COMTOX : A NEW PATHWAY FOR HEAVY METAL AND RADIOACTIVE MATERIAL DISPOSAL

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Abstract:

The Chernobyl and Fukushima accidents have made scientists aware of the nuclear and radiological decontamination issue. How can such pollution be decontaminated in the quickest and most effective manner? Accidental contamination of soils and people by heavy metals remains a recurrent problem which is difficult to treat in our environment other than with physical techniques.
However based on new findings relating to complexing agents properties chemical decontamination seems conceivable.
The objective of this research program is to provide a new "soft" and non aggressive solution to the decontamination of all surfaces contaminated by heavy metals and/or radioactive substances by:

- Developing new molecules capable of complexing heavy metals
- Selecting the most effective ones in terms of complexing these metals,
- Grafting them on a supporting material
- And finally integrating them in the formulation of a multi-purpose product easy to use in the field in case of an accidental contamination and defining an application procedure.

The first stage dealt with the synthesis of new sequestering compounds by exploring two main technological research avenues:

(a) complexing agents mostly with a cyclic structure for the so called soft metals; those contain sulfur, nitrogen or phosphorus.

(b) sequestering agents for the so called hard metals with structure derived from tetronic acid backbone (tetronic acids are sub-units of norbadione, which is a natural sequestering agent of cesium found in certain mushrooms), or from EDTA.

In both cases, studying the fundamental complexing mechanisms led to selecting the most effective molecules.
Finally, to reinforce their efficacy, these complexing units have been grafted on polymers. Since the solubility of polymers is generally low, their molecular weight has been decreased by using oligomers long enough to have the properties of the polymer while being short enough to avoid any major aggregation.

Besides, decontaminating formulations have been developed on the basis of the most effective among these new chelating agents by adding specific surfactant systems, suitable solvents and pH buffers defined for optimum solution pH.

The synthesis of new heavy metal sequestering agents has been successful: tetronic acid derivatives, crown ether-type macrocycles, heterocalixarenes or porphyrins as well as polymer structures obtained by grafting sequestering units on the poly(2-hydroxyethyl) methacrylate . Measuring the sequestering power of heavy metals has lead to identifying two promising pathways: the PHEMA-EDTA polymer (by grafting EDTA on the poly(2-hydroxyethyl)methacrylate) and various tetronic acid derived quadripodal compounds among which CC03 has the rare distinctive property of being an excellent arsenic sequestering agent.

CHALLENGES AND STATE-OF-THE-ART

Unlike organic contaminants which can be destroyed by bio-remediation, oxidization or incineration, heavy metal contamination is permanent and irreversible. Consequently, apart from excavation, washing, and raking techniques, there are no other effective means to decontaminate surfaces that have been soiled by such products.
However based on newly discovered properties of complexing polymers, chemical decontamination is now conceivable.

In particular complexing agents, mainly those with a cyclic structure, are known to work against the so-called soft metals; they contain sulphur, nitrogen or phosphorus. The size of their cycle can be adapted to the nature and the ionic radius of the metal to be complexed.

Moreover, other complexing systems have been under investigation for a few years, more specifically norbadione A, a natural cesium sequestrant, as well as other related fungal pigments: tetronic acids. These compounds are highly interesting on the one hand for their cation complexation properties, especially cesium, and on the other hand for their remarkable antioxidant properties.

Decontamination systems developed within the COMTOX project are based on these two technologies and their objective is to bring a new, non aggressive and easily implemented solution to the decontamination of surfaces that have been contaminated with heavy metals, in particular: Cs, Cd, Pb, As, etc. …

SCIENTIFIC AND TECHNICAL APPROACH

The objective of this programme was in particular:

- to develop new molecules capable of complexing heavy metals on the basis of technological approaches described above,
- to select through physicochemical sorting the most effective for complexing these metals,
- to attempt to find an activity-structure relationship to direct synthesis toward the most effective complexing residues,
- to graft them on a supporting material
- and finally to integrate this material in the formulation of a multi-purpose product easy to use in the field in case of accidental contamination and to define an application procedure.

1 SYNTHESIS OF CYCLIC CHELATORS (CALIXARENES, PORPHYRINS,...)

In this framework, our aim has been to synthesize and study new organic and organometallic structures containing chelating groups such as sulphur, nitrogen, oxygen and phosphorus capable of complexing heavy metals very quickly.
The group's research was aimed at synthesizing and studying cage molecules designed to scavenge such toxic metals as: Cs, Cd, Pb, As, etc. …
Particular attention has been devoted to the following structures: calixarenes, porphyrins, cage structures and crown structures with a cycle that includes oxygen, sulphur and nitrogen atoms.

2 SYNTHESIS OF TETRONIC ACID DERIVED CHELATORS

Several natural compounds contain a 3-acyltetronic acid type moiety which enables them to complex metals; such is the case for tetronasin (figure 1). In the context of this study, we have considered synthesizing a large number of amine- or polyamine- derived compounds containing 3-acyltetronic acid moieties in order to assess their toxic metal complexing properties. The more active compounds should be functionalized with a polymerizable moiety in order to permit the preparation of chelating polymers.

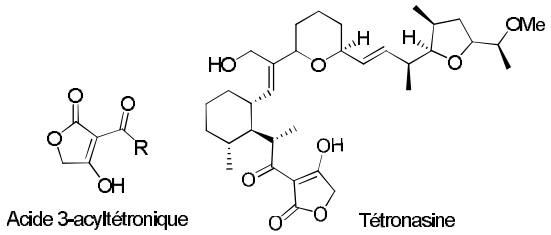

Figure 1: Structures of 3-acyltetronic acid and tetronasin

Calixarene or polyether type moieties are used as spacers between complexing entities.
Several approaches to the synthesis of poly(acyltetronic) compounds have been considered. After various trials, a method using a universal precursor, 3-bromoacetyltetronic acid, has been chosen. The alkylation of various amines or polyamines by this brominated compound permits the synthesis of many poly(acyltetronic) compounds (figure 2).

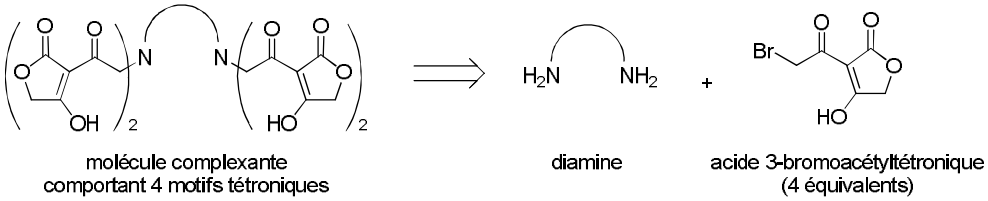

Figure 2: Basic approach to preparing a poly(acyltetronic) compound

3 PREPARATION OF FUNCTIONALIZED POLYMERS WITH CHELATING MOLECULES:

To reinforce their efficacy, these complexing units have been grafted on polymers. To maintain a good solubility in an aqueous medium, grafting was done on oligomers that were long enough to have the properties of a polymer and short enough to prevent too high an aggregation.

4 ASSESSMENT OF THE COMPLEXING POWER OF THE SYNTHETIZED MOLECULES BY MEASURING THEIR AFFINITY IN A LIQUID MEDIUM AND THEIR REMOBILIZATION CAPABILITY.

The determination and spectrophotometric analysis methods together with data processing by the SPECFIT software have allowed measuring the affinities of the synthetized molecules for cadmium, cesium, arsenic, and lead. These measurements were performed by absorption spectrophotometry in neutral and basic aqueous media and in decontamination formulations containing: Demineralized water: 61.5%; ethanol: 30%; 1-(1-methyl-2-propoxyethoxy)-2-propanol: 5%; PLURAFAC LF 401®: 3%; borax: 0.5%
This screening lead to identifying the best chelators by relating structure to activity.

5 DECONTAMINATING COMPOSITION APPLICABLE IN THE FIELD

The last step of the group's mission has been to ensure the development of formulations based on the new chelating molecules selected during the previous steps by stabilizing them, selecting an appropriate solvent and specific surfactant systems to improve the solid phase wettability, and by determining the optimum solution pH.

RESULTS

1 SYNTHESIS OF COMPLEXING AGENTS CONTAINING SEVERAL TETRONIC ACID MOIETIES:

Several cyclic or acyclic compounds have been prepared by T. Le Gall's team at CEA by reacting amines or polyamines with 3-bromacetytetronic acid. The preparation of this precursor and the synthesis of a bis (acyltetronic) **CC01** compound from a primary amine in the presence of base are shown in figure 3.

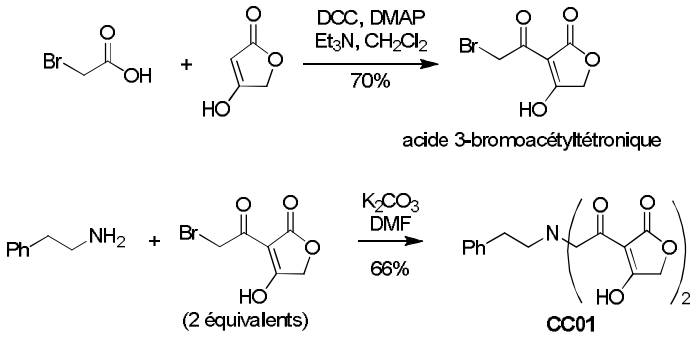

Figure 3: Synthesis of 3-bromacetytetronic acid and of a bis (acyltetronic) derivative.

The compounds prepared through this strategy are shown in figure 4. None of these compounds had been described before this study.

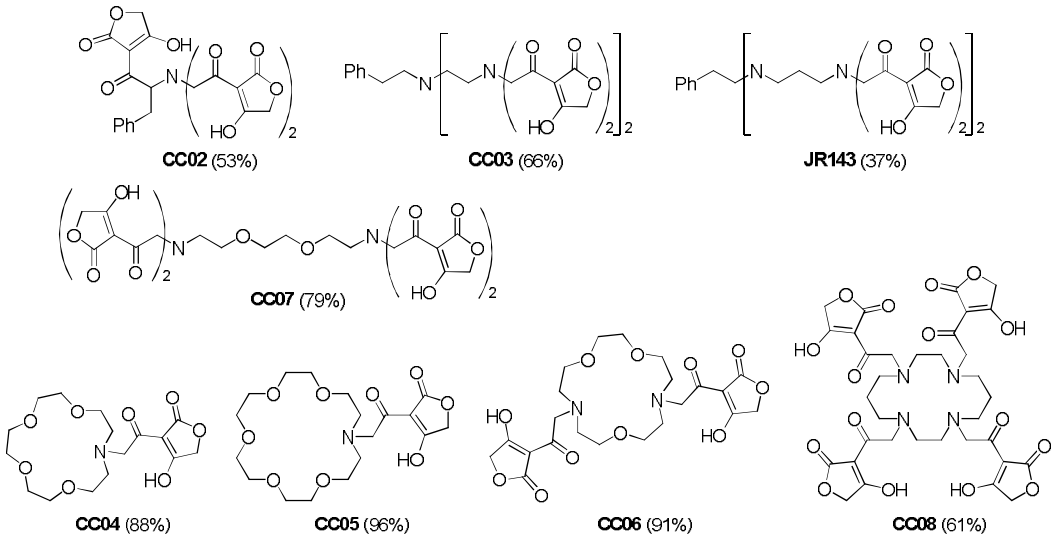

Figure 4: Prepared Poly(acyltetronic) compounds

Among these compounds, derivative **CC03** had very interesting metal complexation properties. This lead us to synthesizing similar compounds having in addition a polymerizable thiophene-pyrrole-thiophene type function. The synthesis of one of them, compound **CC11** is shown in figure 5. An intermediate compound containing two primary amines was obtained from 1,4-di(thiophen-2-yl)butane-1,4-dione in four steps. Four 3-acyltetronic moieties were then incorporated using the brominated precursor in order to complete the synthesis of **CC11**.

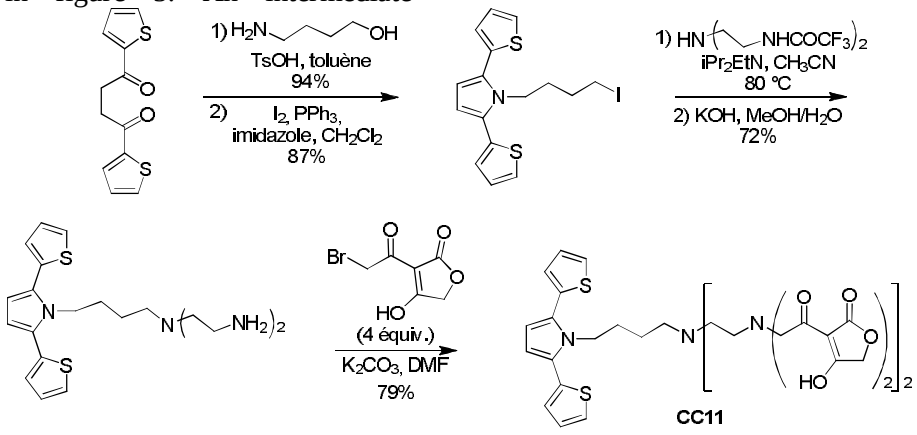

*Figure 5: Synthesis of compound **CC11***

Two other polymerizable derivatives, compounds **CC12** and **JR3-174** were also synthesized (figure 6).

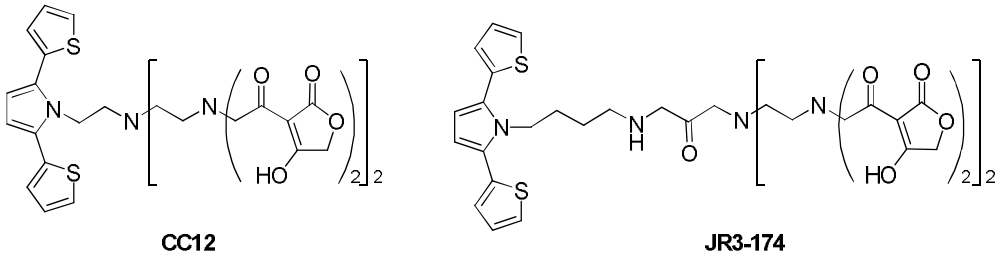

Figure 6: Polymerizable chelating derivatives

The various compounds prepared as remobilization and complexation agents for several metals have been assessed by ITODYS (J.M. El Hage Chahine's team) and by IRFAQ; Studies on the polymerization of derivatives containing a pyrrole-bis(thiophene) moiety were performed at ITODYS (M.Jouini's team).

2 PRODUCTION OF SULPHUR-OXYGEN MIXED MACROCYCLES AND STUDY OF THEIR COMPLEXATION PROPERTIES

G.Rima's team at LHFA have developed new macrocyclic molecules capable of complexing various contaminants. It was considered to functionalize them in order to modulate their physicochemical characteristics or to graft them onto various materials to use them for decontamination purposes.

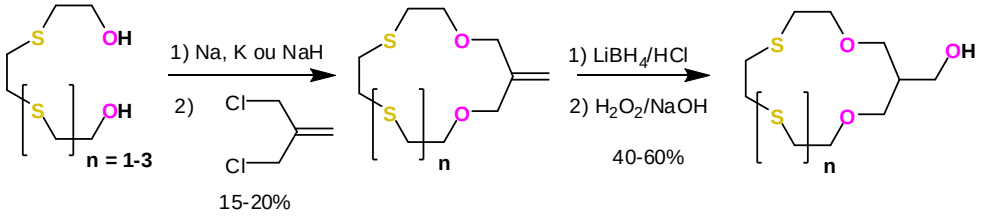

Figure 7: Synthesis of unsaturated and hydroxylated macrocycles

In order to modulate the hard/soft nature of the new cryptands and consequently their complexation properties, various mixed sulphur-oxygen crown ethers were prepared by varying the number of sulphur and oxygen atoms within the structure and the size of the macrocycle (figure 7). This step in the synthesis has required a precise optimization of the reaction conditions by varying factors such as the nature of the salt used in the intramolecular condensation reaction, the dilution of the medium, the speed at which additives are added, the reaction temperature as well as the purification method. The double bond was then oxidized without concomitant oxidization of sulphur atoms in order to allow the formation of hydroxyl group substituted macrocycles. This alcohol group was then used to prepare a library of hydrophilic or lipophilic molecules having various complexation capabilities such as bicyclic tweezer-like structures (figure 8).

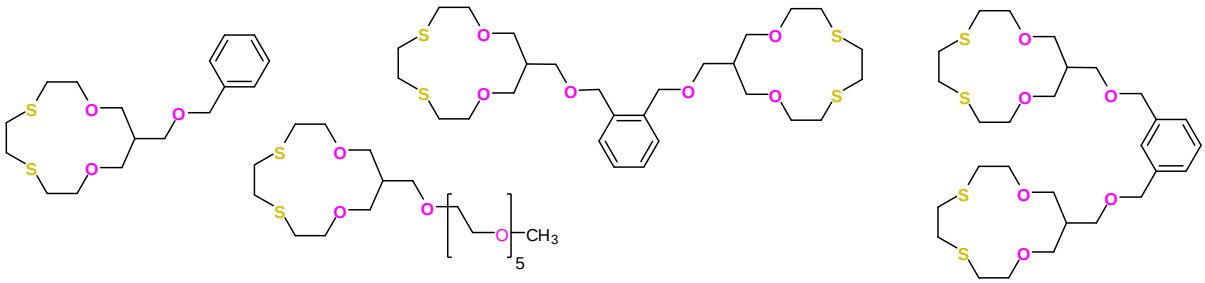

Figure 8 : Examples of macrocyclic functionalized stuctures

An alternative method for modulating the complexation properties of mixed sulphur-oxygen macrocycles is to modify the complexation geometry by varying the oxidization degree of the sulphur atoms. This concept, developed through specific sulphur oxidization without oxidization of the unsaturation (figure 3) was performed on a macrocycle having two sulphur atoms and two oxygen atoms. Depending on the number of oxidization agent equivalents and the reaction conditions it has made it possible to prepare preferentially disulfone, sulfone-sulfoxide and disulfoxide in *meso* or *dl* form. The various structures were characterized by X-ray diffraction.

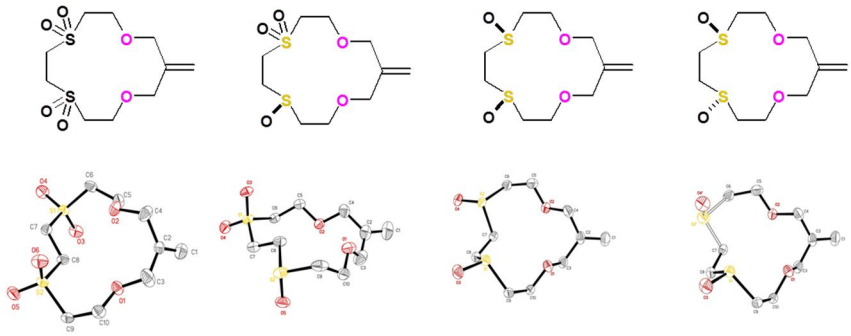

Figure 9: Oxidization products of mixed sulphur-oxygen macrocycles

The complexing properties of the various structures were assessed in relation with the metals leading to palladium or ruthenium monomeric complexes or copper polymeric systems.

3 SYNTHESIS OF GRAFTED CHELATORS ON POLYMERIC STUCTURES

A thiophene or pyrrole based conjugated precursor, SNS butanol was synthesized and functionalized using a chelator. Its polymer obtained by chemical oxidization proved to be a good sequestering agent of arsenic and cesium metallic cations.
Moreover a copolymer was prepared based on SNS and SNS containing the sequestering agent (CC11) (figure 5) in order to achieve its encapsulation through CD and to increase its solubility in water. The condition to obtain the copolymer are now well under control.

4 MEASUREMENT OF THE SEQUESTRATION CONSTANTS OF THE MAIN CHELATING AGENTS

Complexation experiments were performed in an aqueous medium at pH = 7.48 for the 4 metals with all the molecules and at pH = 9.3 for Cs^{+}, As^{5+} et Pb^{2+} with all the molecules since cadmium salt is not soluble in basic media.
The same experiments were performed with CC03 in the compositions formulated by IRFAQ.
The results relating to the formation of complexes between the four metals and all the molecules are given in Table 1 for the aqueous media.

		JR203	CC01	CC02	CC03	CC11	CC12	CC13	CC14	JR160	G10	EDTA	Calixarenes
Cd^{2+}	pH = 7.48	**5.6 ± 0.25 Good**	< 2 Bad	< 2 Bad	**6.8 ± 0.2 Good**	**> CC03 Very Good**	**> CC03 Very Good**	2.6 ± 0.4 Bad	**5.1 ± 0.2 Good**	**> CC03 Very Good**	No complex	13-14	-
	pH = 9.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	15-16	-
Cs^{+}	pH = 7.48	< 2 Bad	< 2 Bad	< 2 Bad	**4.3 ± 0.1 Good**	< 2 Bad	< 2 Bad	No complex	< 2 Bad	3.0 ± 0.3 Bad	No complex	-	~ 8
	pH = 9.3	< 2 Bad	< 2 Bad	< 2 Bad	**4.5 ± 0.1 Good**	< 2 Bad	< 2 Bad	No complex	< 2 Bad	3.1 ± 0.3 Bad	No complex	-	
As^{5+}	pH = 7.48	< 2 Bad	< 2 Bad	< 2 Bad	**5.4 ± 0.1 Very Good**	**4.0 ± 0.1 Good**	< 2 Bad	No complex	< 2 Bad	**3.5 ± 0.2 Moyen**	No complex	-	-
	pH = 9.3	< 2 Bad	< 2 Bad	< 2 Bad	**5.0 ± 0.1 Very Good**	**4.2 ± 0.1 Good**	< 2 Bad	No complex	< 2 Bad	**3.0 ± 0.1 Moyen**	No complex	-	
Pb^{2+}	pH = 7.48	< 2 Bad	< 2 Bad	< 2 Bad	**5.7 ± 0.2 Good**	**> CC03 Very Good**	**> CC03 Very Good**	< 2 Bad	**> CC03 Very Good**	**> CC03 Very Good**	No complex	13-14	-
	pH = 9.3	< 2 Bad	< 2 Bad	< 2 Bad	**6.0 ± 0.2 Good**	**> CC03 Very Good**	**> CC03 Very Good**	< 2 Bad	**> CC03 Very Good**	**> CC03 Very Good**	No complex	17-18	-

ND : not determined

Table 1: Logarithms of the thermodynamic constants in aqueous medium of the formation of the Cd2+, Cs+, As5+ and Pb2+ complexes with the molecules synthetized by the Le Gall and Jouini teams

The same study was performed with the poly(PHEMA/EDTA). A variation is observed in the absorption spectra when cadmium or lead is added. This seems to show a complex has been formed. However with an undetermined level of grafted EDTA, the affinity constant cannot be measured precisely since it is directly related to the concentration in chelating agents.

The results of these tests (in annex 1) show that in water two molecules are suitable:
CC03 which may be considered as a universal chelator with very good affinity for cadmium, cesium, arsenic and lead, and to a lesser extent JR160 which is more specific to cadmium and lead.
These results also show that CC11, which is the polymerizable CC03 analog, has a better affinity for cadmium and lead but loses its highly effective complexing power with cesium and arsenic.
CC12, also a polymerizable CC03 analog but with one ethyl group less between the "CC03 moiety" and the SNS moiety, also shows an enhanced affinity for Cd^{2+} and Pb^{2+} compared with CC03 but totally loses its ability to complex Cs^{+} and As^{5+}.
The very low affinity of CC13 for Cs^{+} and As^{5+} is logical since this molecule is an EDTA derivative known for not being a good chelator of these metals. However the low affinity for Cd^{2+} and Pb^{2+} is strange because EDTA alone is one of the best chelators of these two metals.
The other molecules do not seem to be good candidates for the production of a decontaminating basis.

USING THE RESULTS

We have started an assessment phase of the best sequestering agents in a formulation that could be used in the field. In order to define a method close to operational conditions, the sequestering efficacy measurements - which initially were taken in a homogenous phase - were taken in heterogeneous phase (leaching) in the presence of various substrates. In a first stage, it was decided to measure the chelating power of the compositions containing the best candidates against metals precipitated in the

form of insoluble salts and dispersed into the soil.
Results show that a large part of the sequestrant is bound to the soil and that consequently decontamination of the soil by leaching cannot be done even with the most effective sequestrants.

Further tests in realistic conditions were developed for hardened substrates: concrete, painted metal, etc. … with the most interesting combinations of sequestrants, in particular: CC03, CC11 + EDTA, CC03 + EDTA and PHEMA-EDTA.

Under these conditions (figure 9):

- The good lead sequestering power of PHEMA-EDTA is confirmed. It is of the same order as that of EDTA.
- The cadmium sequestering power of the PHEMA-EDTA polymer is better than that of EDTA.
- The remobilization power of compounds CC11 and CC03 remains inferior to that of polymers PHEMA-EDTA both for cadmium and lead.
- These results confirm those obtained in homogenous solutions

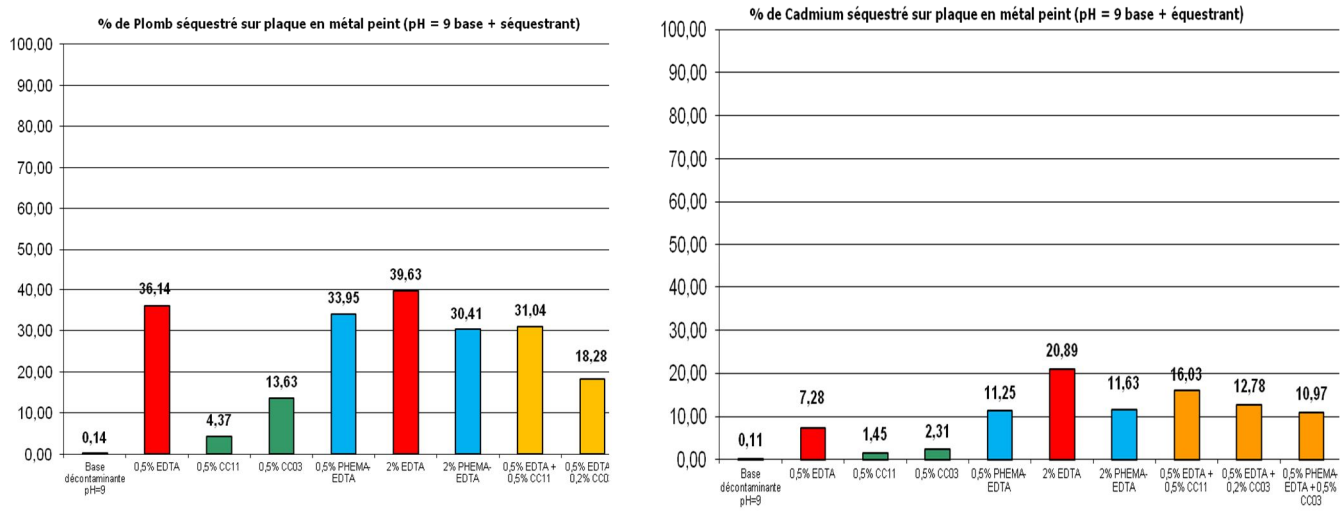

Figure 9: % of heavy metals eliminated from a surface contaminated by their insoluble salts, by a decontaminating solution containing various sequestering agents

CONCLUSIONS

Synthesizing new heavy metal sequestrants has been successful: tetronic acid derivatives, crown ether type macrocycles, heterocalixarenes or porphyrins, and polymeric structures resulting from grafting sequestering units to two types of polymeric supports, poly(2-hydroxyethyl) metacrylate and the thiophene pyrrole thiophene Poly(SNS tetrapod) =PolyCC011 based conjugated polymer.
Trials to optimize these tetrapod compounds through varying the chain length of the "tweezers" were performed; the results obtained for the sequestering power seem to be quite close to but not significantly better than those obtained with compound CC03. A special characteristic of CC03 is to be a very good sequestrant of many heavy metals.

The sequestering efficacy of these materials has been determined by measuring their ability to remobilize water-insoluble salts of various heavy metals on the one hand and by measuring their sequestering constants on the other hand. These two approaches were shown to have convergent results.

Two candidates corresponding to two different synthetic pathways seem particularly promising: the **PHEMA-EDTA** polymer (obtained by grafting EDTA to poly(2-hydroxyethyl) metacrylate and a **tetronic acid derived quadripod compound (CC03)** grafted on a thiophene pyrrole thiophene **(SNS)** based conjugated polymer; the latter compound has the remarkable property of being an excellent **arsenic sequestering agent.**

It has been possible to polymerize compounds such as CC11 and CC12, which contain a pyrrole-bis(thiophene) type polymerizable function but sequestering efficacy of the polymers obtained so far does not seem to be significantly better than that of initial monomers. However these materials are in polymer forms and are consequently easier to recover.

Under operational conditions, using these compounds incorporated in decontaminating formulations is not directly applicable to the treatment of contaminated soils since we have demonstrated that sequestrants themselves bind to certain constituents of these soils (clay, humic salts,...) and consequently do not remobilize precipitated polluting metals to carry them away.

However, the sequestering and remobilizing efficacy of formulations based on builders such as CC03, CC11 and their polymers on the one hand and PHEMA-EDTA on the other hand has been demonstrated (see annex 2) even at low concentrations and **treating contaminated hard surfaces such as metals, painted surfaces, concrete, etc. becomes possible.**