted. The percent of mercury removal raise with the temperature during the treatment of all the matrices. For the slurries of alumina, silica and heat-treated dredging sludge, the mercury removal reach 30–40% already at 370 K. At this temperature  $\text{HgCl}_2$  starts to vaporize [24]. This result confirms that mercury is weakly adsorbed to the inorganic matrices. When these matrices were pre-treated by ultrasound thermal desorption did not improve.

On the other hand, significant thermal desorption of mercury from the real dredging sludge was achieved only above 420 K and only in the temperature range between 470 and 520 K the 50% of

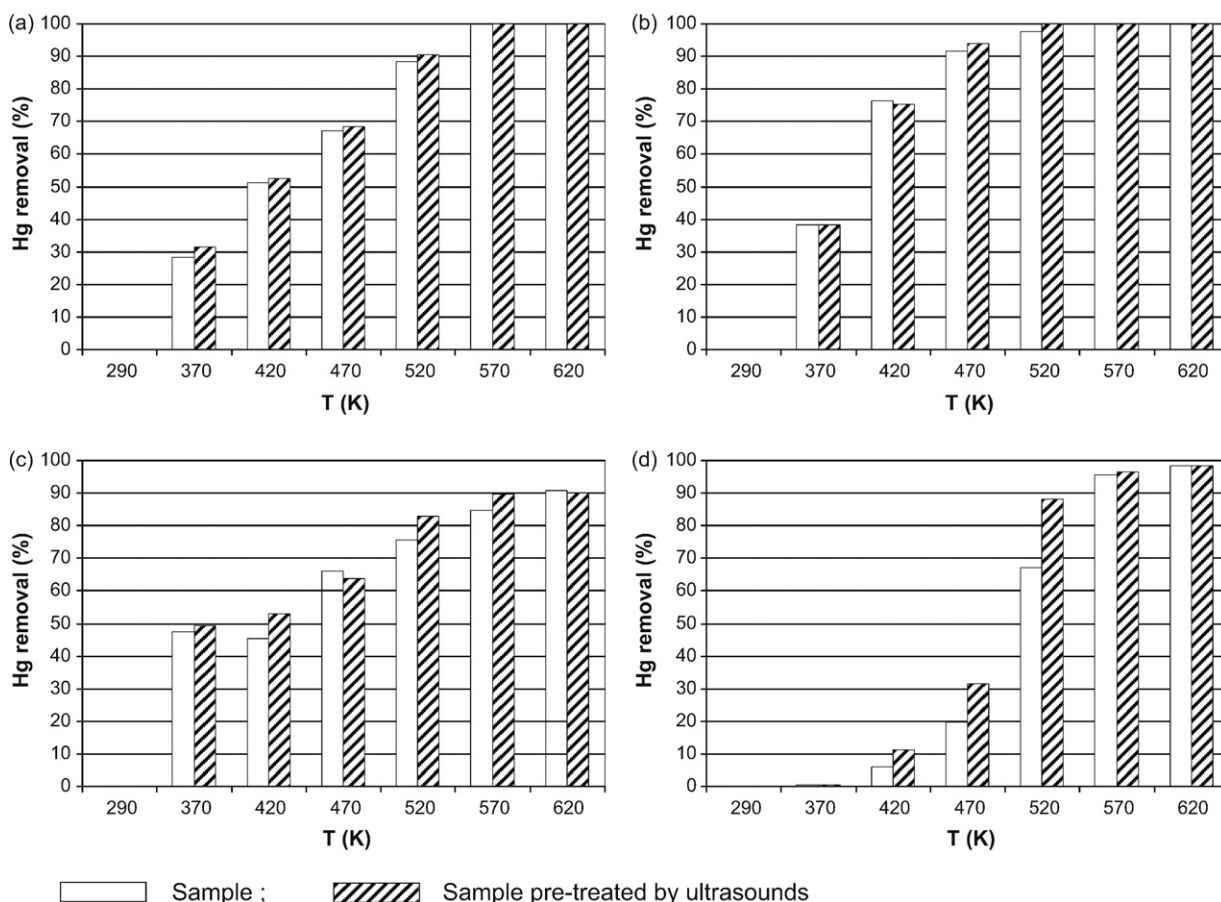


Fig. 4. Comparison of removal efficiencies in thermal desorption from solid matrices. (a) alumina; (b) silica; (c) heat-treated dredging sludge; and (d) dredging sludge.

removal was reached. For dredging sludge slurry, where a measurable humic content is present, the temperature of mercury desorption increased, for constant reaction time, as a result of more effective chemical binding of the contaminant [22,12].

It could be supposed that the evident rise in Hg(II) desorption is related to the burning off of the humic substances which results in a easier release of the contaminant from the sludge. The ultrasound application improves appreciably thermal extraction of mercury from dredging sludge with an enhancement of about 25% in temperature range of 470–520 K. As an hypothesis, this result could be explained considering that the ultrasonic particle size reduction of the slurry provides an enhancement of the partial thermal decomposition of humic substances [22], consequently mercury bound to that material reach about 90% of desorption at lower temperature. In any case some authors reported that below 620 K thermal decomposition of aliphatic structures and polysaccharides occurred together with the elimination of functional groups due to the decarboxylation reactions [28,29], therefore thermal desorption of mercury from dredging sludge could take place at the same time. Further investigations are needed to better explain these observations.

#### 4. Conclusion

The investigation represents a preliminary assay of ultrasound-assisted soil washing and thermal desorption treatment to be applied in the remediation of polluted sites of the Grado–Marano lagoon (North-East Italy) where mercury presence in the dredging sludge has caused a lot of management and environmental problems. Experimental trials were conducted with the aim to obtain

basic information for a scale up in treatment plant design. In particular acid washing and thermal desorption tests were performed on dredging sludge and other solid matrices to assay when low frequency ultrasound was advantageous in order to enhance mercury removal. In this case the ultrasonic supported acid washing and thermal desorption of mercury from four different solid matrices were studied. The work aimed to obtain some information about the possibility to treat total mercury by these techniques and to compare low frequency ultrasound application in the extraction and desorption processes.

Some final issues can be considered:

- Dredging sludge characteristics modified when acid washing was applied resulting in a loss of calcite content although mercury extraction (also ultrasonic aided) was at the same time negligible. This fact lead undoubtedly to a negative evaluation of the remediation process. The acid washing conditions chosen for these case study had revealed a scarce applicability to the mercury extraction from natural dredging sludge even if a potential extraction capability was revealed by tests applied to inorganic matrices.
- Acid washing procedure has given some advantage in mercury extraction from inorganic matrices but dredging sludge was unaffected by this mercury removal process. The tests performed in these case also showed ultrasonic application was not effective in enhance extraction process both if used during acid washing or as pre-treatment on the matrices.
- Thermal desorption of mercury was observed already at 370 K when applied to inorganic matrices but the ultrasound aid has not enhanced removal. In natural dredging sludge a good thermal extraction performance was noted only above 470 K

although a measurable increase of the extraction performance, with an improvement around 25% at 420–520 K, was demonstrated when the ultrasounds were applied as pre-treatment. It has to be stressed that the maximum temperatures of desorption adopted (below 620 K) have to be considered low temperature for a thermal desorption of an ex situ remediation technology, thus in this research the potential of ultrasound-assisted thermal treatment of real dredging sludge was verified and a scale up of a low temperature thermal desorption appears practicable.

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