

Salt-assisted thermal desorption of mercury from contaminated dredging sludge

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ABSTRACT

In this study, we tested a new procedure for the decontamination of mercury-polluted dredging sludge (Marano-Grado Lagoon, northeastern Italy) based on cationic exchange associated with thermal desorption at a low temperature. Four mercury-polluted sludge slurries were treated using thermal desorption at 393 K for 2 h. Three different salts, NaCl (sodium chloride), $(\text{CH}_3)_4\text{NCl}$ (tetramethylammonium chloride) and $(\text{C}_4\text{H}_9)_4\text{NCl}$ (tetrabutylammonium chloride) were used as exchangers. The selected salts have a monovalent cationic part that progressively increases in molecular weight. The results show that the association of cationic exchange with thermal treatment leads to a significant improvement in the removal of mercury from the contaminated material at a low temperature compared to samples that were not treated with salt. The highest levels of decontamination were obtained when the slurries, which had mercury pollution ranging from 20 to 200 ppm, were treated with a 15% solution of $(\text{C}_4\text{H}_9)_4\text{NCl}$. The efficiency of the removal at 393 K (from 24% up to 60%) depended on the nature of the sample. When the samples were treated at a similar temperature without the salt, no remediation of mercury was detected. Our results show that the thermal decontamination temperature can be significantly lowered by this remediation approach, which is the first example based on cationic exchange of the pollutant with an appropriate salt.

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1. Introduction

The Marano-Grado Lagoon in the northeastern part of Italy has experienced significant mercury contamination from mining (Idria Mercury mines of Slovenia) and from a chloro-alkali plant in the area [1–4]. The level of contamination in the lagoon sludge can reach hundreds of ppm of mercury, especially in an industrial impound area. The need to dredge coastal areas and canals for navigation is considered to be a serious management problem that is related to practices required preserving the integrity of the ecosystems [5]. The significant amount of material that needs to be treated and the level of decontamination that needs to be reached (<5 ppm) require efficient and inexpensive remediation techniques. Classical treatments, such as soil washing and thermal desorption, do not completely fulfil these requirements. When applied to mercury removal, soil-washing technologies are generally not efficient enough to reach an acceptable decontamination level. Thermal methods can achieve decontamination levels as low as 2 ppm when a temperature above 623 K is applied for long time [6–9]. As expected, this high tempera-

ture requirement increases the cost of the treatment. Moreover, high temperature treatments should be avoided for sites with uncontrolled organic pollution because the heat can lead to the production of harmful by-products (e.g., dioxins). The aim of this research was to identify treatment conditions that lower the temperature at which mercury can be removed from the sludge.

The release of mercury from contaminated sediments has been reported in many studies in which mercury at low concentrations is volatilised from a sediment surface using air-flows or bio-treatments [10–12]. Our prior published work, as well as some unpublished results, has shown that a significant part of the mercury pollution in the Grado-Marano Lagoon is due to Hg(II) bonded to the organic material of the sediment [13]. The concentration of methyl mercury in the sediments of the contaminated area has been determined to be three orders of magnitude lower than the total mercury present [4]. In particular, a recent study showed that elemental mercury, Hg(0), is the predominant species, while Hg(II) chelated to the organic matter is the second most abundant species present in the lagoon sediment [14]. In aged sediment, Hg(II) chelated to the organic matter becomes the main species. Thermal desorption is a highly efficient but energy intensive remedy for this type of polluted system.

Thermal removal of mercury that is bound to organic material starts at a combustion temperature between 473 and 573 K [15]. We hypothesised that this temperature could be lowered if mercury

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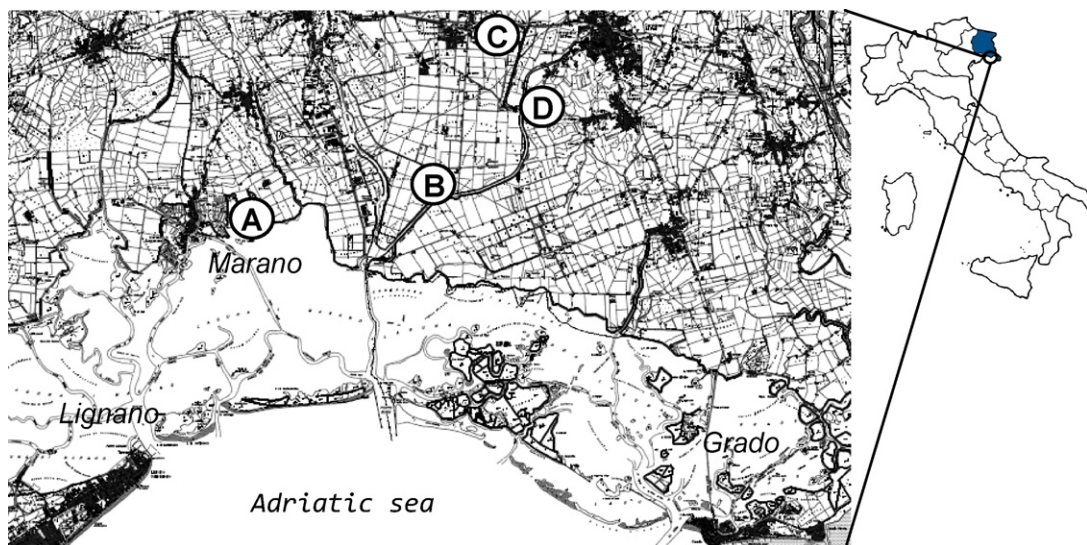


Fig. 1. Map of the area where the samples were drawn.

was first moved as Hg(II) from the organic matrix to the aqueous phase of the slurry.

Normally, a cationic pollutant is bound to a solid matrix through negatively charged sites (organic or inorganic). This binding is reversible, and the equilibrium can be perturbed in through alterations in several conditions, including temperature, pH, concentration of the pollutant in the aqueous phase and cation exchange [16]. The strategy adopted in this work was to move Hg(II), which was immobilised in the sludge, into the aqueous phase by exchanging it with a cation with a higher affinity for the binding sites and/or with a higher concentration than the pollutant [17]. Once the mercury was in the aqueous phase, it could easily be removed at the evaporation temperature of the new compound, which was formed in the water and recovered with existing techniques.

Here, we report the results obtained by treating four samples of mercury-polluted dredging sludge using NaCl, $(\text{CH}_3)_4\text{NCl}$ and $(\text{C}_4\text{H}_9)_4\text{NCl}$ as exchanging salts. These salts, which are listed in increasing order of molecular weight, all have monovalent cations. As in all cases in which we used chloride salts, we ascribed the main desorption to HgCl_2 , which evaporates at 373–393 K [18]. A high Cl^- concentration requirement is easily fulfilled in a saline dredging sludge treatment. At the end of the treatment, the salt used for the exchange can be washed out of the slurry and in principle, it could be treated for reuse. To the best of our knowledge, this is the first example of mercury remediation by cation exchange associated with thermal removal.

2. Materials and methods

2.1. Origin and characterisation of the untreated solid matrices

The sediments used in this work came from four different sites in the Grado-Marano Lagoon (Fig. 1). The sediments were dredged and hand-sampled. One sample was collected from an uncontaminated area (Sample A), a second was taken from a canal point far away from the most polluted area (Sample B), and a third sample was taken from a highly polluted area of the same canal (Sample C). The three samples had similar inorganic compositions including silt (63.5%), clay (22.5%) and sand (14%). The organic matter (mainly humic substances) was found to be 5% in Sample A and approximately 15% in Samples B and C. The concentration of mercury in the unpolluted sample (A) was 0.5 ppm, in Sample B it

was 20 ppm, and in the most contaminated sample (C), it reached 150 ppm.

An additional sample (D) was collected from a different contaminated canal in the same area and was treated to test if the new approach for mercury extraction could be more generally applied. In this sample, the inorganic composition was silt (67.1%), clay (14.3%) and sand (11%). The organic matter (7.6%) was composed mainly of humic substances. The concentration of mercury in the polluted sample (D) was 50 ppm. All the collected samples were stored in the dark and open to air for more than one year. The Hg species is different from the Hg^{2+} and can be considered to be a negligible part of the total mercury to be treated by the assayed method.

In Table 1, the concentrations of other pollution-related metals of the aged samples are reported together with some sediment parameters of natural dredging sludge carried out at the time of sampling.

The sample preparations were carried out following EPA Method 3051, and the analysis was conducted according to the EPA Method 6010B of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

Sample A was used to simulate a matrix with a higher Hg(II) pollution. Unpolluted dredging material (Sample A) was collected from an unpolluted area in the lagoon. It was then dried and successively contaminated with a solution of HgCl_2 following a well-established method [13].

In the spiking procedure, 50 g of the solid matrix was mixed for 24 h with 350 ml of a 0.75 mM aqueous solution of HgCl_2 in a 1 l reactor. Next, the slurry mixture was centrifuged, separated and characterised. After this spiking procedure, the mercury content in Sample A was 200 ppm, and the slurry had an average moisture content of 50%. This sample simulated a naturally polluted sample, but the type of the pollution and age were different.

2.2. Experimental set-up and analysis

The tests were carried out in a simple distillation device at atmospheric pressure as shown in Fig. 2. A 250 ml flask was connected to a condenser water-cooling system and was placed on a heater/magnetic stirrer platform with temperature and stirring controls. The treatment procedure was based on heating a suspension of the polluted samples in a 15% salt solution to the distillation temperature. In this study, we selected three different types of salts,

Table 1
General characteristics of fresh samples and metal composition in aged samples A, B, C and D.

Parameter	Sample A	Sample B	Sample C	Sample D
pH (–)	6.8	7.2	6.7	6.9
Redox potential (mV)	–220	–171	–125	–197
Density (kg/L)	1.7	1.8	1.7	1.9
Porosity	0.555	0.515	0.499	0.489
Void ratio	1.03	1.15	0.53	0.51
Hydraulic conductivity, (10^{-10} m/s)	1.1 ± 0.7	3.2 ± 1.6	5.3 ± 1.7	6.1 ± 2.1
TOC (%C)	5	13.8	14.2	7.6

Parameter	Sample A (ppm DM ^a)	Sample B (ppm DM)	Sample C (ppm DM)	Sample D (ppm DM ^a)
Arsenic	6.90	6.55	8.70	5.70
Cadmium	0.86	1.69	1.52	2.10
Chrome	52.85	82.82	145.10	69.55
Cobalt	8.27	23.66	45.30	21.20
Copper	27.09	106.80	123.12	113.50
Lead	18.70	304.01	360.30	289.05
Mercury	0.5 (200) ^b	20	150	50
Nickel	44.11	44.31	51.70	31.15
Zinc	82.71	109.80	150.45	90.60

^a DM: Dry matter.

^b Doped sludge value.

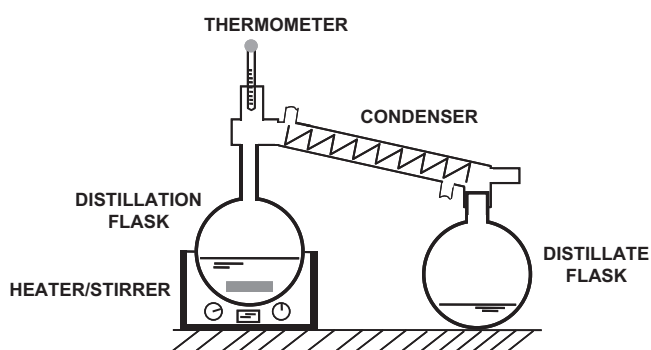


Fig. 2. Schematic drawing of the distillation apparatus used during the experiments.

listed in increasing order of molecular weight: sodium chloride (NaCl), tetramethylammonium chloride ((CH₃)₄NCl) and tetrabutylammonium chloride (C₄H₉)₄NCl. In all of these salts, the cations are monovalent. In fact, one of the aims of this research was to verify whether the efficiency of the exchange was affected by the mass of the cation, as opposed to by its charge. The use of ammonium salts are ideal for answering this question because the cationic mass can be tuned by changing the alchylic substitution on nitrogen. On the other hand, sodium chloride (NaCl) was selected because it is a convenient source of a small monovalent cation. Typically, 1 g of dried mercury-polluted sludge was pre-treated overnight with 25 ml of a 15% aqueous solution of the salt under continuous stirring. The sludge was then heated to the distillation temperature. A fresh, salty aqueous solution was continuously added into the flask while the water was distilled out of the system. A total solution volume of 50 ml was used for the treatment in the experiments performed on spiked Sample A. For the real samples (B, C and D), the treatment volume of the 15% aqueous solution of (C₄H₉)₄NCl was increased up to 200 ml. After 2 h of distillation, the treated sludge was dried and washed with deionised water (total volume 300 ml). The sludge and the washing water were separated by centrifugation. The washing water was then evaporated and residual salt was dried and weighed. The recovery of the salt used for the treatment was quantitative. To verify the processes reproducibility, each extraction test was repeated three times. Finally, the sludge was dried and the mercury content was analysed.

We tried to use a mass balance to verify the mercury extraction from the solid matrix to the distilled water. The results are

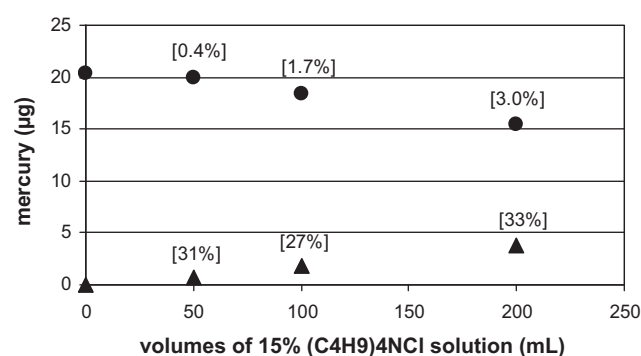


Fig. 3. Mass balance representation of mercury in the solid matrix and in distilled water after treatment of Sample B with increasing volumes of 15% solution of (C₄H₉)₄NCl. Per cent errors are shown in brackets.

reported in Fig. 3. A significant per cent error was made in the measurement of the total mercury in the distilled water. Similar results were obtained for the other samples. Therefore, all of the analyses for treatment performance evaluation were carried out on the solid part.

To calculate the percentage of desorption, the total mercury content of the samples was determined before and after the treatment. To assay of total mercury content, the atomic absorption analytical method was applied using a LECO[®] AMA 254 instrument, which analysed each sample three times with a 5% standard error.

3. Results and discussion

The final goal of this research was to create a mercury recovery-treatment for polluted sludge based on thermal treatment coupled with salt exchange. We based our work on several considerations. In general, the strength of the binding of a polluting cation is related to its charge; the higher the charge, the stronger the binding to the matrix. Therefore, to replace a cation, such as Hg(II), from its binding sites using cationic exchange, we should use a cation with the same charge (i.e., Ca(II)) or a higher charge. If we consider the equilibriums involved in the remediation process based on cationic exchange then we can theorise that a cation with a lower charge but a higher molecular weight could be exploited for exchange purposes. In fact, the heavier the cation used for the exchange, the more insoluble the complex will be with the organic part of the matrix.

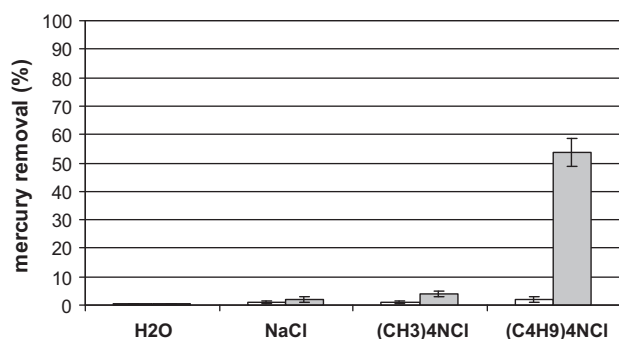
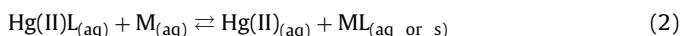


Fig. 4. The cation exchange effect of 15% solutions (total volume 50 ml) of NaCl, (CH₃)₄NCl, (C₄H₉)₄NCl on the removal of mercury from Samples A (grey) and B (white). The treatment was conducted at the distillation temperature (ca. 393 K) for 2 h. The data on the treatment with distilled water ($T=373$ K, $t=2$ h) are given for comparison.

For the sake of clarity, we can simplify the equilibriums involved in this complex system as follows:



where L is a generic organic ligand present in the sediment and M is a generic competitor for mercury binding sites. Charges are omitted for simplicity. If ML is a very insoluble species then it will precipitate out moving the equilibrium towards the release of Hg(II) in solution. Therefore, the crucial point is that the solubility of ML is influenced by the molecular weight of M, which in turn influences the removal of Hg(II) from the sludge; the higher the molecular weight of M, the higher the concentration of Hg(II) in the aqueous phase (from which it is removed by evaporation). An aim of this research was to verify this point; therefore, we selected sodium chloride (NaCl), tetramethylammonium chloride ((CH₃)₄NCl) and tetrabutylammonium chloride (C₄H₉)₄NCl as exchanging salts. The molecular mass of these salts increases progressively (23, 74 and 242 g/mol, respectively). We coupled the thermal treatment to this cationic exchange by exploiting the low temperature evaporation of mercury species, such as HgCl₂. In particular, in our experimental setting, HgCl₂ evaporates in the same temperature range of the salty solution distillation point. The thermal desorption of mercury from the solution during the treatment also has the effect of continuously moving the equilibrium towards the release of new mercury from the sludge to the solution. To avoid this effect, Hg(II) precipitates back into the sediment as hydroxide. The maximum concentration of the salts in solution was set to 15% by mass. The results obtained by treating spiked Sample A and Sample B with the three salty solutions are reported in Table 2a, and the percentages of removal are depicted in Fig. 4. To quantify the influence of the sole temperature on the removal of mercury, we also treated the polluted sludge (A and B) with de-ionised water for 2 h. This non-salty solution boiled at 373 K. The data show that the initial content of mercury was not affected by this treatment. At this temperature, mercury is tightly bound to the organic matrix, and it does not move to the solution phase from which it can evaporate. However, if the heating time was lengthened to 4 h, a 19.5% mercury removal rate was detected, which can be ascribed to a different equilibrium behaviour caused by the thermal effects. Therefore, to evaluate the impact of salt on the thermal treatment, we had to rule out these effects by stopping the process within 2 h.

When a suspension containing spiked-sludge A and 50 ml of the solution with 15% NaCl was heated to the boiling point (ca. 393 K), the mercury removal rate was only 2% after 2 h of treatment (after 4 h it reached 20%, as in the case of de-ionised water). This result shows that the small monovalent cation Na⁺ was not

an efficient competitor for mercury bound to the matrix and that the slight increase in temperature from 373 to 393 K did not significantly improve the decontamination of the sludge. When treatment was performed using (CH₃)₄NCl or (C₄H₉)₄NCl as competitors, the suspension boiled at the same temperature (393 K). After 2 h of treatment, we observed an increase in mercury removal that followed the increase of the molecular mass of the cations. The use of (CH₃)₄NCl (15% aqueous solution) increased the decontamination of the sludge by up to 4% (after 4 h it reached 22%), but when (C₄H₉)₄NCl (15% aqueous solution) was used as an exchanger, the removal of mercury strikingly increased to 54% (after 4 h it reached 74.3%). As expected, the exchange was significant when the molecular mass of the competitor was high and (at least) close to the mass of mercury. To obtain the same percentage of removal of mercury from the same solid sample by thermal treatment in air, we had to raise the temperature to 503 K (unpublished results). Therefore, we conclude that the use of an appropriate salt exchange treatment allows for mercury remediation at a significantly lower temperature. Importantly, a temperature of 393 K does not affect the nature of the soil grain size distribution and mineralogy [7]. Moreover, at this temperature, the sludge organic content is not burned, and potentially harmful by-products are not formed. Another important consideration is the recovery of the salt after treatment. As stated in Section 2, in our experiment, the recovery of the salt used for the treatment was quantitative. Optimising the process of salt recovery after treatment could help cut costs and reduce environmental impacts when applying this methodology. Further works related to salt recovery are in progress.

To test the validity of the new extraction approach on a sample drawn from a real polluted area, we applied the same procedure to Sample B. Sample B had a total mercury content of 20 ppm and is representative of most of the polluted sludge that needs to be dredged. The results are reported in Fig. 4, and they show that when 1 g of Sample B was treated for 2 h at 393 K, with a total volume of 50 ml of 15% aqueous solution of NaCl, (CH₃)₄NCl or (C₄H₉)₄NCl, no removal of mercury was observed. Obviously, in this sample the nature of mercury pollution is somehow different than the mercury pollution in the simulated sample [14]. Moreover, Table 1 shows that, in Sample B (as well as in Samples C and D), there was a high concentration of different metallic cations, which can efficiently compete with Hg(II) for cationic exchange with the salt. Accordingly, we had to use a higher amount of cation exchanger compared to spiked Sample A to observe extraction of mercury from Sample B (the same was found for Samples C and D). Tetrabutylammonium chloride was chosen as a competitor because, in spiked Sample A, it demonstrated the best extraction efficiency. Compared to other cationic interfering species in the sludge, the Hg(II) cation is volatile (as i.e., HgCl₂) at the distillation temperatures. Therefore, it is reasonable to propose a salt-assisted thermal process for its treatment.

The data obtained in these tests are reported in Fig. 5 and Table 2b. In these experiments, 1 g of Sample B was treated with different volumes of 15% aqueous solutions of tetrabutylammonium chloride. We treated the sample with increasing volumes of the salty solution to increase the amount of salt available for the exchange. As the treatment volume was increased from 50 to 200 ml, we observed a parallel improvement in the removal of mercury from 2% up to 24% (Table 2c).

To rule out the effect of increasing volume on the removal performances, we treated 1 g of Sample B with 50 ml of a 25% tetrabutylammonium chloride solution (the total mass of salt in the solution was 12.5 g). The percentage of mercury removal was found to be 9.5%, which was comparable to the amount of removal obtained by treating the same sample with 100 ml of a 15% solution of tetrabutylammonium chloride solution (the total mass of salt in the solution was 15 g). In our opinion, these data demonstrate that the total

Table 2a

Actual concentrations of total mercury and percent removal of each sample in experimental with the three salts [percent error].

	Actual concentrations (ppm)				Percent removal (%)			
	H ₂ O	NaCl	(CH ₃) ₄ NCl	(C ₄ H ₉) ₄ NCl	H ₂ O	NaCl	(CH ₃) ₄ NCl	(C ₄ H ₉) ₄ NCl
Sample A	B ^a : 200.0 [5%] A ^b : 197.8 [3%]	B: 200.0 [5%] A: 195.7 [4%]	B: 200.0 [5%] A: 191.4 [7%]	B: 200.0 [5%] A: 92.4 [6%]	0.5 [0.5%]	2.1 [1%]	4.3 [1%]	53.8 [5%]
Sample B	B: 20.0 [3%] A: 19.9 [4%]	B: 20.0 [3%] A: 19.7 [2%]	B: 20.0 [3%] A: 16.5 [3%]	B: 20.0 [3%] A: 19.3 [2%]	0.5 [0.5%]	1.0 [0.5%]	1.6 [0.5%]	2.2 [1%]

^a Before treatment.^b After treatment.**Table 2b**Actual concentrations of total mercury and percent removal of each sample in experimental with three different volumes of (C₄H₉)₄NCl [percent error].

	Actual concentrations (ppm)			Percent removal and [error] (%)		
	50 ml	100 ml	200 ml	50 ml	100 ml	200 ml
Sample B	B ^a : 20.0 [3%] A ^b : 19.6 [5%]	B: 20.0 [5%] A: 18.2 [5%]	B: 20.0 [3%] A: 15.1 [7%]	2.1 [0.4%]	9.1 [1.7%]	24.2 [3%]
Sample C	B: 150.0 [7%] A: 147.1 [6%]	B: 150.0 [8%] A: 134.8 [8%]	B: 150.0 [7%] A: 61.6 [5%]	1.9 [1%]	10.1 [2.8%]	58.9 [13.3%]
Sample D	B: 50.0 [5%] A: 48.5 [3%]	B: 50.0 [4%] A: 44.4 [6%]	B: 50.0 [3%] A: 19.3 [5%]	2.5 [1%]	11.2 [1%]	61.5 [8.1%]

^a B = Before treatment.^b A = After treatment.

amount of salt available for exchange is the key factor for extraction efficiency.

Similar performance values were determined for Sample C and Sample D (Fig. 5 and Table 2b). Sample C was drawn from the same canal as Sample B but from a different area, and Sample D was drawn from a different canal in the polluted area. The three real samples had quite similar contents of polluting metals (Table 1), but they had different mercury contents and organic matter contents (see Materials and Methods). Accordingly, when 1 g of Sample C or D was treated with 50 ml of the 15% aqueous solution of (C₄H₉)₄NCl, no removal of mercury was observed. We progressively increased the total volume of the treatment solution, and we observed a corre-

sponding increasing in mercury extraction. The removal of mercury from Sample D reached 61%, while the removal from Sample C reached 58.9%. To prove the crucial importance of the assistance of the salt for the mercury removal in this temperature range, we heated 1 g of the three samples (B, C and D) at 423 K for 2 h in an oven. The results are reported in Fig. 6, and they clearly demonstrated that if an appropriate salt is not available for the exchange then the removal of mercury from the sludge is negligible in this range of low temperatures.

In conclusion, despite the different mercury species compositions in the various samples, we ascribe the different removal performances to the different organic matter contents and

Table 2cActual concentrations of total mercury and percent removal of each sample in salt assisted (200 ml of (C₄H₉)₄NCl) and 423 K thermal experimental comparison [percent error].

	Actual concentrations (ppm)		Percent removal and [error] (%)	
	Salt assisted	Thermal at 423 K	Salt assisted	Thermal at 423 K
Sample B	B ^a : 20.0 [3%] A ^b : 15.1 [5%]	B: 20.0 [5%] A: 19.5 [4%]	24.2 [3%]	2.1 [0.8%]
Sample C	B: 150.0 [7%] A: 61.6 [5%]	B: 150.0 [8%] A: 145.7 [7%]	58.9 [13.3%]	2.8 [1%]
Sample D	B: 50.0 [3%] A: 19.3 [4%]	B: 50.0 [3%] A: 44.1 [5%]	61.5 [8.1%]	11.2 [3%]

^a Before treatment.^b After treatment.

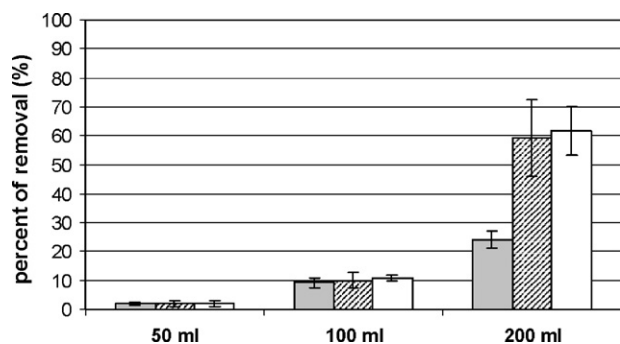


Fig. 5. The effect of increasing volumes of a 15% solution of $(C_4H_9)_4NCl$ on the removal of mercury from Samples B (grey), C (dashed) and D (white). The treatment was conducted at the distillation temperature (ca. 393 K) for 2 h.

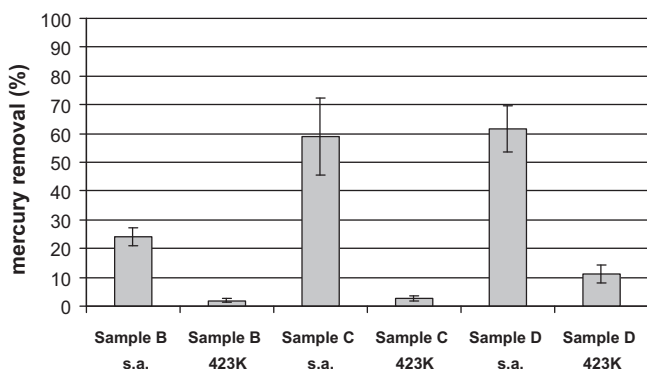


Fig. 6. Comparison of mercury removal from Samples B, C and D between the salt-assisted method (s.a.) (200 ml of 15% solution of $(C_4H_9)_4NCl$ at the distillation temperature for 2 h) and the classical thermal treatment where the same samples were heated at 423 K in an oven in an air atmosphere.

exchangeable cations contents of the samples. Nevertheless, the extraction of total mercury from all of the polluted dredging sludge that we evaluated was clearly observable.

4. Conclusions

In our research, we have pioneered a new procedure for decontaminating mercury pollution from dredging sludge using cationic exchange associated with thermal desorption at a low temperature. Although the percentage of removal obtained in the salt-assisted thermal treatment and the experimental method could be considered far from an acceptable decontamination criterion, we believe that this is an important result because it represents a proof of concept that thermal decontamination temperatures can be significantly lowered using cationic exchange of the pollutant with an appropriate salt. These findings open the possibility for re-evaluating thermal treatment methods that might become economically competitive compared to other remediation methods.

Importantly, temperatures up to 393–423 K are considered low and can easily be obtained by recovered steam (e.g., from the energy production industry or other industrial processes).

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