Heavy metals removal from anaerobically digested sludge

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To my parents - my first instructors

To my brother - my first friend

ABSTRACT

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Although studies in the field of heavy metals removal from sewage sludges are numerous, knowledge gaps still exist, which are the reason for the low attention paid to the implementation of techniques for this purpose. Such techniques still remain in laboratory and pilot plant scale. This work aims to contribute to the further applicability of technologies that might be used to remove heavy metals from anaerobically digested sludge.

A physical classification scheme based on wet-sieving was applied and showed that heavy metals prevailed in the fractions < 0.063 mm, constituting 70 % of the total sludge mass and 78-85 % of the heavy metals present in the sludge. In all the separated fractions, however, most of the metals concentrations exceeded the Dutch standard for sludge application on land. To determine the chemical forms of heavy metals in the sludge, three sequential chemical extraction (SCE) schemes were tested: Tessier (1979), Veeken (1998), and Sims & Kline (1991). Modified versions of the original schemes were also applied as a tentative to investigate the differences among them. Despite uncertainties, the SCE method gives useful information concerning metals availability. The results demonstrated that Cr (65-67 %) and Cu (65-87 %) were released in an oxidizing environment. Zinc (78-86 %) was extracted by a reducing agent, whereas Pb was solubilized at strong acidic conditions and high temperature. A chelating agent released considerable amounts of Cr (56-57 %), Pb (57-78 %) and Zn (50-62 %). About 70 % of Cu was also extracted at a pH of 12.6. The modified schemes were valuable to interpret the differences in the results of the original schemes.

To assess the heavy metals solubilization, several organic and inorganic acids were tested at different conditions of pH, reaction time, and redox potential. Oxidation with aeration or H_2O_2 was also investigated. The best results achieved with the most effective acid (HCl) were: Cr: 85 % with H_2O_2, Cu: 100 % with H_2O_2, Pb and Zn: 100 % with aeration and H_2O_2. Moreover, Cu solubilization was highly influenced by oxidation. The effect of bioleaching on heavy metals extraction, with application of elemental sulfur

and ferrous iron, was studied. The results were compared to those obtained by chemical leaching with H_2SO_4 and HCl. With addition of ferrous iron, the maximum extraction achieved for Zn was 80.8 % with a pH of 2.7. For Cu, it was 65.5 % with a pH of 2.5. Chromium was solubilized only when the pH was 2.5 and less than 1 % of Pb was extracted by bioleaching. HCl is more effective than H_2SO_4 to solubilize all the metals studied.

After metals solubilization, the next step was the separation of the sludge solids from the metal-rich acidic liquid (leachate) by centrifugation and filtration. The filtered leachate was submitted to hydroxide precipitation with NaOH and sulfide precipitation with Na_2S, both separately and in combination. Each precipitation step was followed by filtration. The results showed that, when Fe and Al are present in the sludge (as it was the case), adsorption and/or coprecipitation of the heavy metals to ferric or aluminium hydroxide precipitate might occur. This was especially observed when hydroxide precipitation was solely applied. The use of NaOH at a pH of 4-5 followed by filtration and further addition of Na_2S to the filtered liquid at a pH of 7-8 considerably decreased the dosage of the second precipitant, when this was exclusively applied. The best removal efficiencies achieved were: Pb: 100 %, Cr: 99.9 %, Cu: 99.7 %, and Zn: 99.9 %.

Two conceptual designs of a treatment process to be applied in practice for heavy metals removal from sewage sludge were discussed. One referred to a physical-chemical treatment and the other to a biological-physical-chemical treatment. In the first concept, heavy metals solubilization is achieved with HCl and an oxidative pre-treatment with aeration or H_2O_2. In the second concept, the approach is the use of the bioleaching to solubilize heavy metals. This system consists of an aerobic bioreactor fed with S^o. A biological sulfate-reducing reactor, where sulfate is converted into sulfur, is included and a closed sulfur cycle is achieved. Based on a brief technical, environmental and economical evaluation, the biological-physical-chemical process seems to be more attractive than the physical-chemical process. In further development of the process to a practical scale, attention has to be paid to the reuse possibilities of heavy metals recovered from the sludge and how to deal with the remaining liquid residues.

CONTENTS

Chapter 1

General introduction

ORIGIN OF SEWAGE SLUDGE

Increasing urbanization and industrialization has culminated in a dramatic growth in the volume of municipal wastewater produced worldwide. This wastewater contains all the substances that enter in human metabolism, such as food, beverages, pharmaceuticals, a great variety of household chemicals and the substances discharged from trade and industry to the sewer system (Kroiss, 2003). Moreover, rain water and its contact materials also contribute to this composition. As a result, the constituents of the municipal wastewater discharged into the sewer system are a mirror of our civilization and of human and urban metabolism.

Besides the gas production (e.g., carbon dioxide and methane), municipal wastewater treatment results in two products, which are closely related in their chemical composition (Kroiss, 2003):

- Treated wastewater to be discharged to the receiving surface water;
- Wastewater sludge to be treated and disposed or reused without creating new (environmental) problems.

The several levels of the municipal wastewater treatment are known as preliminary, primary, advanced primary, secondary (without/with nutrient removal), and tertiary (or advanced) treatment. The description of each treatment level, as given by Metcalf and Eddy (2003) is shown in Table 1.1.

Table 1.1 - Levels of wastewater treatment (Metcalf and Eddy, 2003)

Treatment level	Description
Preliminary	Removal of rags, sticks, floatables, grit, and grease that may cause maintenance or operational problems with the treatment system
Primary	Removal of a portion of the suspended solids and organic matter by a physical operation
Advanced primary	Enhanced removal of suspended solids and organic matter. Usually performed by chemical addition or filtration
Secondary	Removal of biodegradable organic matter and suspended solids by biological or chemical processes. Disinfection is also typically included in the definition of conventional secondary treatment
Secondary with nutrient removal	Removal of biodegradable organics, suspended solids, and nutrients (nitrogen and/or phosphorus)
Tertiary	Removal of residual suspended solids (after secondary treatment), usually by granular medium filtration or microscreens. Disinfection and nutrient removal are also often included
Advanced	Removal of dissolved and suspended materials remaining after normal biological treatment when required for various water reuse applications. Usually accomplished by combined processes

To treat municipal wastewater streams, biological methods are usually applied. The overall objectives of the biological treatment of domestic wastewater are:

- To transform dissolved and particulate biodegradable components into acceptable end products;
- To capture and incorporate suspended and non-settleable colloidal solids into a biological floc or biofilm;
- To remove or reduce the concentration of organic and inorganic compounds (e.g., heavy metals);
- To remove pathogens and other microorganisms;
- To transform or remove nutrients, such as nitrogen and phosphorus;
- In some cases, to remove specific trace organic constituents and compounds;
- To produce effluent that can be discharged to surface water.

A conventional biological treatment process, which is worldwide used in practice to treat municipal wastewaters, is the activated sludge system (see scheme in Figure 1.1). Such system is basically constituted of a bioreactor in which the microorganisms responsible for the treatment are kept in suspension and aerated.

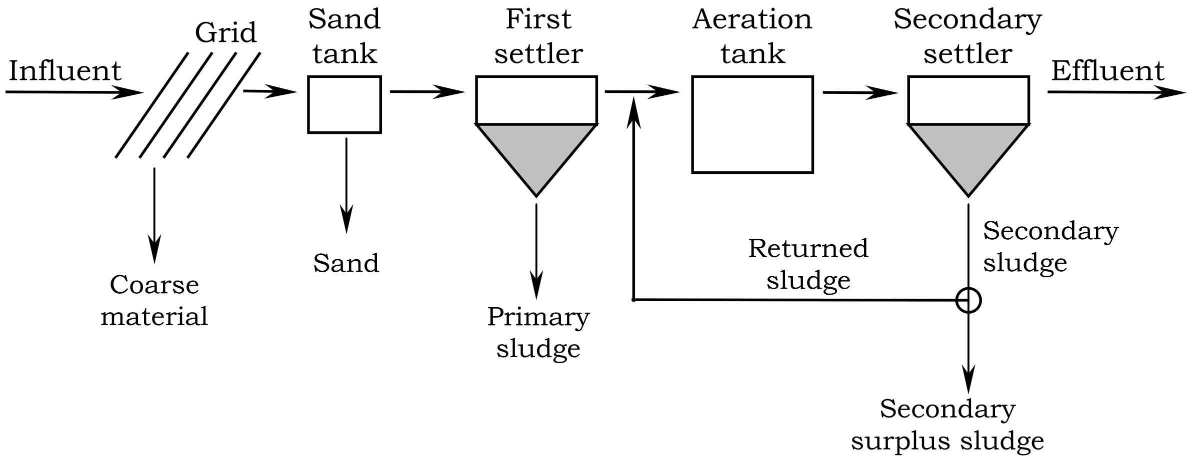

Figure 1.1 - Scheme of an activated sludge system

After the preliminary and primary treatment phases, the liquid is kept in the reactor for about 6 hours and flows into a settling tank. The biomass and fine solids settle as sludge and the treated liquid can be discharged. The settled sludge is partly returned to the aeration tank and the surplus amount is mixed with the primary sludge and normally stabilized biologically at anaerobic conditions. This process is carried out in closed biologic reactors, known as anaerobic digesters. Despite the relatively high quality effluent produced by this type of system, it has the serious drawback of excessive sludge production.

The main focus on municipal treatment over the last 30 years has been on improving the quality of the effluent by including the construction of secondary and advanced wastewater treatment units in the treatment plant. As such, higher levels of treatment have been achieved not only for the common wastewater constituents but also for the removal of specific compounds such as nutrients and heavy metals. A by-product of these approaches is the increased amount of sludge generated. Sludge processing, reuse, and disposal represent the most complex problem facing the engineer in the field of municipal wastewater treatment. Sludge treatment often represents more than 50 % of the total costs of municipal wastewater treatment (Rulkens 2003a).

COMPOSITION OF SEWAGE SLUDGE

The problems dealing with sewage sludge are complex because it is largely constituted of those substances responsible for the offensive character of untreated wastewater (Metcalf and Eddy, 2003). Besides the potentially hazardous materials, however, sludge also contains valuable materials. To identify potential alternatives for a sustainable treatment, it is useful to evaluate the composition of the sludge. This composition can be roughly characterized by five groups of components, which are present in the sludge (Rulkens, 2003b):

- Non-toxic organic carbon compounds, Kjeldahl-N, phosphorus containing components;
- Toxic pollutants:
  - Heavy metals, such as Zn, Pb, Cu, Cr, Ni, Cd, Hg, As (varying from more than 1000 ppm to less than 1 ppm);
  - PCBs, PAHs, dioxins, pesticides, endocrine disrupters, linear-alkyl-sulfonates, nonyl-phenols, etc.
- Pathogens and other microbiological pollutants;
- Inorganic compounds such as silicates, aluminates, calcium and magnesium containing compounds;

- Water, varying from a few percent to more than ninety five percent.

Nitrogen, phosphorus, and organic carbon containing compounds can be considered as valuable compounds, as well as some inorganic compounds. A sustainable treatment includes the recovery and useful reuse of the valuable products and the minimization of the possible adverse environmental and human impact of sewage sludge. The management of the solids and concentrated contaminants present in the sludge is still one of the most difficult and expensive problems in the field of wastewater engineering.

SEWAGE SLUDGE PROCESSING

The principal methods used for sludge solids processing are listed in Table 1.2 (partly adapted from Metcalf and Eddy, 2003):

Table 1.2 - Sewage sludge processing

Method	Function
Thickening	Volume reduction
Stabilization	Removal of easy biodegradable compounds
Conditioning	Improve dewaterability
Dewatering	Volume reduction
Drying	Volume reduction
Incineration	Volume reduction, energy production
Wet oxidation	Conditioning, volume reduction
Gasification	Volume reduction, energy production
Pyrolysis	Volume reduction, energy production
Landfill	Disposal
Land application	Beneficial use
Cement and bricks production	Beneficial use
Conveyance and storage	Solids transport and storage

Thickening, conditioning, dewatering, and drying are used primarily to remove moisture from the sludge. These processes are important, for example, when the sludge is to be incinerated. For avoiding any external energy input in the incineration process, the sludge must be dewatered to a cake solids content of at least 30-35 % (Priestley, 2001). Another example is when the sludge is to be disposed to controlled landfills. In this case, the sludge volume should be minimized to reduce transport costs and dumping areas.

Controlled landfill still continues to be used widely for the disposal of sludges, either in sludge-only monofills or along with municipal solid waste. The number and capacity of landfills, however, have been reduced, and new landfill locations that attend to public and regulatory acceptance as well as economic requirements are increasingly difficult to find. In many cases, the easiest and least costly way of reuse of the valuable compounds of the sludge is the application of the sludge on land for agricultural purposes. This improves soil structure, cation-exchange capacity, water holding capacity, water infiltration, tilth, and soil aeration. It also helps in plant growth due to the supply of nutrients, such as nitrogen, phosphorus, potassium, iron, zinc, manganese, etc. Moreover, the nutrients in the sludge also substitute partially expensive chemical fertilizers. Depending on the sludge composition, however, it might be necessary to remove undesirable substances (e.g., heavy metals) present in the sludge before its application as agricultural fertilizers. Nevertheless, if the beneficial use of sludge in agriculture is not possible or feasible, other technical solutions for final sludge disposal, such as use for landscaping, re-cultivation and landfill disposal can be applied (Kroiss, 2003).

Anaerobic digestion is one of the oldest processes used for the stabilization of sludges. It comprises the decomposition of organic matter and inorganic matter (especially sulfate) in the absence of molecular oxygen. Anaerobic digestion is mainly applied in the stabilization of concentrated sludges resulted from the treatment of municipal and industrial wastewater. In anaerobic digestion, part of the volatile compounds is converted into biogas (methane), which can be applied as an energy resource either at the wastewater treatment plant itself or elsewhere.

The biological conversion of organic matter in aerobic digestion occurs in the presence of oxygen, usually in an open-top tank. This process is much simpler to operate than an anaerobic digester, but no usable gas is produced. The process is energy-intensive because of the power requirements necessary for mixing and oxygen transfer (Metcalf and Eddy, 2003).

With respect to composting, this process involves aerobic degradation of organic matter, as well as a potential decrease of the sludge water content.

In essence, the activity of microorganisms causes both an increase in temperature, hence pathogen destruction, and a release of energy, carbon dioxide, water, and other components. The costs are elevated when sludge is composted, in contrast to, for example, direct application of sludges in agriculture. However, the market and health aspects such as pathogen risk, odor, and nutrient control often emphasize and require the demand for alternative solutions, justifying composting as a promising stabilization option (Coulomb and Myrope, 1997).

A common possibility for sludge volume reduction is incineration. This process involves the total conversion of organic solids to oxidized end products, primarily carbon dioxide, water, and ash. The major advantages (A) and disadvantages (D) of incineration, according to Metcalf and Eddy (2003) are:

- Maximum volume reduction, decreasing disposal requirements (A);
- Destruction of pathogens and toxic compounds (A);
- Energy recovery potential (A);
- High capital and operating cost (D);
- Highly skilled operating and maintenance staffs required (D);
- The residuals produced (air emissions and ash) may have adverse environmental effects, such as green house effect (McBean *et al.*, 1995) (D);
- Disposal of residuals, which may be classified as hazardous wastes, if they exceed prescribed maximum pollutant concentrations (D).

In the last fifteen years, several technologies have been developed with the objective to reuse sludge within a city. Among them, brick making sounds attractive, due to its simple operation and marketability (Okuno and Takahashi, 1997). The process, developed in Japan, can produce bricks from 100 % of incinerated sludge ash without any additives, yielding the least amount of end products. Moreover, according to Okuno and Takahashi (1997), no heavy metals leach out from the brick, even at a rough environment of pH levels below 3. In general, however, the supply of the sewage bricks exceeds the demand and the production costs of the traditional ones. As such, an alternative destination of sewage sludge is its utilization as raw material for Portland cement production, which is being developed in Japan also (Taruya *et al.*, 2001). The authors defend that the direct injection of dewatered sludge into Portland cement kilns was more attractive than sludge incinerator ash and dried powder sludge.

Wet oxidation, pyrolysis and gasification processes have attracted a lot of attention as potentially attractive ways of recovering value from waste, but these technologies are relatively new and are still for a large part under development. In wet oxidation the organic content of sludge is oxidized in specific reactors at high temperatures (200-300 °C) and low/high pressure systems (30-150 bar) (Utvik and Matter, 1997). Both pyrolysis and gasification turn wastes into energy rich fuels by heating the waste under controlled conditions. In contrast to incineration, which fully converts the input waste into energy and ash, these processes limit the conversion so that combustion does not take place directly. Instead, they convert the waste into valuable intermediates that can be further processed for materials recycling or energy recovery (Schwager, 2001).

SEWAGE SLUDGE MANAGEMENT POLICY WORLDWIDE

Current aspects

The correct management of sewage sludge and other biodegradable wastes requires the development of proper normative and regulations to maximize the use of waste material and energy and minimize the impact of waste on the environment (Spinosa and Lattarulo, 2003). Especially in the developed countries, several attempts have been made to improve regulations that protect public health and the environment. In addition, some of those regulations are under review or improvement to further reduce the risks derived from reuse practices. In the EU, the revision of the Directive 86/278/EEC on sludge land application, and the development of a Biowaste Directive have been planned as necessary actions (Spinosa and Lattarulo, 2003). In certain cases, however, developing countries face the problem of adapting regulations with little or no modifications. This situation is not always feasible and acceptable, since the sludge characteristics are strongly site-dependant (Jiménez and Spinosa, 2001).

In developing countries, wastewater treatment hardly reaches 10 % of the volume generated, and only in a few of the existing plants, sludge treatment is carried out. As a consequence, these countries are in a position that allows the application of new or different strategies to reuse or dispose the sludge, compared to those applied in developed countries. The beneficial use of sludge for land application, instead the use of commercial fertilizers, is an example of such strategy, but its development requires that the countries execute industrial pre-treatment programs, as well as the integral management of sludge to avoid diseases spreading (Jiménez and Spinosa, 2001).

Many countries are at many different levels of development in sludge regulation and management. Even within countries there can be a vast diversity of approaches, as in Brazil only 66.2 % of the country's 170 million population (IBGE, 2000) is connected to sewers and only 25.6 % of this population is connected to treatment plants (SNIS, 2001). In fact, only recently the number of wastewater treatment plants is increasing in Brazil, and consequently the sludge production is growing. According to Santos and Tsutiya (1997) the estimated total sludge production will be a volume of 750 dry tons per day in São Paulo state in the year 2015. The city of Jundiaí, in São Paulo state, is an example of the environmental contrast existent in the country. This city has installed over 95 % piped sewerage cover, and all the sewage from 320 000 people and many industries is fully treated. A well-developed sludge management policy intends to use all of the dewatered and dried sludge applied in sugar cane plantations and reforested land (McCann, 2002). Moreover, the cities of Curitiba and Brasília are nowadays applying the sludge in large scale in agriculture, whereas the sludge generated in the metropolitan region of São Paulo is fully landfilled (Fernandes *et al.*, 2001).

In Vietnam, large volumes of sludge generated in municipal wastewater treatment plants from big cities such as Ho Chi Minh City and main economic areas of the south are, so far, disposed to open field. This results in serious problems due to the shortage of disposal capacity and leaching of heavy metals to underground water, surface water and soil (Marchioretto *et al.*, 2002).

In the USA, regulatory influences on both federal and state levels have encouraged the beneficial use of sewage sludge (biosolids). Research and technology in the field have helped alleviate public concern regarding the human health and environmental impacts of sludge. In addition, education and marketing efforts have been improving public perceptions in some areas of the USA about the beneficial use of sludge, although public acceptance problems persist in other areas (U.S.EPA, 1999). The Part 503 Biosolids Rule clearly defines sludge quality requirements for use or disposal and has become a useful tool for sludge managers in marketing efforts.

The solutions for sludge management will vary over time and regions and economic criteria will play an important role (Kroiss, 2003). Nevertheless experiences from all over the world should be shared to increase the knowledge and establish certain criteria to reach a successful sludge management program. Moreover, education and communication play an important function in increasing public acceptance towards sludge reuse. In addition, standardized techniques for sludge sampling and analysis need to be established to ease the enforcement of local and international regulations. Different aspects, like soil characteristics, economics, technical capabilities, and health levels are issues that cannot be neglected when developing regulations. Also, adequate monitoring and enforcement policies are important for future management programs (Jiménez *et al.*, 2003).

Sustainable sewage sludge treatment

Future sludge treatment should be progressively focused on an improved efficiency and environmental sustainability of the process. In this context, special attention must be paid to those processes that are simultaneously concentrated upon the elimination of the risks for environment and human health and on the recovery or beneficial use of the valuable compounds in the sludge.

There are five basic approaches to tackle the sludge problem (Rulkens, 2003b). Such approaches are often applied in combination with each other, particularly if the treatment process is applied in practice:

- Beneficial use of organic carbon and inorganic compounds;
- Recovery of phosphates from sludge for reuse;
- Reduction of the total amount or volume of sludge;
- Change in treatment scenario of municipal wastewater:
    - Centralized treatment primarily based on physical-chemical treatment with attention to complete removal of colloidal and suspended particles;
    - Decentralized sanitation applied to avoid discharge of heavy metals and other pollutants from point sources or diffuse sources.
- Sludge quality improvement:
    - Prevention of discharge of pollutants to the sewer and disconnection of the rainwater;

- Removal of colloidal and suspended particles from the influent as a first treatment step;
- Removal of toxic organics and pathogens;
- Removal of heavy metals – this thesis is primarily focused on this issue.

REMOVAL OF HEAVY METALS FROM SEWAGE SLUDGE

Today much is known about the health effects of heavy metals. Exposure to heavy metals has been linked with developmental retardation, various cancers, kidney damage, and even death in some instances of exposure to very high concentrations. Despite abundant evidence of these deleterious health effects, exposure to heavy metals continues and may increase in certain areas with the absence of planned policy actions. For instance, mercury is still extensively used in gold mining in many parts of Latin America. Arsenic, along with copper and chromium compounds, is a common ingredient in wood preservatives. Lead is still widely used as an additive in gasoline. Increased use of coal in the future will increase metal exposures because coal ash contains many toxic metals and can be breathed deeply into the lungs (Nriagu, 1996).

Heavy metals can be removed from sewage sludge by chemical leaching with inorganic and organic acids or by bioleaching. With these methods, a substantial reduction in heavy metal concentration can be achieved especially in case of very strongly polluted sludges. The benefits of heavy metals removal from this type of sludge include:

- Sludge can be disposed to landfills with lower risk of heavy metals leaching to surface and groundwater or uptake by plants;
- Sludge can be used as soil improver;
- Sludge can be applied with lower risk as energy source in co-incineration. In addition, the off-gas treatment system would be less complex than when the sludge is metal polluted;
- Dewatered sludge or sludge fly ashes can be applied with lower risk as raw material for Portland cement and bricks production.

State of the art of the most common techniques for heavy metals removal from sewage sludges

Basically there are three approaches (Rulkens *et al.*, 1989) available to reduce the concentration of heavy metals in sewage sludges. The first approach is control of industrial sources and other point sources of wastewater discharges to the sewer system. However, the source control might be a difficult task, as it is very difficult to identify all these sources. In some places, there is even the presence of illegal factories discharging their effluents direct to the sewer. A second approach is control of diffuse sources, for instance by using lead-free gasoline, copper-free tap water transport systems and uncoupling rain water discharge on the sewerage system. The third approach is the extractive removal of heavy metals from sewage sludge.

The widespread use of anaerobic digestion in the treatment of sewage sludges in recent years underlines the importance of investigations in the field of heavy metals removal from anaerobically digested sludges. Heavy metals can be present in (anaerobically digested) sewage sludge in a number of forms. They can be dissolved in the water phase either as ions, as organic and inorganic complexes (this amount is in general negligible), precipitated as salts or hydroxides, co-precipitated with metal oxides, adsorbed to suspended solids, or associated with biological residues. The distribution of the metals over these forms depends on the chemical properties of the specific metal and on the sludge characteristics, which are determined by pH, temperature, redox potential, and presence of complexing agents.

The choice of the most worthwhile speciation technique to determine metals distribution is difficult. Currently, despite its limitations, sequential chemical extraction (SCE) procedures may provide useful information concerning the availability of the metals in the sludge. Furthermore, an additional tool to the evaluation of metals mobility in the sludge is the application of acidification tests, with progressive pH variations. With a rational combination of the existing methods, it will be possible to draw consistent conclusions about the heavy metals speciation in the sludge, so that proper extraction technologies can be designed. But still, basic research is necessary for the validation of extraction tests in relation to the actual field conditions.

A treatment process to remove heavy metals from (anaerobically digested) sludges is generally accomplished by four steps. The first treatment step consists of solubilization of the heavy metals. The second step comprises the separation of the water phase containing the mobilized heavy metals and the sludge particles. The sludge particles are removed as a concentrated sludge and the liquid containing the solubilized metals (leachate) is subjected to the third treatment step, in which the heavy metals will be precipitated and removed from the leachate in a fourth treatment step.

To promote the solubilization of heavy metals it is mainly necessary to decrease the pH of the sludge to values around 1-2 with a previous increase in the redox potential of the sludge, especially in the case of anaerobically digested sludge. The combination of these two conditions will favor, for example, the formation of soluble metal complexes, oxidizing insoluble reduced metal forms (e.g., Cu_2S) to soluble forms (e.g., $CuSO_4$). The solubilization step can be accomplished by means of chemical leaching and bioleaching.

In the case of chemical leaching, a previous oxidation step might be executed in order to raise the redox potential of the (anaerobically digested) sludge. This can be performed by aeration or by the addition of an oxidating agent, like H_2O_2 (Yoshizaki and Tomida, 2000). Then the acidification step takes place. According to literature, several acids have been tested and the most common are inorganic acids such as hydrochloric acid (Fytianos *et al.*, 1998), nitric acid (Naoum *et al.*, 2001), sulfuric acid (Cheung, 1988), and phosphoric acid (Yoshizaki and Tomida, 2000). Organic acids like citric and oxalic acid (Veeken and Hamelers, 1999) are also used. Chelating agents such as EDTA (Pérez-Cid *et al.*, 2002) and NTA (Samanidou and Fytianos, 1990) are employed as well. Depending on the conditions that these chemicals are applied, such as pH, redox potential, and reaction time, high heavy metals solubilization efficiencies can be achieved.

A promising alternative to the chemical leaching is the microbiological leaching (bioleaching) of heavy metals, which is mediated by acidophilic bacteria (genus *Thiobacillus*) able to produce acid. The acid added in the chemical leaching process is now replaced by an electron donor addition such as elemental sulfur or ferrous iron. Under aerobic conditions, these components are oxidized by *Thiobacillus* and converted to sulfuric acid. Over the last two decades bioleaching of heavy metals from sewage sludge has been widely studied (e.g., Lombardi and Garcia Jr., 2002; Filali-Meknassi *et al.*, 2000; Sreekrishnan and Tyagi, 1996; Couillard and Mercier, 1994; Hayes *et al.*, 1980). Nevertheless, the application of this technique in the solubilization of heavy metals from sewage sludge still prevails under laboratory and pilot plant scale. On this regard, investigations must be carried out to elucidate the bioleaching process scale-up.

The second step in the sludge treatment aiming at heavy metals removals is the separation of the water phase containing the mobilized heavy metals and the sludge particles. This separation step can be accomplished in a centrifuge, a hydrocyclone, a settler, a flotation tank or a filtration device. The “clean” sludge particles are removed as a concentrated sludge, which, after dewatering and pH corrections, can be landfilled, applied as soil improver, used as raw material for Portland cement production, or even incinerated. Moreover, it is likely that the extreme pH conditions applied during the (bio)leaching step causes a reduction of the pathogens organisms.

To remove the solubilized heavy metals from the acidic liquid (leachate), the precipitation process followed by a separation step is a feasible option. Common precipitating reagents used include alkalis such as CaO, NaOH, $NaHCO_3$, etc. Sulfides such as Na_2S, H_2S, NaHS, or FeS can be also used, as it has been found for industrial wastewaters containing heavy metals (Brooks, 1991). The lower solubility of the metal sulfides in the acid region below pH value of 7 permits reduction of metal solubility to values that are orders of magnitude lower than are attainable by hydroxide precipitation. Nowadays, a combination of hydroxide and sulfide precipitation for optimal metals removal is also being considered (U.S.EPA, 1998).

SCOPE AND OUTLINE OF THIS THESIS

Although numerous studies have appeared in the field of heavy metals removal from sewage sludges, less attention has been paid to the implementation of techniques for this purpose. Such techniques still remain in the laboratory and pilot plant scale. The main objective of this thesis is to gain more scientific and practical insights into the heavy metals removal from anaerobically digested sludge, and to develop some conceptual designs that may be applied in practice.

Chapter 2 describes the materials and main analysis procedures used in the experimental part of the research, and shows the physical and chemical characteristics of the applied sludge. The concentration of the heavy metals present in the sludge is emphasized and legal standards for metals disposal on land are shown and discussed. A physical classification scheme, based on differences in the particle size of sludge is applied in order to determine the heavy metal content of the various fractions of the sludge. An analytical approach for determining the chemical forms of heavy metals in the sludge based on sequential chemical extraction procedures is executed.

Chapter 3 deals with the chemical leaching process applied in the crucial step of the sludge treatment aiming heavy metals removal: the metals solubilization step. Moreover, the study stresses the possibility of using chemical leaching as an applicable part of the treatment. For this aim, several acids are tested at different conditions of pH, reaction time and redox potential. The effect of acidification is intensively tested for liquid samples of the sludge and briefly tested for dried and crushed sludge samples. In addition, the influence of the chemical oxidation on the heavy metals solubilization is also investigated by applying aeration or adding hydrogen peroxide.

Chapter 4 evaluates the application of bioleaching in the solubilization of Cr, Cu, Pb and Zn from anaerobically digested sludge. The aim of this chapter is to get more comprehension concerning the practical application of bioleaching, its advantages and shortcomings. Bioleaching using elemental sulfur and ferrous iron as substrates is investigated and compared with chemical leaching with sulfuric acid. Finally, there is a comparison of these results with those of the literature and of the previous experiments with hydrochloric acid described in Chapter 3.

Chapter 5 refers to the precipitation of heavy metals from the leachate that is obtained after metals solubilization and separation from the sludge particles. On the basis of literature, hydroxide precipitation with NaOH and sulfide precipitation with Na_2S are investigated here. Both precipitating agents are applied solely and in combination.

An overall evaluation of the investigated topics is presented in Chapter 6. In addition, the practical implementation of the sewage sludge treatment process aiming at heavy metals removal is also discussed.

Finally, a summary of all the chapters is presented in Chapter 7.

Chapter 2

Sludge characterization

Abstract

The materials and main analysis procedures used in this research are described, and the physical and chemical characteristics of the sludge are evaluated. A physical classification scheme, based on differences in particle sizes was first applied to determine the heavy metal content of the various size fractions of the sludge. Metals were mostly concentrated in the fractions < 0.063 mm, but in all the separated fractions, most of the metals concentrations exceeded the Dutch standard (BOOM). Sequential chemical extraction (SCE) was used, starting with Tessier (1979), followed by Veeken (1998) and Sims & Kline (1991) schemes. Afterwards, modified versions of Tessier and Veeken schemes were applied. Despite some bottlenecks, SCE procedures provide useful information about the availability of the metals. The modified schemes were useful for interpretation of the differences between the results of the original schemes. The SCE results showed that Cr (65-67 %) and Cu (65-87 %) were effectively released in an oxidizing environment. Zinc (78-86 %) was extracted by a reducing agent at 96 °C and pH of 2, whereas Pb (62-81 %) was solubilized in strong acidic conditions at 150 °C in the microwave oven. A chelating agent was able to release considerable amounts of Cr (56-57 %), Pb (57-78 %) and Zn (50-62 %). About 70 % of Cu could be extracted with application of high pH (12.6) at 20 °C.

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INTRODUCTION

Digested sludge is a complex mixture of primary mineral grains and fragments of biological and industrial materials. This mixture is held in a matrix of bacterial fragments and organic colloids, together with secondary precipitates of the ions released during anaerobic digestion (MacNicol and Beckett, 1989).

The physical-chemical forms of heavy metals in solid matrices are usually determined by a two-step approach (Veeken, 1998). In the case of sewage sludge, it can be first physically separated into different particle-sized fractions by a wet-sieving operation, after which, the organic and mineral particles in one size class can be separated by a water-elutriation process. Second, the total heavy metal concentration is determined in each size class and the sludge and its particle-sized fractions are subjected to a sequential chemical extraction (SCE) procedure.

Physical characterization

The main components of digested sewage sludge are (MacNicol and Beckett, 1989):

- Primary or detrital components:
    - Mineral grains of all sizes (0.002-2 mm);
    - Plastics, hairs, pigments, and organic residues including plant detritus.
- Secondary components:
    - Inorganic precipitates;
    - Amorphous degraded organic matter;
    - Digester biomass;
    - Microbial detritus.

Together forming the organic matrix.

According to the mentioned authors, however, to achieve a complete fractionation of digested sludge is a difficult task, since many of the sludge components are coated on, or embedded in each other. In practice, to evaluate the distribution of heavy metals between the principal constituents of digested sewage sludge, not only the particle sizes, but also the particle densities should be considered. Nevertheless, to find an accurate technique to determine the distribution of heavy metals in each sludge component is still difficult. In the case of the present work, a wet-sieving operation was employed to separate the sludge sample into different particle-sized fractions. This procedure might provide a sufficient basis for the physical characterization of the heavy metals in the sludge.

Chemical characterization

Total concentration of heavy metals in sewage sludges indicate the extend of contamination, but give little insight into the forms in which the metals are present, or their potential for mobility and bioavailability after dispersal in the environment (Lombardi and Garcia Jr., 1999; Pérez-Cid *et al.*, 1999; Zufiaurre *et al.*, 1998; McBride, 1995).

An experimental approach commonly used for studying the mobility, transport and bioavailability of metals in sludges is the use of sequential chemical extraction (SCE) procedures (Forstner *et al.*, 1989). Such techniques comprise the utilization of a series of chemical extractants in a sequence of reagents of increasing harshness. For each extraction step, a particular chemical form of the metal is expected to dissolve. Although varying in manipulative complexity, SCE techniques usually fractionate metals in sludges (or soils) into more or less five extraction steps (Lake, 1987):

1. Exchangeable phase: extraction by an electrolyte solution ($MgCl_2$, KNO_3, $BaCl_2$ or NH_4Ac) at a pH value of 7;
2. Carbonate phase: extraction at a pH value around 5, with NaAc, and HAc;
3. Reducible phase: incorporating metals absorbed by iron and manganese oxides. Extraction is usually by an acidified reducing agent (NH_2OH), eventually coupled with HAc or HCl, at a pH value between 2-4;
4. Oxidizible phase: incorporating metals bound to organic matter and sulfides. Hot H_2O_2 in an HNO_3 medium (pH value of 2) is generally used;
5. Residual phase: consisting of metals held within the crystal lattices of primary and secondary minerals. Extraction involves digestion with mixtures of strong acids, such as HF or HNO_3 and HCl.

Among SCE schemes, that developed by Tessier *et al.* (1979), has been widely employed, especially in soils and sediments (Pérez-Cid *et al.*, 1999; Zufiaurre *et al.*, 1998; Veeken, 1998; McGrath, 1996). Pérez-Cid *et al.* (1999) compared the five-stage Tessier and the four-stage BCR (proposed by the European Community Bureau of Reference) SCE schemes for metals partitioning in sewage sludge and found similar extractable metal contents. After critical evaluation of SCE with respect to the selectivity of reagents, Veeken (1998) chose the Tessier scheme as the basis for determining the chemical distribution of heavy metals in biowaste. As biowaste is largely composed of organic matter, an additional step was included to distinguish between metals adsorbed to organic matter and metals incorporated in organic matter.

In this way, both Tessier and Veeken SCE schemes were chosen to be applied and compared in this research. In addition, to make the comparisons more complete, a third SCE scheme was tested. This scheme was proposed by Sims and Kline (1991) for soils and was used by Walter and Cuevas (1999) in soil samples repeatedly amended with sewage sludge. This SCE scheme was chosen due to its relatively experimental simplicity comparing to Tessier and Veeken SCE schemes, since it is made-up of four fractions carried out at 20 °C (except in the residual step).

Important aspects of SCE schemes

Problems associated with the application of SCE techniques in wastewater matrices and soils include the diversity of reagents used to extract specific metal forms, as well as the variety of extraction procedures employed (Lombardi and Garcia Jr., 1999). As reviewed by Veeken (1998), the disadvantages of SCE techniques include:

1. Lack of specificity: extraction reagents cannot destroy one phase without solubilizing the other phases;
2. Absence of selectivity: extraction reagents cannot release metals bound to one specific phase and not to other phases;
3. Readsorption: heavy metals that are solubilized by an extracting agent can be readsorbed to the remaining solid phases;
4. Dependence on many factors, such as type of sample, size of particulates, pH, temperature, contact time, concentration of extractant, and solid-to-liquid ratio.

Despite uncertainties, the use of SCE procedures provides qualitative information that may allow for the prediction of the biological and physical chemical availability, mobilization and transport of heavy metals (Clevenger, 1990; Lake, 1987).

Scope of the study

The present chapter describes characteristics of the anaerobically digested sludge applied in this research. In order to understand better the contributions of the various grain size classes to the total heavy metal content, the sludge was divided into different physical fractions by means of wet sieving. The chemical distribution of some heavy metals in the sludge was also investigated, following sequential extraction procedures used for the evaluation of these elements in the sludge.

EXPERIMENTAL

Origin of the sludge

The sludge applied in this research originated from an anaerobic digester of a wastewater treatment plant (WWTP) located in Schijndel, the Netherlands. This plant has a capacity of 10 000 m^3/day and receives both industrial (about 35 %) and domestic (about 65 %) influents. The treatment is based on a two-stage activated sludge system followed by anaerobic digestion of the primary and secondary sludges. After digestion, the sludge is transported to another WWTP, dewatered, mixed with other sludges, incinerated, and disposed to a landfill. After being collected from the anaerobic digester, the sludge used in the present work was stored at 4 °C when not directly used.

Physical and chemical characteristics of the sludge

Table 2.1 shows some physical and chemical characteristics of the sludge applied herein. To have insights about the applicability of this research to other anaerobically digested sludges coming from different locations, some characteristics of the sludge applied in this research are compared to those of a Brazilian sludge. This sludge is produced in a WWTP located in the Metropolitan Region of São Paulo, Barueri. This plant has a capacity of 820 800 m^3/day and is similar to the Dutch WWTP in terms of mixed influent, conventional treatment and digestion of the primary and secondary sludge. The difference between the two WWTP's is the final destination of the sludge. After digestion, the Brazilian sludge is dewatered and sent directly to a landfill. Despite this fact, both sludges are comparable in terms of dry matter, organic matter, and COD (see Table 2.1).

Table 2.1 - Some characteristics of the Dutch anaerobically digested sludge and comparisons with a Brazilian sludge

Parameter	Dutch sludge - Schijndel -	Brazilian sludge - Barueri -
Dry matter (g/L)	26.5	22.7
Organic matter (g/L)	14.8	12.4
Humidity (%)	97.3	[c]
COD (g/kg DM[a])	950	1000
BOD (g/kg OM[b])	0.03	[c]
$N_{kjeldahl}$ (g/kg DM[a])	71.6	[c]
S (g/kg DM[a])	11.6	[c]
Sulfide (g/kg DM[a])	0.9	[c]
P (g/kg DM[a])	25.5	[c]

[a] Dry matter; [b] Organic matter; [c] Not available.

To continue with comparisons, some metals concentrations are shown in Table 2.2. In addition, the Dutch standard for sludge disposal to agricultural soils - BOOM (SDU, 1991) is presented. The Brazilian standard for heavy metals disposal to agricultural land, which follows, with some exceptions, the limits established by U.S.EPA-40 (U.S.EPA, 1993), CFR Part 503.13, is also given. For further comparison, the proposed standard by EU Commission is included in Table 2.2.

Table 2.2 - Some metals content of the Dutch sludge and comparisons with the Brazilian sludge and legal standards

Element	Dutch sludge[a] - Schijndel - (mg/Kg DM[b])	Brazilian sludge - Barueri - (mg/Kg DM[b])	BOOM (mg/Kg DM[b])	U.S.EPA-40 CFR 503.13 (mg/Kg DM[b])	EU Commission (mg/Kg DM[b])
Al	25 660-30 500	[c]	[c]	[c]	[c]
Ca	37 100-41 500	[c]	[c]	[c]	[c]
Cd	2-3	40	1.25	39	2
Cr	345-495	542	75	3 000	[c]
Cu	745-1050	1 180	75	1 500	600
Fe	18 800-24 500	[c]	[c]	[c]	[c]
K	5 800-7 000	[c]	[c]	[c]	[c]
Mg	4 600-5 400	[c]	[c]	[c]	[c]
Mn	280-420	[c]	[c]	[c]	[c]
Na	3 700-4 700	[c]	[c]	[c]	[c]
Ni	20-40	288	30	420	100
Pb	185-205	313	100	300	200
Zn	1 320-2 330	1 772	300	2 800	1 500

[a] Data from the present research; [b] Dry matter; [c] Not available.

Table 2.2 demonstrates that the concentrations of Cr, Cu, Pb and Zn in the Dutch sludge are comparable to those of the Brazilian sludge. These similarities (see Table 2.2 and Table 2.1) are of interest for the general applicability of the results of the present research. They indicate, roughly, that similar sewage sludge treatment methods might be applicable to different countries.

According to Table 2.2, both sludges are exceeding the allowed limits of the Dutch standard, which is very strict. Both sludges are also surpassing the limits of the EU Commission standard (with exception of Ni in the Dutch sludge). In contrast, according to U.S.EPA-40, the Dutch sludge could be disposed to agricultural land. Comparisons among total amount of heavy metals, however, is very general and implies that all forms of a given metal are equally soluble (Van Herck and Vandecasteele, 2001) and exert the same impact on the environment (Solís *et al.*, 2002). The total heavy metals concentration values are excellent criteria to define the extend of metals contamination in the sludge and in the soil, when this is the final destination of the sludge. But to forecast the ecological impact, the total content is of little value, since it has been observed that plant metal concentrations are not only correlated with soil total metal content (Gupta *et al.*, 1996). Besides the determination of the total metals concentration, a deep investigation of the metals speciation in the sludge, emphasizing the mobility capacity of these metals should be done.

Physical distribution of heavy metals in the sludge

To evaluate the metals distribution in the solid and liquid parts of the sludge, centrifugation was applied to the sludge during 20 minutes at 4000 rpm and the supernatant was analysed for its heavy metal content. In addition, experiments concerning the physical fractionation of the sludge were performed based on wet sieving operation. The vibrating sieving system (Retsch Labor-Siebmachine Type VIBRO) was equipped with stainless steel sieves of mesh sizes 5.0, 1.0, 0.5, 0.2, 0.09, 0.063, 0.032, and 0.02 mm (see scheme in Figure 2.1). The fraction collected in each sieve and the remaining liquid (fraction smaller than 0.02 mm) was analysed for its heavy metals content. The experiments were performed in triplicate.

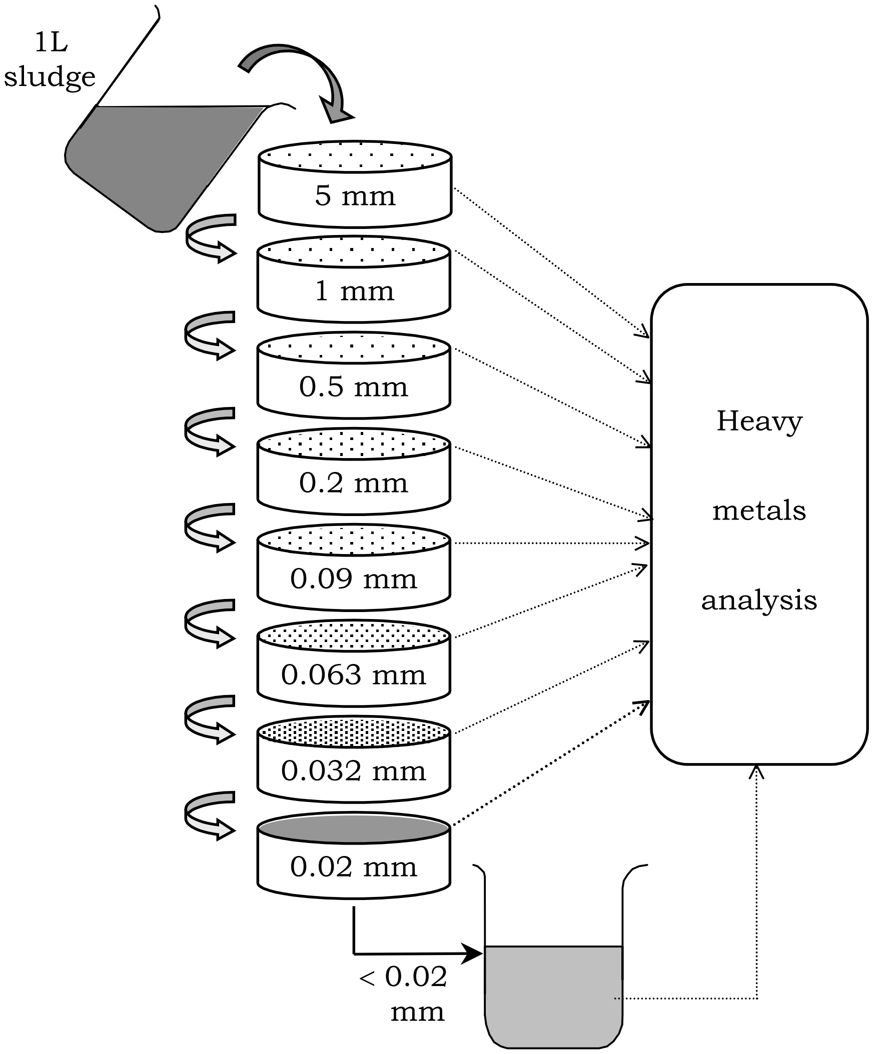

Figure 2.1 - Scheme of the sieving experiments

Sequential chemical extraction (SCE)

Three sequential chemical extraction schemes were tested in this research: Tessier (1979), Veeken (1998), and Sims & Kline (1991). Table 2.3 shows a resume of these three schemes. Each experiment was carried out in duplicate. Samples of 2-g dried (103 °C) sludge (Tessier), 10-g dried (40 °C) sludge (Veeken), 2-g dried (40 °C) sludge (Sims & Kline) were put into 250 ml polypropylene centrifuge tubes. After each extraction step, samples were centrifuged at 4000 rpm for 30 minutes. The supernatant was analyzed for its heavy metal content and the subnatant was washed (centrifuged) with distilled water prior to extraction, in the proportion: 8 ml/g (Tessier), 10 ml/g (Veeken), and 25 ml (Sims & Kline). The details about the SCE schemes, chemicals used, pH, temperature, and reaction time conditions are presented in Table 2.3.

Table 2.3 - SCE schemes

	Step	Reagent	Time and Temperature
Tessier	Exchangeable	MgCl$_2$ 1M, pH= 7, 8 (v/w)^a	1h - 20 °C
	Bound to carbonates	NaAc^b 1M, pH= 5, 8 (v/w)^a	5h - 20 °C
	Bound to Fe-Mn oxides	NH$_2$OH.HCl 0.04M, 20 (v/w)^a, pH= 2	6h - 96 °C
	Bound to organic matter	HNO$_3$ 0.02M, 3 (v/w)^a, 30 % H$_2$O$_2$, 5 (v/w)^a, pH= 2, 30 % H$_2$O$_2$, 5 (v/w)^a NH$_4$Ac^b 3.2M, 5 (v/w)^a	2h - 85 °C 3h - 85 °C 30min - 20 °C
	Residual	5ml H$_2$O, 4ml HNO$_3$ 70 %, 1ml HCl 35 %, 2ml HF 48 %	26min - MO^e
Veeken	Exchangeable	NH$_4$Ac^b 0.5M, pH= 7, 10 (v/w)^a	3h - 20 °C
	Bound to carbonates	NaAc/HAc^b 0.1M, pH= 5.5, 10 (v/w)^a	5h - 20 °C
	Bound to Fe-Mn oxides	NH$_2$OH.HCl 0.1M, 20 (v/w)^a, pH= 4	6h - 20 °C
	Bound to org-inorganic matter	EDTA 0.1M, pH= 4.5, 20 (v/w)^a	16h - 20 °C
	Incorporated in organic matter and organic-mineral aggregates	HNO$_3$ 0.02M, 3(v/w)^a, 30 % H$_2$O$_2$, 5(v/w)^a, pH= 2, 30 % H$_2$O$_2$, 5 (v/w)^a NH$_4$Ac^b 3.2M, 5 (v/w)^a	20h - 85 °C 30min - 20 °C 4h - MO^e
	Residual	Aqua regia - HCl : HNO$_3$ - 3 : 1	30min - MO^e
S & K^d	Exchangeable	KNO$_3$ 0.5 M, 12.5 (w/w)^c, pH= 6.2	16h - 20 °C
	Bound to organic matter	NaOH 0.5 M, 12.5 (w/w)^c, pH= 12.6	16h - 20 °C
	Inorganic precipitate	Na$_2$EDTA 0.05 M, 12.5 (w/w)^c, pH= 4.5	6h - 20 °C
	Residual	HNO$_3$ 4 M, 12.5 (w/w)^c, pH= 0.6	16h - 80 °C

^{a} Liquid-to-solid ratio (v/w): v is the volume of the extractant (ml); w is the mass of the sample (g); ^{b} Acetate; ^{c} Weight-to-weight (w/w): w is the mass of the extractant (g); w is the mass of sample (g); ^{d} Sims & Kline; ^{e} Microwave oven.

As a second study concerning SCE, modified versions of Veeken and Tessier schemes were applied as a tentative to investigate the causes of the differences between both schemes. In this regard, some conditions were slightly altered from original ones. These modifications are presented in Table 2.4.

Table 2.4 - Modified steps of Tessier and Veeken SCE schemes

Tessier Scheme		Veeken Scheme	
Step	Conditions	Step	Conditions
Bound to organic and inorganic matter	Na$_2$EDTA 0.05M, pH= 4.5, 20 (v/w), 6h - 20°C (from Sims & Kline scheme)	Bound to Fe-Mn oxides	NH$_2$OH.HCl 0.04M, pH= 2, 20 (v/w), 6h - 96 °C (from Tessier scheme)

The new extraction step included in the modified Tessier scheme was set before the step bound to organic matter in the original version, which was then named incorporated in organic matter and organic-mineral aggregates, as proposed by Veeken (1998).

Analysis and apparatus

The heavy metals chosen to be studied in this research are chromium, copper, lead, and zinc. The choice was based on the relatively high concentration of these metals in the sludge compared to other metals such as nickel and cadmium (as shown in Table 2.2). Moreover, the concentration of these metals exceeds the Dutch standard (BOOM).

The heavy metals were analysed by the Inductively Coupled Plasma - Mass Spectrometry Method (ICP-MS, Elan 6000, Perkin Elmer). Liquid samples (resulted from the extraction experiments) for heavy metals analysis were filtered with paper filters (Schleicher & Schuell nº 595½, black ribbon, 12-25 μm), diluted 10 times with HNO_3 (0.14 M), and stored at 4 °C before analysis. Solid samples and liquid samples of the original sludge were previously digested in the microwave (MDS-2100 CEM) with addition of aqua regia ($HCl:HNO_3$ - 3:1) before final dilution for ICP-MS measurement, following the Dutch norm NEN 6465, as described by Veeken (1998).

Heavy metal extraction efficiency was calculated as the ratio between the solubilized metal in the sludge after the extraction and the non-solubilized metal in the sludge before the extraction.

ICP-AES (Spectro-Flame FVM04) was used to measure Al, Ca, K, Mg, Mn, Na, and S.

BOD was determined with the Oxitop method. COD and Kjeldahl-N were determined according to the Standard Methods. Sulfide was measured with a Spectronic 20 Genesys.

pH was determined with Knick type 510 pH-meter. Oxidation-reduction potential was measured with a WTW-OXI 197.

For samples agitation, a mixer Snijders Scientific was used and the samples were centrifuged in an IEC Centra MP4.

The chemicals used in the experiments were pure for analysis (Merck).

RESULTS AND DISCUSSIONS

Physical distribution of heavy metals in the sludge

Figure 2.2 shows the proportion of heavy metals present in the supernatant of the centrifuged sludge in relation to the total heavy metals content of the original sludge (HM-OS). Metals are mostly present in the solid fraction of the sludge and must be therefore dissolved in the liquid, before being removed from the sludge.

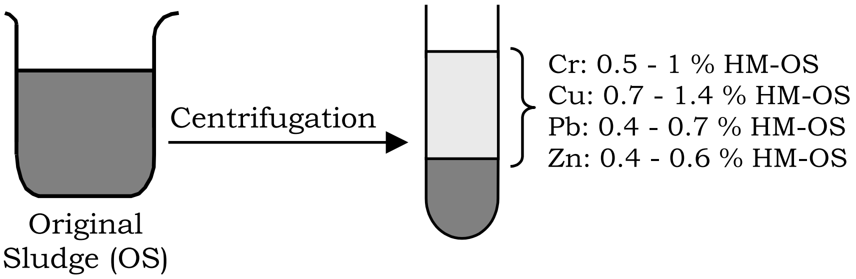

Figure 2.2 - Heavy metals proportion present in the liquid fraction of the sludge

The heavy metals distribution in the different size fractions of the sludge is presented in Table 2.5. The Dutch standard for sludge disposal on agricultural soils (BOOM, 1991) is also included, for comparison. Relative standard deviations for triplicates were < 8 %.

Table 2.5 - Some characteristics of the anaerobically digested sludge

Fraction	Contribution % (on DM[a] basis)	Organic matter % DM[a]	Heavy metal content mg/kg DM[a]			
			Cr	Cu	Pb	Zn
Original Sludge	-	60	452	893	160	2 032
5.0-1.0 mm	7.0	89	122	232	52	708
1.0-0.5 mm	3.8	82	199	318	88	902
0.5-0.2 mm	5.2	64	256	389	139	1 360
0.2-0.09 mm	13.3	58	358	589	152	1 484
0.09-0.063 mm	15.7	59	447	935	166	1 903
0.063-0.032 mm	26.0	54	499	1 014	186	2 142
0.032-0.02 mm	7.0	56	568	1 172	197	2 440
< 0.02 mm	22.0	54	468	1 013	166	2 230
BOOM (1991)	-	-	75	75	100	300

[a] Dry matter.

From Table 2.5 it is clear that heavy metals are largely concentrated in the fractions < 0.063 mm, constituting about 70 % of the total sludge mass and contributing 78-85 % of the heavy metals present in the sludge. MacNicol and Beckett (1989), observed that most of the Cu and Zn present in an anaerobic sludge were held in the particle-sized fraction > 0.04 mm. Besides the predominance of heavy metals in the fractions < 0.063 mm of the studied sludge, in almost all the fractions the amount of metals exceeded the Dutch standard. This suggests that if land application is considered, then the whole sludge has to be treated, without previous separation.

Sequential chemical extraction (SCE)

Figure 2.3 shows the extraction percentages of Cr, Cu, Pb and Zn obtained with the three SCE schemes. To make the comparisons of the SCE schemes more consistent, the extraction results of all experiments were recalculated to 100 %. Differences between duplicates were within 3 %.

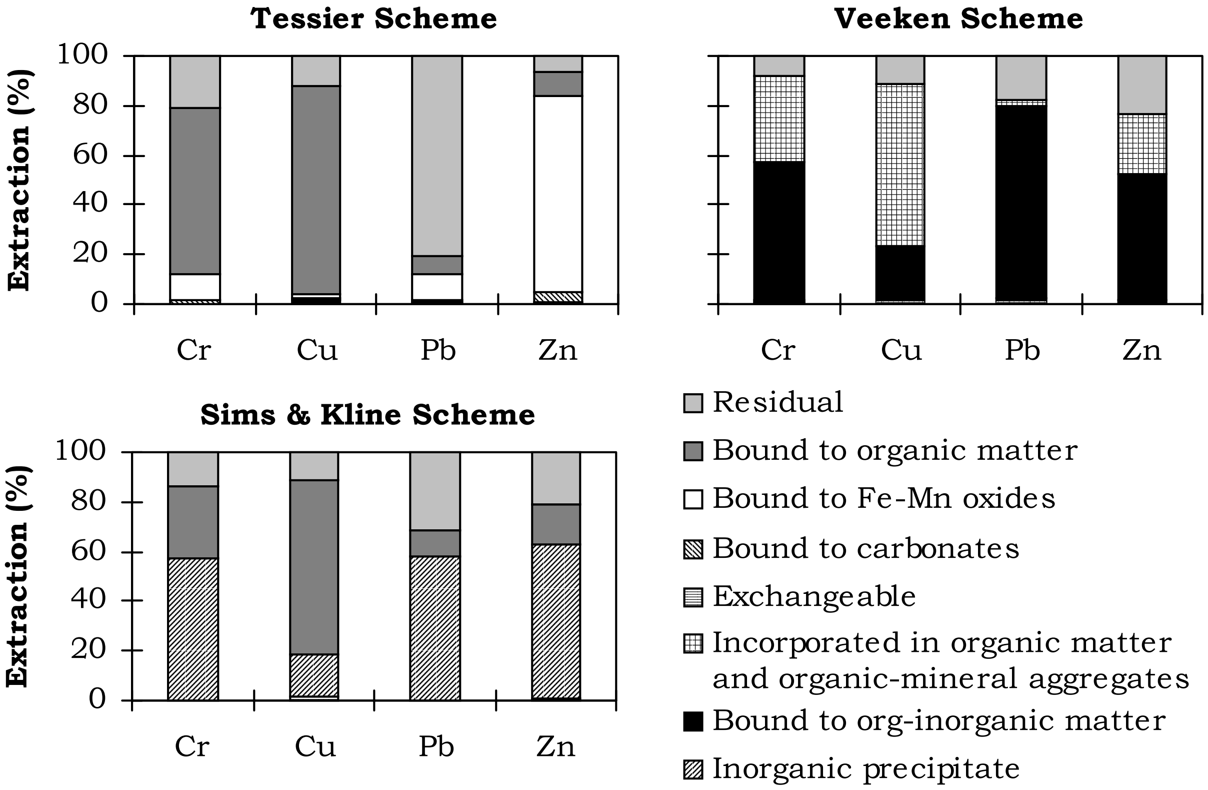

Figure 2.3 - Results of the three SCE schemes

According to Figure 2.3, 67 % of Cr was bound to organic matter in Tessier scheme, 56 % bound to organic and inorganic matter in Veeken scheme and

57 % present as inorganic precipitate in Sims & Kline scheme. The predominance of Cr in the organic matter fraction of the sewage sludge is in accordance with Qiao and Ho (1996), who found about 62 % of Cr in this fraction, based on a Tessier scheme. Also using a Tessier scheme, Zufiaurre *et al.* (1998) concluded that about 40 % of Cr was present in the organic and sulfidic fractions of a sewage sludge sample. In contrast, Pérez-Cid *et al.* (1999; 1996) and Solís *et al.* (2002) observed that Cr was prevalent in the residual fraction of sewage sludge samples, obtained according to the application of Tessier and BCR schemes.

Copper was mainly found in the organic matter fraction according to the three schemes applied. These results agree with the literature referring to Cu speciation in sewage sludges (Solís *et al.*, 2002; Zufiaurre *et al.*, 1998; Qiao and Ho, 1996). On the other hand, Pb was 81 % present in the residual fraction of Tessier scheme, 78 % bound to organic and inorganic matter in Veeken scheme and 58 % found as inorganic precipitate in Sims & Kline scheme. Zufiaurre *et al.* (1998) observed that about 60 % of Pb was extracted in the residual fraction of a sewage sludge sample with Tessier scheme application.

About 79 % of Zn predominated in the fraction bound to Fe-Mn oxides in Tessier scheme, bound to organic and inorganic matter in Veeken scheme (51 %) and inorganic precipitate in Sims & Kline scheme (62 %). Zufiaurre *et al.* (1998) and Qiao and Ho (1996) detected about 32 % of Zn also in the fraction bound to Fe-Mn oxides of a sewage sludge sample with Tessier scheme application. In contrast, Gupta *et al.* (1990), Oake *et al.* (1984), and Stover *et al.* (1976), found that most of Zn was present in the organic fraction of sewage sludge samples with Stover scheme application. In the present research, it is difficult to know whether Zn was indeed extracted by the reducing agent or by the conditions of pH and temperature applied in Tessier scheme. This uncertainty remained when Veeken scheme was applied. In this case, most of Zn was not extracted by the reducing agent, since the pH and temperature conditions in this scheme were milder than those applied in Tessier scheme.

Comparing the heavy metals behavior in all the fractions among the three SCE schemes, the results of Veeken and Sims & Kline schemes are consistent, although it is difficult to distinguish between what is bound to organic and to inorganic matter in Veeken scheme. On the other hand, the Tessier and Veeken schemes are different in several aspects. One possible reason for that is due to the experimental conditions (see Table 2.3) employed in the fraction bound to Fe-Mn , such as temperature, molarity of the chemical and pH value. Another cause might be the absence of EDTA in the Tessier scheme.

Because Tessier and Veeken schemes gave very different results, it was decided to slightly modify both procedures as a tentative to investigate the causes of the differences between them. Modified steps of Tessier and Veeken SCE schemes are present in Table 2.4. Figure 2.4 indicates the extraction efficiency of metals for both modified versions.

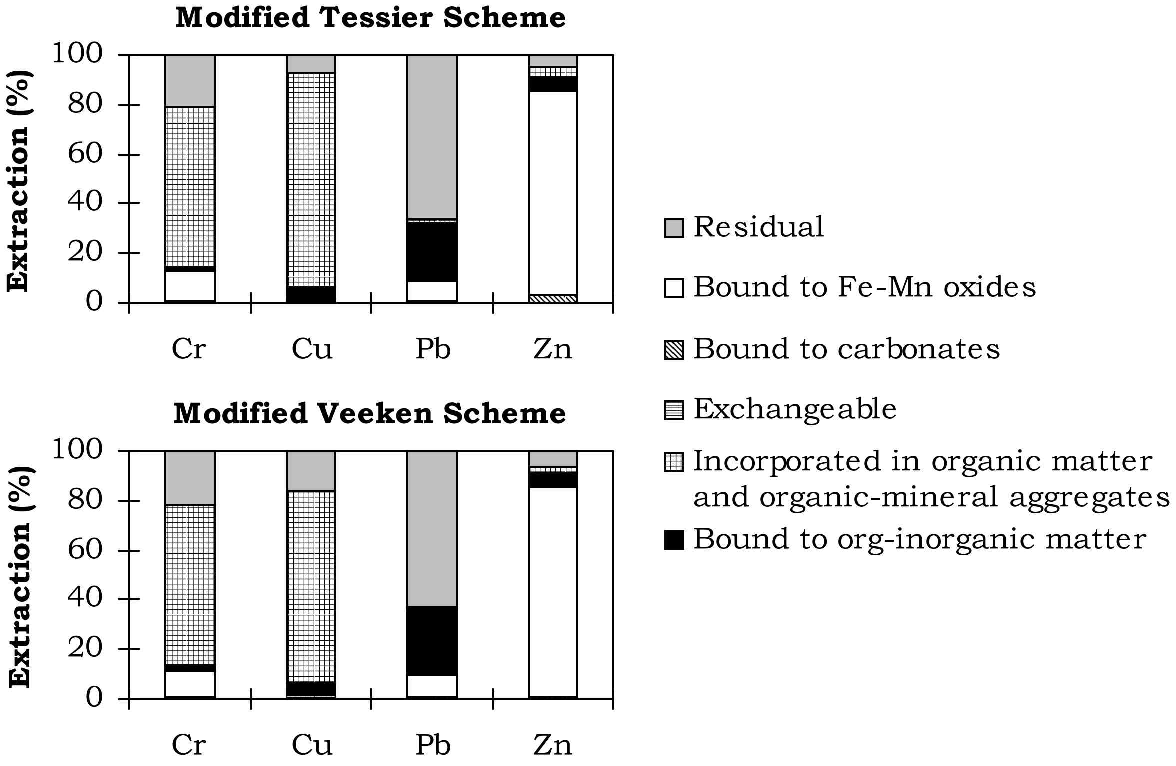

Figure 2.4 - Results of the modified SCE schemes

The fraction profile given in Figure 2.4 shows that the heavy metals behavior in the two modified schemes is very similar. In both modified and original SCE schemes the extraction percentages for heavy metals in the fractions exchangeable and bound to carbonate of both modified schemes were negligible. With respect to the fraction bound to Fe-Mn oxides, the extraction percentage for Zn was relatively high in the two schemes (82.5 to 85.5 %), while less than 12.5 % of Cr and 9 % of Pb were detected in this fraction and the percentage for Cu was very low. These results differ highly from the original Veeken scheme, because at a low pH value (around 2) and at a high temperature (96 °C), hydroxylamine can easily reduce ferric iron to ferrous iron and, in this way, ferric hydroxides precipitates are dissolved.

A small proportion of the metals was bound to the organic and inorganic matter fraction, with exception of Pb. Results obtained for modified and original Veeken schemes are very dissimilar. In the modified Veeken scheme all the metal extraction efficiencies were lower than in the original version. The reason might be that before the fraction bound to organic and inorganic, almost all metals were already extracted with hydroxylamine in acidic medium at high temperature. About 78 % of Pb was bound to organic and inorganic matter in the original Veeken scheme and only 23 % in the modified version. Comparing to Pb, the extraction level of Cr was even lower (2 %) using EDTA in the modified version. Chromium and Cu were mainly incorporated in organic matter and organic-mineral aggregates, according to the modified schemes. The extraction percentages in the residual fraction for both modified schemes were similar. In contrast, concerning Veeken scheme, the extraction percentage for Pb was higher in the residual fraction of the modified version.

The results demonstrated that the two modified schemes provided valuable information for interpretation of the differences in the results obtained with the application of the original schemes.

The heavy metals speciation given by the five SCE schemes applied clearly demonstrated the uncertainty of the SCE method with respect to selectivity and specificity, leading to difficulties in the interpretation of these results. It is important to realize that the results of the SCE procedure are influenced by the type of leaching solutions, as well as the conditions (pH, temperature, contact time) and sequence in which they are applied. These observations serve to highlight the problems inherent in attempting rigorous division of metal species within sludge, when such species are likely to be involved in a diversity of interactions. It seems more rational that, instead of calling a fraction “bound to organic matter” or “bound to inorganic matter”, the type of chemicals used would better determine a fraction designation. For instance, when a combination of H_2O_2 and HNO_3 are applied, this phase could be simply named “oxidizible phase”.

In order to reinforce this idea, Table 2.6 summarizes the most relevant percentages of the heavy metals extracted in the several fractions of the five SCE schemes tested. This table shows that, despite the differences among the fractions names given by the authors of the SCE schemes, the type of extracting agents applied to release one specific metal are very similar.

Table 2.6 - Most relevant extractions of the heavy metals obtained with the application of the SCE schemes

Metal	Extraction (%)	Temp.(°C); pH	Extraction situation	Fraction name
Cr	67(T)	85; 2	Oxidizing agent	Bound to organic matter
	64(T’); 65(V’)	85; 2	Oxidizing agent	Incorporated in org. matter and org.-mineral aggregates
	56(V)	20; 4.5	Chelating agent	Bound to org.-inorg. matter
	57(S & K)	20; 4.5	Chelating agent	Inorganic precipitate
Cu	84(T)	85; 2	Oxidizing agent	Bound to organic matter
	65(V); 87(T’); 77(V’)	85; 2	Oxidizing agent	Incorporated in org. matter and org.-mineral aggregates
	71(S & K)	20; 12.6	High pH	Bound to organic matter
Pb	81(T); 66(T’); 63(V’)	150; <1	Strong acids	Residual
	78(V)	20; 4.5	Chelating agent	Bound to org.-inorg. matter
	58(S & K)	20; 4.5	Chelating agent	Inorganic precipitate
Zn	79(T); 83(T’)	96; 2(T, T’)	Reducing agent	Bound to Fe-Mn oxides
	85(V’)	20; 4(V’)	Reducing agent	Bound to Fe-Mn oxides
	51(V)	20; 4.5	Chelating agent	Bound to org.-inorg. matter
	62(S & K)	20; 4.5	Chelating agent	Inorganic precipitate

T: Tessier scheme; V: Veeken scheme; S & K: Sims and Kline scheme; T’: Modified Tessier scheme; V’: Modified Veeken scheme.

Table 2.6 shows that it is indeed easier to evaluate the SCE schemes according to the type of chemicals used (Van Herck and Vandecasteele, 2001), associated, of course, to the experimental situations applied. The table demonstrates that at least 50 % of Cr, Pb and Zn were extracted by EDTA at a pH value of 4.5 and 20 °C. However, this was not the best extracting condition for Zn, which was better released by a reducing agent at a pH value of 2 and 96 °C. In contrast, at a pH value around 12.6 and 20 °C, Cu was efficiently extracted. Copper was also released in an oxidizing environment. In this case, as oxidation occurred and Cu bound (or incorporated) to the organic fraction of the sludge was solubilized, other reduced forms that might be present in the sludge were also oxidized, such as Cu_2S to $CuSO_4$.

For further experiments, the selection of metal leaching agents will mainly focus on oxidizing agents and strong acids. EDTA will not be applied, because according to the results of the SCE schemes, the chelating agent did not satisfactorily remove Cu. Moreover, it must be investigated whether the metals extracted by EDTA (e.g., Cr, Pb, and Zn) will be also extracted by an oxidizing agent or not. When it was included in a SCE scheme, the chelating step always came before the oxidizing step.

In this way, the results given by the SCE procedures must be evaluated carefully. Their interpretation is only qualitative and the selectivity of the method is not good enough to investigate the real speciation of the metals in the sludge (van Herck and Vandecasteele, 2001). Yet the SCE procedure provides a way of obtaining useful information concerning the availability of the metals. It also allows for the determination of the chemical differences between samples and thus may indicate the differences in availability (Clevenger, 1990). From a SCE scheme, it can be deduced whether a large fraction of the sludge material dissolves in water or acid or whether oxidizing or reducing conditions are necessary. This renders the SCE schemes an important tool for predicting metals mobilization in the sludge matrix and a complementary support in results discussions when the sludge is submitted to further treatment aiming at heavy metal removal.

Quevauviller *et al.* (1996) pointed out that basic research is still necessary for the validation of extraction tests in relation to the actual field conditions. This research would, however, probably take a long time and a faster validation of existing tests is required in legislation. A strategy could be, in the short-term, to validate the existing tests required by the regulations through interlaboratory studies and initiate a project with a broad scope, which would, in the long-term, allow more accurate, harmonized procedures adapted to the different purposes and matrices to be developed. Additionally, models should be developed as a systematic approach for selecting the tests adapted to specific case studies (Quevauviller *et al.*, 1996). Frontline research on NMR (nuclear magnetic resonance) might also provide further information. It is still doubtful, however, that further research will substantially increase the insight of the heavy metals binding to sludge.

CONCLUSIONS

Heavy metals solubilization

The proportion of heavy metals present in the water phase of the studied sludge is not higher than 1.5 % in relation to the total heavy metals present in the original sludge. This leads to the conclusion that as mostly the metals are present in the solid fraction of the sludge, they must be dissolved in the liquid, before being removed from the sludge.

Physical distribution of heavy metals in the sludge

Besides the predominance of heavy metals in the fraction < 0.063 mm of the sludge, in almost all the sized-fractions the amount of metals exceeded the Dutch standard for heavy metals disposal on agricultural soils. This indicates that if land application of the sludge is considered, then the full sludge must be treated, without prior fractionation.

Sequential chemical extraction (SCE)

The results of the heavy metals speciation given by the five SCE schemes clearly demonstrated the uncertainty of the method with respect to the selectivity and specificity, leading to difficulties in the interpretation of these results. The results of SCE procedures are influenced by the type of leaching solutions, as well as the conditions (pH, temperature, contact time) and sequence in which they are applied.

Despite some bottlenecks, the SCE procedure provides a way of obtaining useful information concerning the availability of the metals. This renders the SCE schemes a complementary tool for evaluating metals mobilization in the sludge matrix and a complementary support for discussing further results achieved with a sludge treatment technique.

The SCE results of the investigated sludge showed that Cr (65 - 67 %) and Cu (65 - 87 %) could be effectively released in an oxidizing environment (85 °C, pH= 2). Zinc (78 - 86 %) could be extracted by a reducing agent (96 °C, pH= 2), whereas Pb (62 - 81 %) could be solubilized at strong acidic conditions at high temperature (150 °C in the microwave oven). Furthermore, a chelating agent (20 °C, pH= 4.5) was able to release considerable amounts of Cr (56 - 57 %), Pb (57 - 78 %), and Zn (50 - 62 %).

About 70 % of Cu could also be extracted with application of high pH (12.6) at 20 °C.

Chapter 3

Chemical leaching of heavy metals

Abstract

This work evaluates, firstly, the chemical leaching using progressive acidification as the most common technique applied in the study of heavy metals mobilization in sewage sludge. Secondly, the study emphasizes the possibility of using chemical leaching as an applicable part of the sludge treatment aiming at heavy metals removal. Organic acids (citric and oxalic) and inorganic acids (nitric, hydrochloric and phosphoric) were tested at different conditions of pH, reaction time, and oxidation-reduction potential. The effect of acidification was intensively tested for liquid samples of the sludge and briefly tested for dried and crushed sludge samples. In addition, the influence of the chemical oxidation on the heavy metals solubilization was also investigated by applying aeration or adding hydrogen peroxide. The results showed that the option including chemical oxidation with either aeration or hydrogen peroxide followed by acidification with HCl resulted in the highest extraction yields of most heavy metals. Especially Cu extraction was highly influenced by oxidation. The best results achieved were: Cr: 85 % with H_2O_2, Cu: 100 % with H_2O_2, Pb: 100 % with aeration or H_2O_2, and Zn: 100 % with aeration or H_2O_2.

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INTRODUCTION

Usually, in sewage sludges, heavy metals are so tightly incorporated or absorbed in minerals and organic solids that only under extreme acidic conditions achieved by chemical leaching or bioleaching, these metals can be satisfactorily solubilized. It is known, however, that chemical leaching has the drawback of high cost due to the acids addition. Despite this fact, it is still very useful to consider chemical leaching as a practical method for heavy metals extraction. Especially from such a complex matrix as sewage sludge, which may contain a mixture of several heavy metals. Each metal might behave differently from one another and, in most cases, their solubilization occur only at high redox-potential conditions and with the application of acidification techniques, such as chemical leaching and bioleaching.

This work starts with an evaluation of the chemical leaching using progressive acidification as the most common technique applied in the study of heavy metals mobilization in sewage sludge. Second, the study emphasizes the possibility of using chemical leaching as an applicable technique for the sewage sludge treatment, aiming at heavy metals removal. To be removed from the sewage sludge particles, heavy metals must be previously released into the liquid. Then this liquid containing the solubilized heavy metals (leachate) is separated from the sludge particles (e.g., by centrifugation) and sent to a precipitation step. The heavy metals are then precipitated and removed from the liquid by a physical separation technique.

Heavy metals speciation and extraction

Because of the wide spectrum of results that can be obtained from different extraction procedures, as observed in Chapter 2, the choice of the most worthwhile speciation technique remains a difficult task. As such, it seems wise to subject the sludge to both SCE (sequential chemical extraction) procedures and single extractions with progressive acidification. With a rational combination of these methods, it might be possible to draw more consistent conclusions about the heavy metals profile in the sludge. This was an important aspect for the set-up of the present research. Continuing the study of heavy metals speciation started in Chapter 2 with SCE schemes, chemical leaching of heavy metals based on single acidification techniques are discussed here.

The starting point of the present research is the investigation of a progressive acidification technique (PAT) applied for the dried and crushed sewage sludge. The PAT comprises the progressive decrease of the initial pH of the sludge by adding acid, followed by heavy metals analysis in the liquid fraction. This technique can be more advantageous comparing to SCE schemes for routine analysis of potential heavy metal availability. It can be executed more easily and rapidly than SCE and it is not limited by fraction definition (Rudd *et al.*, 1988). In addition, making the sludge sample more homogeneous by drying and crushing it before the PAT application is a useful reference for further comparison with PAT applied to the original sludge slurry.

Dried versus liquid sludge

Differences observed in the behavior of the liquid and dried forms of the sludges using PAT are that metals are more readily solubilized from dried samples (Rudd *et al.*, 1988). In contrast, the same authors quote that the SCE indicates that drying of the sludges effectively reduced the extractability of fractions that are readily available in the slurry form.

Although sludges may be dewatered to have their final volume reduced before, for instance, land disposal, it is more realistic and useful to use the original sludge slurry for experimentation (Rudd *et al.*, 1988). Furthermore, the process of drying and crushing the sludge does not seem to be feasible in real and large scale, from a practical and economical point of view. This last point must be considered when the acidification process is applied not only with the purpose of heavy metals speciation, but also to solubilize heavy metals for their further removal.

Solubilization control parameters

Heavy metals can be mobilized from sludge particles by changes in pH and ORP (oxidation-reduction potential) conditions and by complexing with synthetic complexing agents (NTA, EDTA), inorganic complexing agents (Cl^-, NO_3^-, S^{2-}, PO_4^{3-}, CO_3^{2-}), or with natural chelating agents such as soluble humic substances (Samanidou and Fytianos, 1990).

The pH is one of the most powerful parameters to control the metals transfer from immobile solid-phase forms to more mobile, and therefore more bioavailable, solution-phase forms. This parameter influences adsorption equilibria, the stability of organomineral complexes and ORP (Lake, 1987). Sometimes instant heavy metals solubilization (Zn for example) can be achieved by merely lowering the pH (Tyagi *et al.*, 1988). Hayes *et al.* (1980), however, observed that a low pH value is not always enough to promote a satisfactory metals release from anaerobic sludge particles to the liquid, unless acidification is preceded by a rise in the sludge ORP. The ORP of the anaerobic sludge can be raised either by means of biological (see Chapter 4) or chemical oxidation, which can be achieved through aerobic conditions. Chemical oxidation can also occur by addition of an oxidizing agent like hydrogen peroxide. Under reducing conditions, which prevail in anaerobic digestion, extremely insoluble metal sulfides are formed (Couillard and Zhu, 1992). Chemical oxidation applied before acidification increases the ORP of the sludge, promoting the oxidation of the non-soluble metal forms to crystal forms that would be dissolved at low pH. Particularly when hydrogen peroxide is applied, the highly oxidizing hydroxyl radicals ($OH^{\bullet}$) can be formed, if there is enough iron present in the sludge. These reactions, known as Fenton reactions, occur as follows (Walling, 1975):

$$Fe^{2+} + H_2O_2 \Leftrightarrow Fe^{3+} + OH^- + OH^{\bullet} \tag{4.1}$$

$$Fe^{3+} + H_2O_2 \Leftrightarrow Fe^{2+} + OOH^{\bullet} + H^+ \tag{4.2}$$

The standard oxidation potential of $OH^{\bullet}$ is $E_{OH\bullet} = -3.06$ V, so application of H_2O_2 can lead to locally extreme high oxidation-reduction potentials.

Scope of the study

In this chapter, the chemical leaching process was applied to assess the mobilization of heavy metals present in the sludge and the possibility of using chemical leaching as an applicable part of the treatment aiming at heavy metals removal from sewage sludge. In this way, organic acids (citric and oxalic) and inorganic acids (nitric, hydrochloric and phosphoric) were tested at different conditions of pH, reaction time, and oxidation-reduction potential. The effect of acidification was intensively tested for liquid samples of the sludge and briefly tested for dried and crushed sludge samples. In addition, the influence of the chemical oxidation on the heavy metals solubilization was also investigated by applying aeration or adding hydrogen peroxide. Although chemical leaching is an expensive process owed to the high costs of acid addition, this technique can still be considered as a practical step in the heavy metals removal from anaerobically digested sludges.

EXPERIMENTAL

Anaerobically digested sludge

The origin and main characteristics of the sludge as well as the chemical and physical distribution of heavy metals in the sludge applied in this research are described in Chapter 2.

Analysis

The procedures and equipments for heavy metals and pH analysis are mentioned in details in Chapter 2.

Experiments with the dried and crushed sludge: chemical leaching using progressive acidification

Effect of leaching agents

In order to evaluate the mobilization of heavy metals in the sludge, extraction by acids was performed. Therefore, three acids were tested separately: nitric, oxalic and citric. As recommended by Veeken and Hamelers (1999), oxalic and citric acids were chosen because extraction can be performed at mildly acidic conditions and because they are biodegradable. Nitric acid was used for comparison as it is a strong acid and because of its oxidative character. A scheme of the experiments is shown in Figure 3.1.

For each acid, seven bottles in duplicate containing 2-g air-dried sludge (40 °C) were filled with 40 ml of distilled water followed by the acid addition in such doses (see Table 3.1) to vary the pH values from 1 to 7. The bottles were stirred continuously (125 rpm) during 30 minutes at room temperature (20 °C) and the pH was monitored. From each bottle, two samples of 10 ml were collected and centrifuged at 4000 rpm during 20 minutes. The supernatant was filtered through a paper filter and further analyzed in duplicates for its heavy metals content.

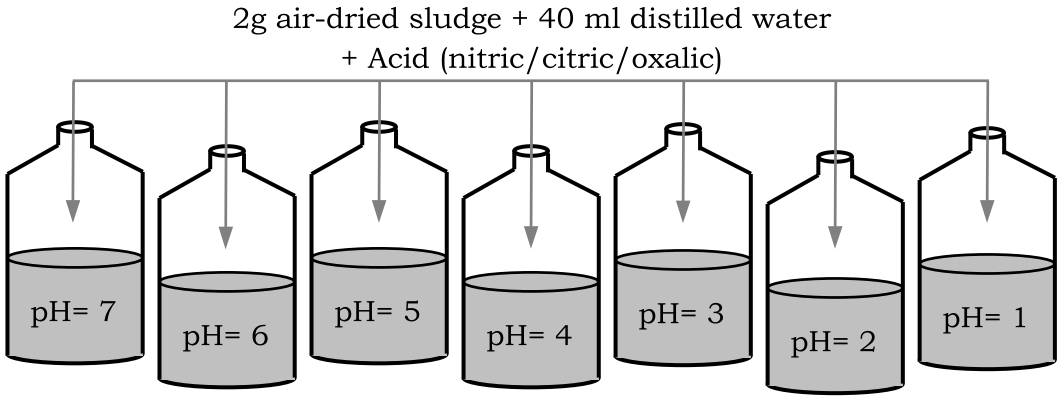

Figure 3.1 - Scheme of the progressive acidification experiments: effect of leaching agents

Table 3.1 - Acid dosages applied in the progressive acidification experiments (effect of leaching reagents)

pH	Nitric acid		Citric acid		Oxalic acid	
	g/L	mM/L	g/L	mM/L	g/L	mM/L
7	0.2	3.6	7.7	40	1.1	12.5
6	0.4	6	15.4	80	1.8	20
5	1.1	18	28.8	150	4.5	50
4	2.3	37	54.3	283	7.2	80
3	4.4	70	115.2	600	12.6	140
2	6.4	102	[a]		28.8	320
1	17.6	280	[a]		[a]	

[a] The required dosage of citric acid (pK_1= 3.14) to achieve pH= 2 was too high and was not considered. The same explanation is given by oxalic acid (pK_1= 1.23) to achieve pH= 1.

Leaching experiments as a function of time

The influence of the extraction time in the mobilization of the heavy metals present in the sludge was checked. For that, three acids were tested: nitric, citric and hydrochloric. Oxalic acid was no longer applied because according to the experiments concerning the effect of leaching agents, oxalic acid appeared to be not an effective extracting agent. Thus, for each acid, three bottles in duplicate containing 7-g air-dried sludge (40 °C) were filled with 140 ml of distilled water and the pH was settled to 3 (for the three acids), 2 and 1 (for nitric and hydrochloric acids) (see applied dosages in Table 3.2). Samples in duplicate were collected from each bottle after 30 minutes, 2 hours, 6 hours, 1 day, 5 days, and 7 days. The experiments and sampling were accomplished following the same procedure applied in the previous section. A scheme of these experiments is shown in Figure 3.2.

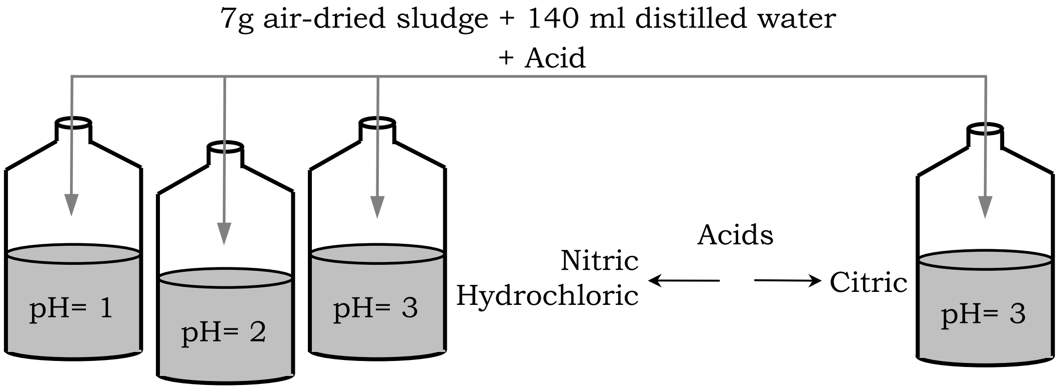

Figure 3.2 - Scheme of the progressive acidification experiments: effect of leaching time

Table 3.2 - Acid dosages applied in the progressive acidification experiments (effect of leaching time)

pH	Nitric acid		Hydrochloric acid		Citric acid	
	g/L	mM/L	g/L	mM/L	g/L	mM/L
3	4.4	70	3.3	90	115.2	600
2	6.4	102	6.8	187	[a]	
1	17.7	280	11.7	320		

[a] The required dosage of citric acid (pK_1= 3.14) to achieve pH= 2 was too high and was not considered.

After carrying out experiments with dried and crushed sludge samples, and choosing the most effective situation in terms of leaching results, the next step was to apply this situation to the original liquid sludge sample and compare the results. On this basis, the next experiments were set up.

Experiments with the liquid sludge: effect of oxidation with aeration

Aeration influence on heavy metals extraction

Five bottles in duplicate filled with 150 ml of the original sludge were submitted to five different experimental situations, at 20 °C (see scheme in Figure 3.3). Aeration before and after acidification, simultaneous aeration and acidification, only aeration and only acidification were the conditions studied. Aeration and acidification with 13.9 g/L (380 mM/L) of HCl (to achieve a pH value of 1) were both applied during 24 hours with continuous agitation (125 rpm). In the situation with simultaneous application, the total experimental time was 24 hours. The sampling procedure was identical to that followed in the former section.

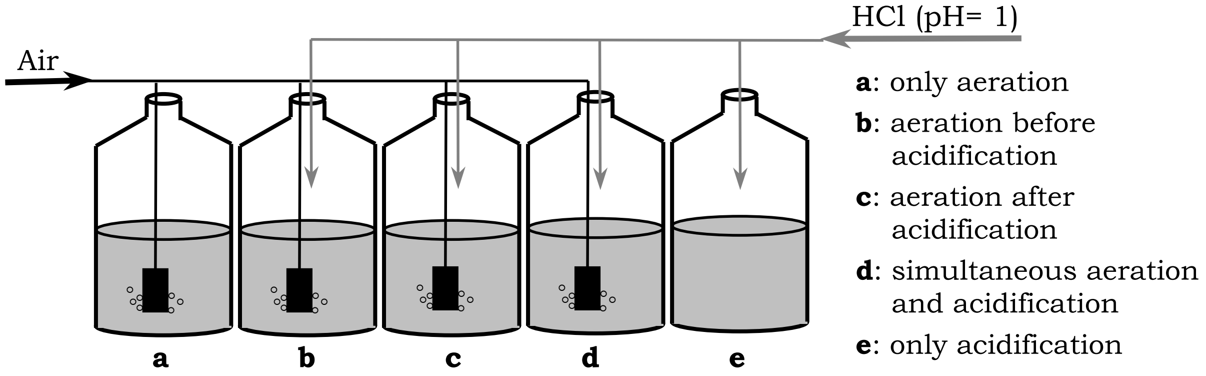

Figure 3.3 - Scheme of the experiments with different situations of aeration and acidification

Effect of acidification time and aeration on heavy metals solubilization

To assess the most effective acidification time on metals solubilization and the influence of aeration on that, these experiments were carried out. Two bottles in duplicate filled with 150 ml of the original sludge were submitted to acidification during 24 hours with HCl at a pH value of 1 with continuous shaking (125 rpm) at room temperature (20 °C). One of the bottles was aerated during 24 hours before aeration, as this was the best condition found in the previous experiments. The acidification time was varied at 30 minutes, 5 hours, 1 day, 4 days, and 8 days. The sampling procedure was the same applied in the former section.

Effect of aeration time and acidification time on heavy metals solubilization

These experiments were accomplished to investigate the best combination of aeration and acidification regarding the application time. A scheme is shown in Figure 3.4.

Five bottles in duplicate filled with 150 ml of the original sludge were aerated during 0, 3, 5, 9, and 24 hours. Then the bottles were acidified during 0.5, 2, 5, and 24 hours with HCl (pH= 1). Aeration and acidification were carried out with continuous shaking (125 rpm) at 20 °C. The sampling procedure was identical to that of the former section.

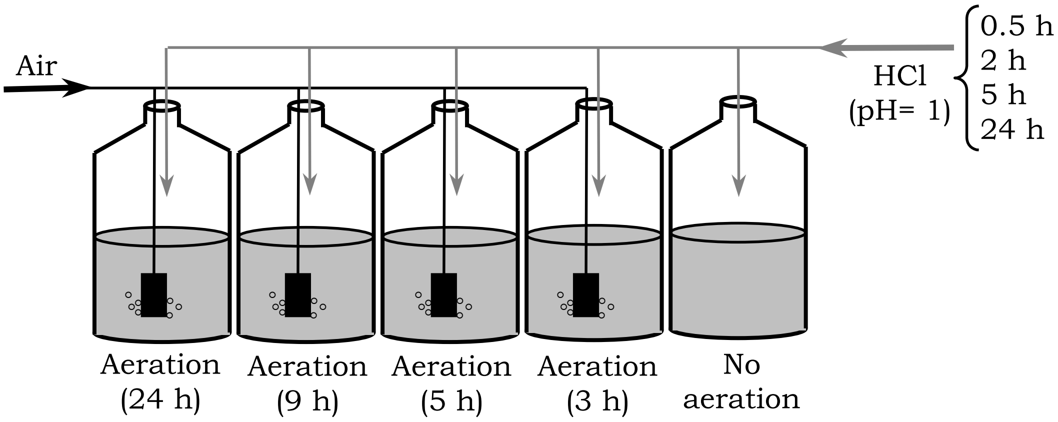

Figure 3.4 - Scheme of the experiments with aeration and acidification time variations

Experiments with the liquid sludge: effect of oxidation with H_2O_2

Effect of H_2O_2 dosage on heavy metals extraction

The influence of H_2O_2 was studied to verify whether its effect on heavy metals extraction would be higher than the aeration effect or not (see scheme in Figure 3.5).

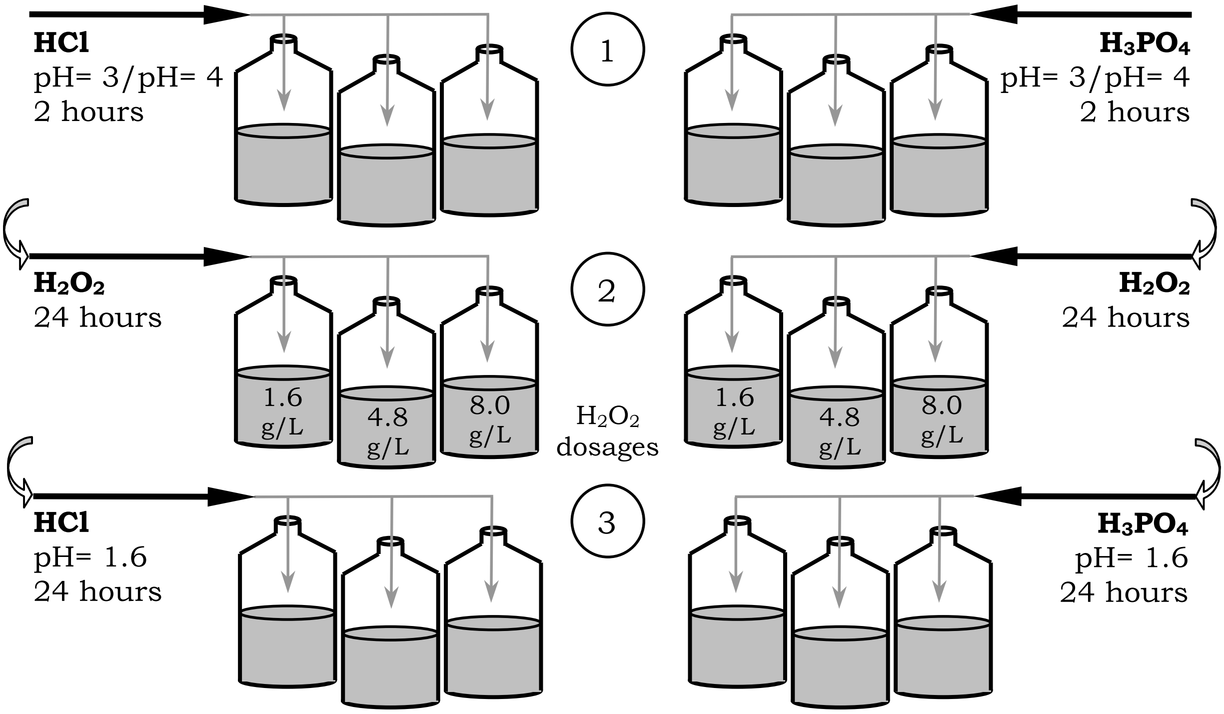

Figure 3.5 - Scheme of the several steps of the experiments with H_2O_2 dosage variation

In this way, H_2O_2 dosage was varied according to the concentration of iron present in the sludge to have the ideal proportion of Fe:H_2O_2 necessary for the occurrence of the Fenton reaction. According to Walling (1975), the typical ranges are 1:5-25 - Fe:H_2O_2. Thus, the H_2O_2 dosages applied were: 1.6 g (47 mM) H_2O_2/L sludge (1:5 - Fe:H_2O_2), 4.8 g (141 mM) H_2O_2/L sludge (1:15 - Fe:H_2O_2), and 8 g (235 mM) H_2O_2/L sludge (1:25 - Fe:H_2O_2). After H_2O_2 application, the samples were kept shaking during 24 hours (Figure 3.5).

Before the H_2O_2 addition, the pH value of 300 ml sludge was decreased with HCl and H_3PO_4, till the values of 3 and 4, as the pH range for the Fenton reaction is between 3-5 (Walling, 1975). The samples were kept shaking during 2 hours. The combination of H_3PO_4 and H_2O_2 was introduced here, following recommendation of Yoshizaki and Tomida (2000). After the addition of H_2O_2 and the shaking time of 24 hours, the pH was decreased till 1.6 with both acids (lowest pH value achieved with H_3PO_4 in the experiments) and the samples were kept shaking during 24 hours.

The experiments were carried out in duplicate, at 20 °C and the sampling procedure was identical to that of the former sections (Figure 3.5). The dosages of HCl used were: 48 mM/L (1.75 g/L) for pH= 4, 93 mM/L (3.4 g/L) for pH= 3, and 190 mM/L (6.9 g/L) for pH= 1.6. The dosages of H_3PO_4 used were: 156 mM/L (15.3 g/L) for pH= 4, 208 mM/L (20.4 g/L) for pH= 3, and 580 mM/L (56.8 g/L) for pH= 1.6.

Effect of oxidation time on heavy metals extraction

The influence of the H_2O_2 and the aeration application times were studied and compared. A scheme of the experimental steps is shown in Figure 3.6.

The H_2O_2 application followed the same procedure of the previous experiments. But now only the pH value of 3 was tested with HCl and H_3PO_4 and the H_2O_2 dosage was 4.8 g/L, as these were the best conditions found in the last experiments. The oxidation times of 6 hours and 24 hours were tested for both aeration and H_2O_2 application. The experiments were carried out in duplicates, at 20 °C and the sampling procedure was identical to that mentioned in the last section.

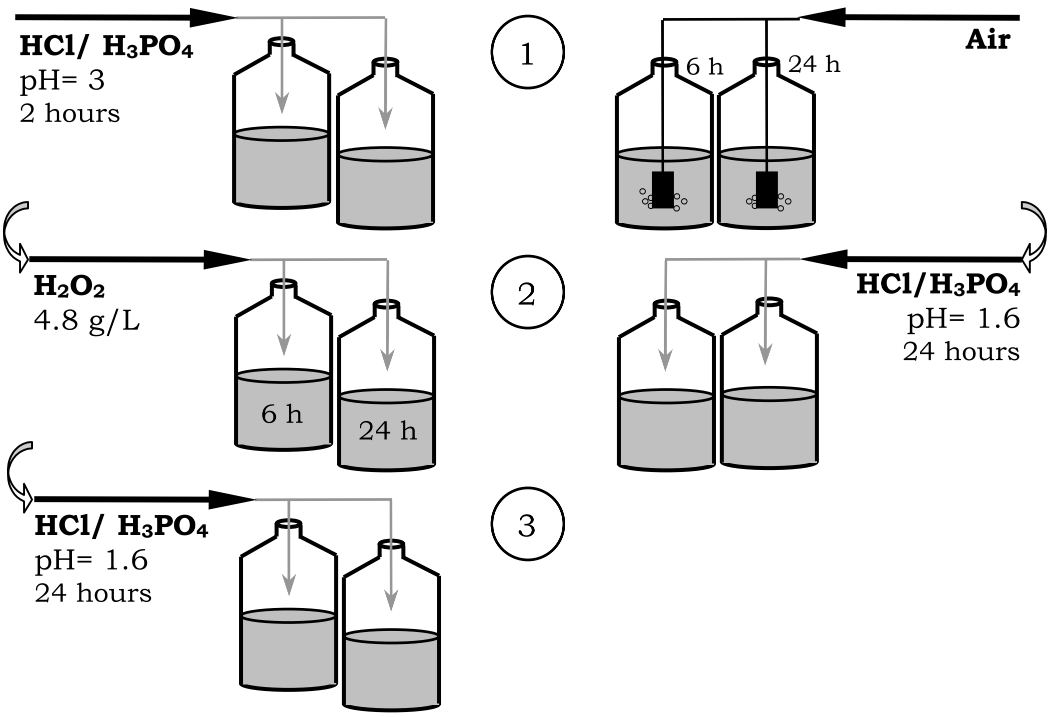

Figure 3.6 - Scheme of the several steps of the experiments with oxidation time variation

RESULTS AND DISCUSSIONS

Experiments with the dried and crushed sludge: chemical leaching using pH progressive changes

Effect of leaching agents

The effect of the pH on the heavy metals extraction with nitric acid (HNO_3), citric acid ($C_6H_8O_7$), and oxalic acid ($C_2H_2O_4$) are shown in Figure 3.7. Differences between duplicates were within 3.8 %.

Figure 3.7 demonstrates that, in the presence of complexing agents such as oxalic acid and citric acid, Cr extraction was not primarily governed by the pH decrease. The complexing capacity of the oxalate and citrate are clearly shown for Cr by comparing the extraction efficiency between nitric acid and the organic acids at the same pH values. The potential of complexing agents to form complexes with Cr (III) is consistent with the results obtained in the SCE schemes, shown in Chapter 2.

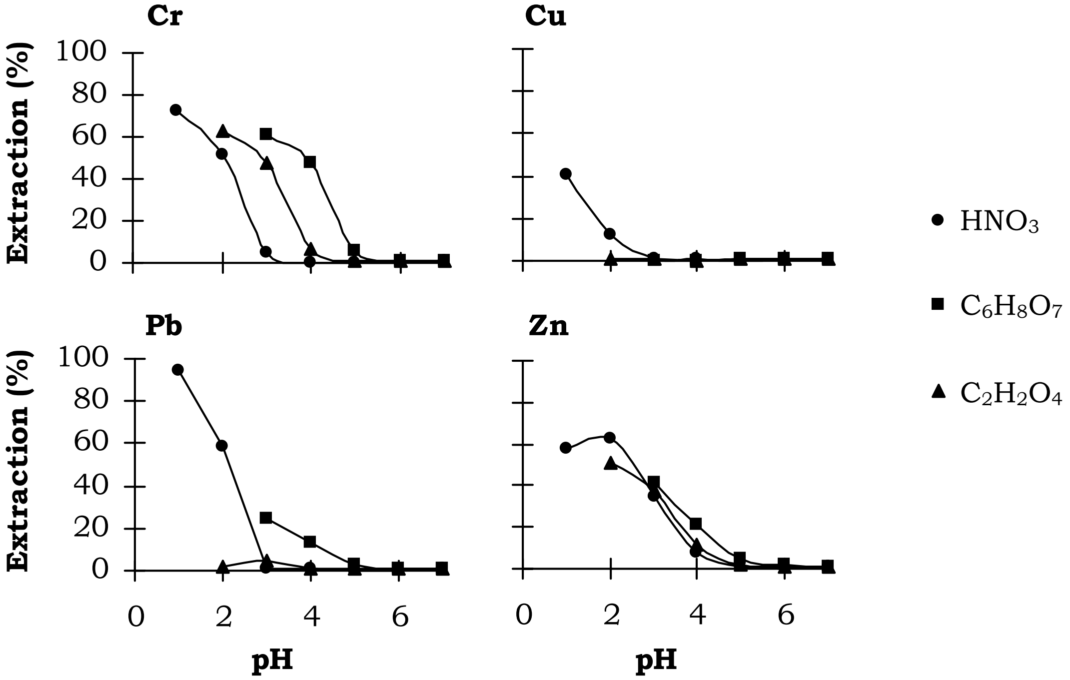

Figure 3.7 - Heavy metals extraction by nitric, citric and oxalic acid as function of pH
(Initial concentrations in mg/Kg: Cr= 473, Cu= 911, Pb= 167, Zn= 2330)

According to Veeken (1998) and Sims and Kline (1991) schemes, about 57 % of Cr was extracted by EDTA at a pH value of 4.5. As such, when a complexing agent like citric acid, oxalic acid or EDTA are applied, Cr can be solubilized at a higher pH value (3-5) than when a strong acid such as HNO_3 is applied (pH value < 3). In the Tessier (1979) scheme, about 65 % of Cr was extracted by HNO_3 and H_2O_2 at a pH value of 2. From Figure 3.7, citric acid was able to solubilize about 60 % of Cr, at a pH value of 3. Approximately the same amount was solubilized by oxalic acid at a pH value of 2 and by nitric acid at a pH value of 1.5. Despite the fact that Cr extraction started at the pH value of 5 with citric acid, the best extraction yield for Cr (72.3 %) was achieved with nitric acid at a pH value of 1.

The difference between citric and oxalic acid in the solubilization of Cr could be due to the chemical structure of both acids. Citric acid is formed by three carboxylic groups whereas oxalic acid contains two carboxylic groups. A high number of carboxylic groups might favor the complexing (or chelating) capacity of the compound. Extraction based on chelation involves the coordination of two or more donor atoms present in the chelating ligand to the same metal ion in such a way so as to form a heterocyclic ring termed a chelate (Lake, 1987). Citric acid, for example, is a tridentate ligand (i.e., contains three donor atoms capable of coordination to a single metal ion), which forms three chelate rings when all donor atoms are coordinated to a metal. Oxalic acid is a bidentate ligand.

Another reason for the better Cr extraction yielded with citric acid than with oxalic acid is defended by Veeken and Hamelers (1999). When calcium is present in the medium, as is the case of the present sludge, the calcium oxalate precipitate causes that oxalate become less available for heavy metals leading to a lower extraction comparing to citric acid extraction (Veeken and Hamelers, 1999).

About 40.5 % of Cu was extracted by nitric acid at a pH value of 1, starting at a pH value around 2, as observed by Lake (1987), and Wozniak and Huang (1982). The organic acids were not efficient in Cu solubilization. This might be due to the low pH value required for Cu to solubilize and to the short acidification time of 30 minutes applied in these experiments (see next section). Speciation schemes (see Chapter 2 and further discussion) suggested that Cu was predominantly incorporated in the organic fraction of the sludge and this makes its solubilization difficult. Therefore, an oxidating agent like HNO_3 might be more efficient to solubilize Cu, as confirmed by the speciation schemes. In addition, as Cu presents high affinity for organic complexes, it might be that the formation of Cu-citrate or Cu-oxalate complexes was limited by the reactions kinetics. Perhaps a prolonged reaction time would promote the formation of Cu soluble complexes.

Lead achieved its maximum extraction yield (94 %) with nitric acid at the pH value of 1, starting at a pH value around 3. At a pH value of 5 Pb extraction with citric acid started, achieving its maximum value (24.4 %) at the pH value of 3. Although there is an influence of the complexing agent citrate in Pb solubilization, this metal extraction is highly affected by low pH value. This is in agreement with Lake (1987), Kiekens and Cottenie (1984), and Wozniak and Huang (1982), who reported that the threshold of pH value for Pb mobilization is near to 2.

The curves of Zn demonstrated that this metal solubilization is affected by the decrease in the pH value, independent on the type of acid applied. Zinc started to solubilize at the pH value around 5 with the three acids. The best extraction yield for Zn (62.5 %) was achieved with HNO_3 at the pH value of 2. At the same pH value, around 51 % of Zn was extracted by oxalic acid.

The relatively low concentrations of soluble heavy metals measured at a pH value of 7 in the progressive acidification experiments could be comparable to those extracted by the exchangeable fraction in the SCE (see Chapter 2).

Leaching experiments as a function of time

Data related to the time influence on the extraction of Cr, Cu, Pb and Zn are shown in Figure 3.8. Differences between duplicates were within 3.5 %. Copper extraction was the most affected by the time from all the metals studied, followed by Zn. When citric acid was applied, Cr and Pb solubilizations improved as long as the time increased (Figure 3.8).

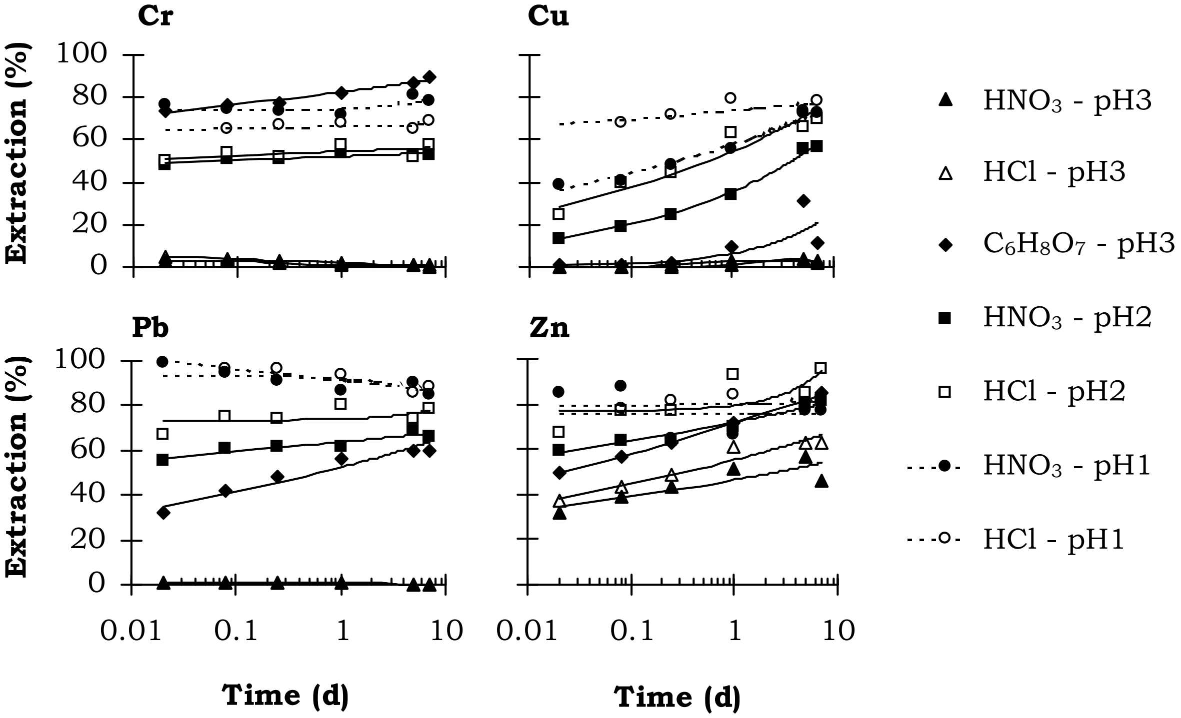

Figure 3.8 - Heavy metals extraction with nitric, hydrochloric and citric acid at different pH values as functions of time
(Initial concentrations in mg/Kg: Cr= 473, Cu= 911, Pb= 167, Zn= 2330)

The best extraction yield for Cr (89.6 %) was achieved with citric acid at a pH value of 3 after 7 days. This might be explained by the Cr speciation in the sludge and the tendency of Cr (III) to form complexes with organic acids. In general, there was no difference between nitric and hydrochloric acid to solubilize Cr. The best extraction yields for Cr with these two acids were obtained at a pH value of 1, with no considerable differences due to a change in the acidification time. These results are in accordance with those presented in Figure 3.7. Chromium solubilization is first governed by the presence of a chelating agent and this influence becomes stronger with an increase in the acidification time. When other acids are applied, however, their interference in Cr solubilization becomes almost competitive with the chelating agent at the point in which the pH value decreases till 1.

As mentioned before, copper was found predominantly incorporated in the organic fraction of the sludge (see Chapter 2 and further discussion). Thus, as a strong bounded heavy metal, it takes a longer time to reach equilibrium (Veeken and Hamelers, 1998; Hayes *et al.*, 1980). The effect of citric acid in Cu solubilization appeared after 6 hours, reaching the maximum extraction (30.9 %) after 5 days. The maximum extraction yield (79 %) of Cu was achieved with HCl at a pH value of 1 after one day.

Almost 100 % of Pb was extracted after 30 minutes with HNO_3 and HCl. Here the influence of the complexing agent citrate in Pb solubilization was clear, but the minimum pH value of 3 achieved with this acid was not enough to promote the almost 100 % extraction yielded with the other acids at a pH value around 1.

Zinc solubilization was affected by the leaching time, especially at the highest pH values. From Figure 3.8 it seems that there is no big difference between the results obtained with HCl application at both pH values of 2 and 1. There is no consistent explanation for the immediate fall in the nitric acid curve at pH value of 1 between 2 and 6 hours. The best extraction yield (96 %) for Zn was obtained with HCl at the pH value of 2, after 7 days followed by 93 % after 1 day.

Comparing the leaching effectiveness of all the acids as well as respective pH values and leaching times applied in this research, the use of HCl at a pH value of 1 during 24 hours was selected as the reference leaching situation for further investigations. Citric acid was only effective in Cr solubilization and HNO_3 was as effective as HCl to promote Cu solubilization only after a leaching time of about 5 days.

The progressive acidification process and the SCE schemes gave some indication of the potential behaviour of heavy metals under conditions of reduced pH value. In terms of sludge disposal to land, it should be wise to apply again the SCE schemes in the sludge after the acidification process, in order to evaluate whether the remaining heavy metals distribution has changed or not. Rudd *et al.* (1988) applied a SCE scheme to the residues obtained following sewage sludge acidification. According to these authors, Cu and Pb forms were relatively stable, but Zn speciation was likely to change with decreasing pH. The solubility of Zn, in particular at pH around 4-5 (see Figure 3.7), emphasizes its importance as a limiting metal, as its threshold pH can approach the pH values of some soils. In the presence of organic acids Cr and Pb can also be available at a pH value around 5.

Experiments with the liquid sludge: effect of oxidation with aeration

Aeration influence on heavy metals extraction

Figure 3.9 shows the effect of aeration applied in different situations on heavy metals extraction. Differences between duplicates were within 2.5 %. The aeration process considerably influenced copper extraction.

When aeration was solely applied, about 11 % of Cu was extracted, whereas less than 5 % of Cr, Pb and Zn was extracted. Speciation schemes (see Chapter 2) suggested that Cu exists as an organic complex in the sludge, as also observed by Tyagi *et al.* (1988), and Oliver and Carey (1976). For metals that are organically bound, a prolonged exposure under more extreme acid conditions would be required to bring about removal and recovery of heavy metals, as confirmed by Figure 3.8 and investigations of Tyagi *et al.* (1988).

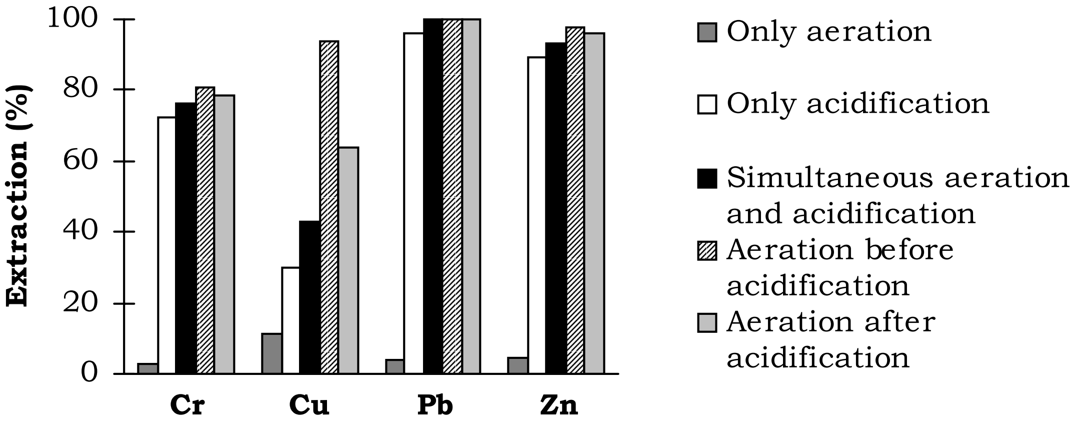

Figure 4.3 - Aeration influence on heavy metals extraction with HCl at pH= 1
(Initial concentrations in mg/L: Cr= 10.1, Cu= 23.8, Pb= 5, Zn= 43)

According to Hayes *et al.* (1980), in anaerobic sludges the heavy metals are present usually in their most reducible form, e.g., metal sulfides. Accordingly, besides the predominance of Cu as bound to the organic fraction of the sludge, Cu is also present as the insoluble Cu_2S (solubility product: K_{sp}= 2.5 x 10^{-48}) in the sludge (Hayes *et al.*, 1980). To solubilize Cu is necessary to oxidize Cu_2S to the more soluble form $CuSO_4$ (stability constant: K_o= 250).

Byukx *et al.* (2000) observed that Cu speciation in sulfide-rich freshwater sediment was not affected by aeration. In the present case, Cu speciation might have changed, because the effect of aeration on Cu extraction is clearly demonstrated by Figure 3.9.

The situation where aeration is applied before acidification is the best one for Cu and, to a lower extend, for Cr and Zn solubilizations. This is in agreement with Hayes *et al.* (1978) who observed that only decreasing the pH for anaerobic sludge does not end in a shift of metal sulfides to the soluble ionic form until acidification is preceded by a raise in the sludge ORP. The original ORP of the sludge was around – 90 mV. After aeration the ORP value increased to + 674 mV.

For Cr, Zn and especially Cu, the results obtained when aeration was applied after acidification were better than the results obtained when simultaneous aeration and acidification were applied. This can be due to the application times of aeration and acidification. During the simultaneous aeration and acidification, the total extraction time was 24 hours whereas in the other situations, acidification was applied during 24 hours followed by another 24 hours of aeration.

The extraction yields of Cr, Pb and Zn resulted from all the situations studied, are not considerably different from each other. The extraction percentages are relatively high and do not differ much from the maximum. The differences among the situations without aeration and aeration applied before acidification are smaller (Cr: 8.6 %, Pb: 3.9 %, Zn: 8.9 %) comparing to Cu (64.3 %).

<u>Comparison of the best extraction results achieved with the dried and crushed sludge and the liquid sludge</u>

Table 3.3 shows that the results achieved for the liquid sludge sample with application of aeration (24 hours) before acidification (with HCl, at pH= 1, during 24 hours) are better than the results attained for the dried and crushed sludge sample with application of HCl (at pH= 1, during 24 hours).

Table 3.3 - Comparison of some extraction results (%) obtained with the liquid sludge and the dried and crushed sludge

Situation	Cu (%)	Cr (%)	Pb (%)	Zn (%)
Liquid sludge: only acidification[a]	30	72	96	89
Liquid sludge: aeration before acidification[a]	94	81	100	98
Dried and crushed sludge[b]	79	68	94	84

[a] Liquid sludge: 25gDM/L; [b] Dried sludge: 50gDM/L; Organic matter: 550g/KgDM.

Table 3.3 shows that, without aeration, the extraction yields for Cr, Pb and Zn were approximately the same for the liquid and the dried sludge samples, despite the differences in the solids content between the both sludges. Copper extraction from the liquid sludge sample, however, required aeration to be competitive to the extraction obtained with the dried sludge sample. Rudd *et al.* (1988) observed that the differences in the behavior of the liquid and dried forms of the sludges using the progressive acidification were that the metals were more readily solubilized from the dried samples. On the other hand, the SCE schemes indicated that drying of the sludges effectively reduced the extractability of fractions that were readily available in the liquid form (Rudd *et al.*, 1988). The authors suggested that during the drying process the organic matter is oxidized and a mineralization might occur. Based on this, the size of the minerals particles are reduced and homogenized during the crushing process. This might favors Cu extraction, since this metal predominates in the organic fraction of the sludge.

In relation to the total solids concentration, Sreekrishnan *et al.* (1993), reported that an increased concentration of solids in the sewage sludge intensifies the buffering capacity, nutrient concentration and organic matter content in the sludge. Thus, an increase in the buffering capacity of the sludge will lead to a smoother and more gradual decrease in the pH value. Therefore, the sludge solids concentration does not interfere directly with the metal solubilization process, but affects by controlling the rate at which the sludge is acidified, in terms of required acid dosage and leaching time. Thus, the total solids concentration might interfere with the initial acidification process, but not in the final result of heavy metals solubilization.

Effect of acidification time and aeration on heavy metals solubilization

Figure 3.10 shows the influence of the acidification time on the solubilization of Cu, Cr, Pb and Zn, in the situations without aeration and with aeration applied before acidification. Differences between duplicates were within 3.2 %. In the absence of aeration, the heavy metals (especially Cu) needed a prolonged acidification time to solubilize effectively.

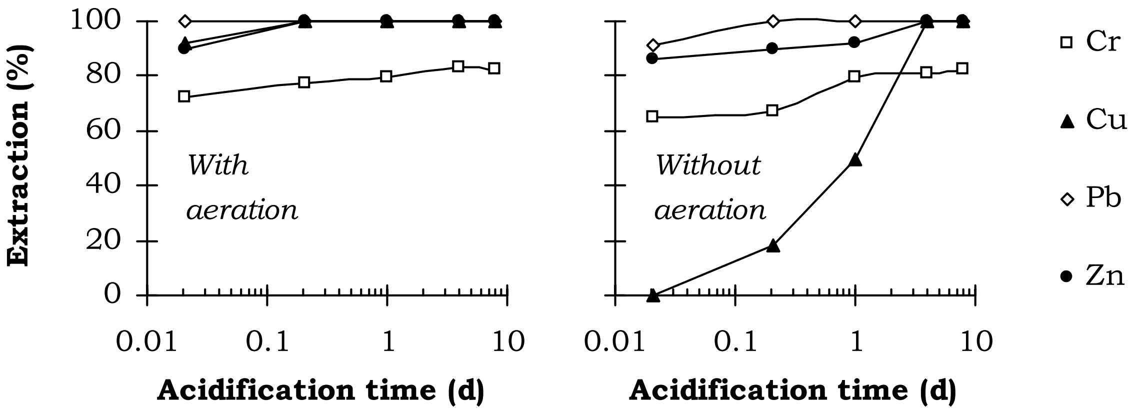

Figure 3.10 - Effect of acidification time on heavy metals extraction with HCl at pH= 1
(Initial concentrations in mg/L: Cr= 9.8, Cu= 24.3, Pb= 4.9, Zn= 43)

Comparing both graphs, when aeration was applied, satisfactory extraction yields were achieved with an acidification time of 5 hours for all the heavy metals. Without aeration, however, only after 3-4 days Cu achieved sufficient solubilization level.

Effect of aeration and acidification time on heavy metals solubilization

The effect of aeration and acidification time on heavy metals solubilization is shown in Figure 3.11 in form of surface contours. Differences between duplicates were within 3.0 %. The results show that each metal had a different extraction profile concerning aeration and acidification times.

The solubilizations of Cu and, to a less extend, of Zn were related to the aeration time rather than to the acidification time. To achieve an extraction yield of around 100 % Cu and Zn always needed 24 hours of previous aeration, but the acidification time could be reduced to 5 hours, or even less in the case of Zn. The surface contours of Cr demonstrate that its solubilization depended equally on the acidification and aeration times. However, to follow the tendency of Cu and Zn to minimize the acidification time and maximize the aeration time, with an acidification time of 20 hours about 80 % of Cr could be solubilized.

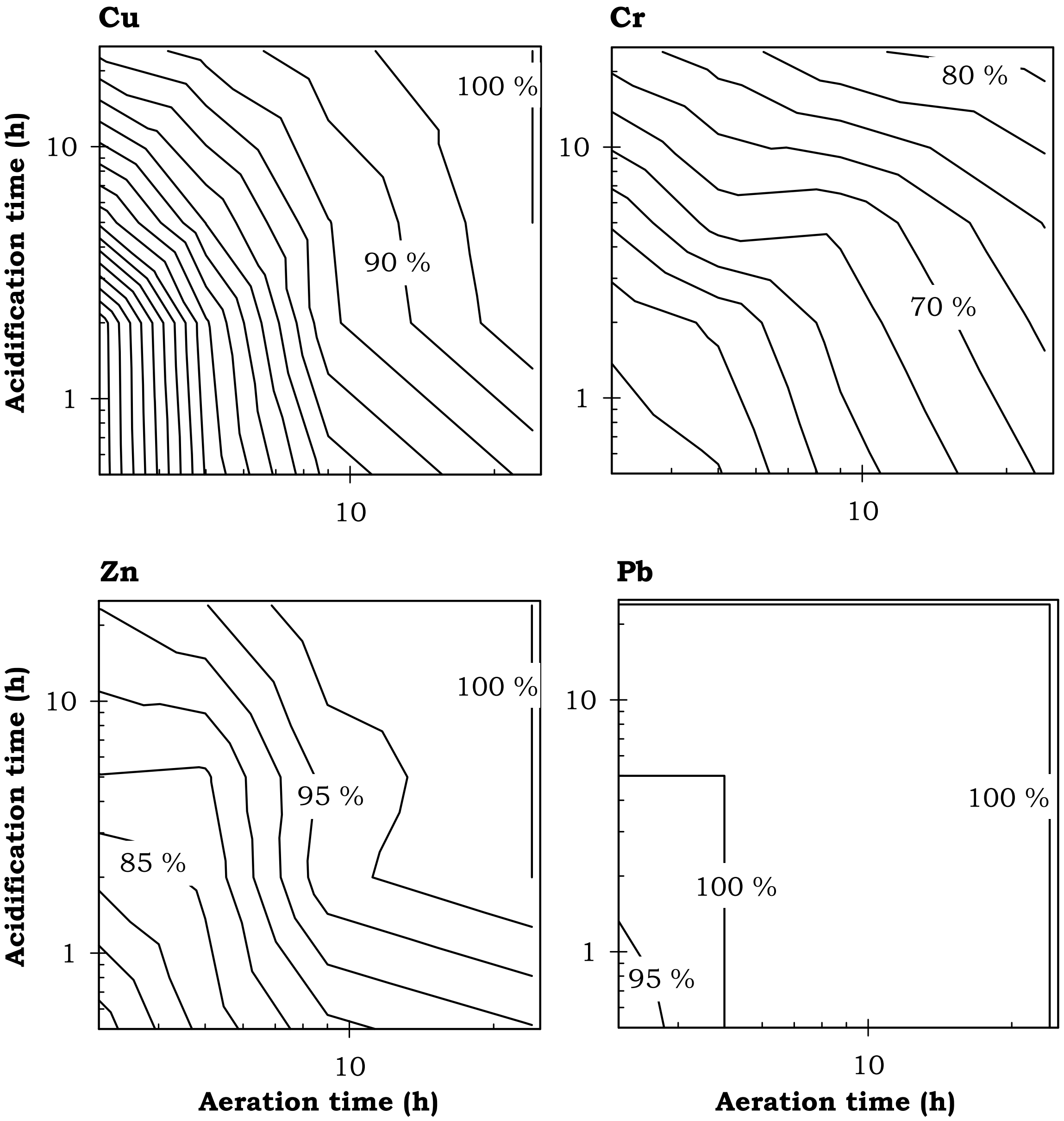

Figure 3.11 - Heavy metals extraction as function of acidification and aeration time
(Initial concentrations in mg/L: Cu= 22.2, Cr= 9.6, Pb= 5.1, Zn= 45.3)

About 100 % of Pb was already solubilized after 5 hours of aeration and acidification. For the present work it is important to find the situation that provides the most effective solubilization of all the metals studied. Thus, the situation in which both aeration and acidification are applied during 24 hours will be considered as reference in further study.

Experiments with the liquid sludge: effect of oxidation with H_2O_2

Effect of H_2O_2 dosage on heavy metals extraction

Figure 3.12 shows the extraction yields of Cr, Cu, Pb and Zn achieved with HCl and H_3PO_4 at initial pH values of 3 and 4, followed by H_2O_2 application at different dosages and a second acid dosage to pH value of 1.6. Differences between duplicates were within 4.5 %.

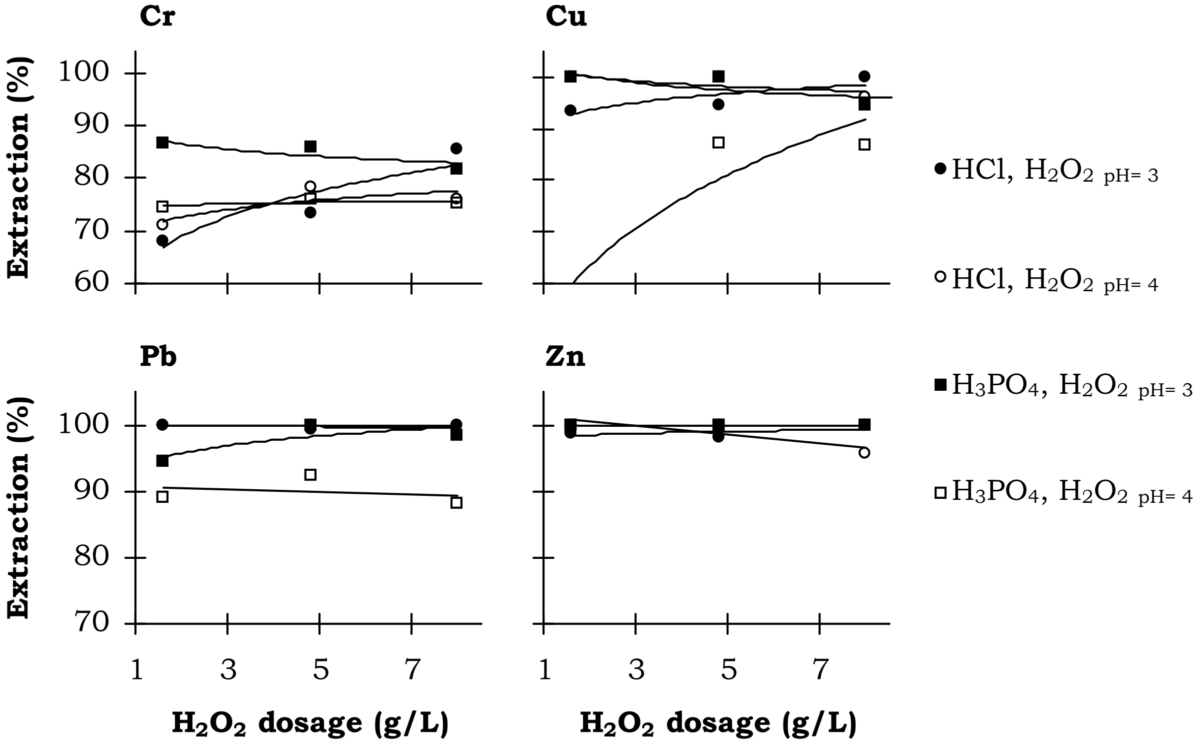

Figure 3.12 - Heavy metals extraction by HCl and H_3PO_4 as function of H_2O_2 dosage
(Initial concentrations in mg/L: Cr= 13.1, Cu= 27.8, Pb= 5.4, Zn= 53)

Despite the clear differences in the heavy metals behaviour, there were two situations that promoted high heavy metals extraction. One of them was with H_3PO_4 application at the initial pH value of 3 and 4.8 g H_2O_2/L. Similar results were found in the situation with HCl at initial pH value of 3 and the highest H_2O_2 dosage (8 g/L).

The fact that H_3PO_4 required a smaller H_2O_2 dosage than HCl to promote similar Cr, Cu, Pb and Zn extraction might be due to the function of the H_3PO_4 in the process. Phosphoric acid molecule might exert a positive effect on the Fenton reactions. Phosphate is commercially used to block catalytic surfaces, which promote the decomposition of H_2O_2 by the reaction:

$$2H_2O_2 \Rightarrow O_2 + 2H_2O \qquad (4.3)$$

Zinc was the easiest metal to be extracted in all the situations. Even with HCl at initial pH value of 4 and H_2O_2 dosage of 8 g/L, about 95.8 % of Zn was extracted. In general, when H_3PO_4 was applied, the pH value of 3 was more adequate to promote the Fenton reaction than the pH value of 4, as also observed for Cr, Cu and Pb. Mostly high differences between the two initial pH values did not affect heavy metals extraction with HCl. For further study, the best situation with H_3PO_4 and HCl will be considered those with initial pH value of 3 and H_2O_2 dosage of 4.8 g/L. Both conditions provided satisfactory extraction yields for all the metals studied.

Effect of H_2O_2 addition, aeration, and acidification with HCl and H_3PO_4 on the heavy metals extraction

Figure 3.13 shows the extraction percentages of Cr, Cu and Zn obtained at different process conditions regarding way of oxidation (H_2O_2 or aeration), acidification (HCl or H_3PO_4) and oxidation time (24 or 6 hours). Differences between duplicates were within 6 %. The oxidation-reduction potential of the sludge after H_2O_2 application was +723 ± 50 mV. The figure corresponding to Pb is not shown here, since about 100 % of this metal was extracted in all the situations studied.

Figure 3.13 highlights that when comparing both oxidation times, in general, there are no considerable differences in applying 24 or 6 hours of oxidation. In addition, Cu was not satisfactorily solubilized by the combination of H_3PO_4 and aeration.

Generally the differences between the extraction yields for Cr with the oxidation times of 24 and 6 hours were around 3 %, except in the situation that H_3PO_4 and aeration were applied, with a difference between the extraction efficiencies of 15.8 %. Comparing HCl and H_3PO_4, there were no considerable differences between both acids in the Cr extraction. Aeration was less effective (from 5 to 17 %) than H_2O_2 addition to solubilize Cr. This is consistent with the speciation schemes of Tessier (1979) and Veeken (1998), in which 58-65 % of Cr was detected in the fraction including H_2O_2 as reagent (see Chapter 2).

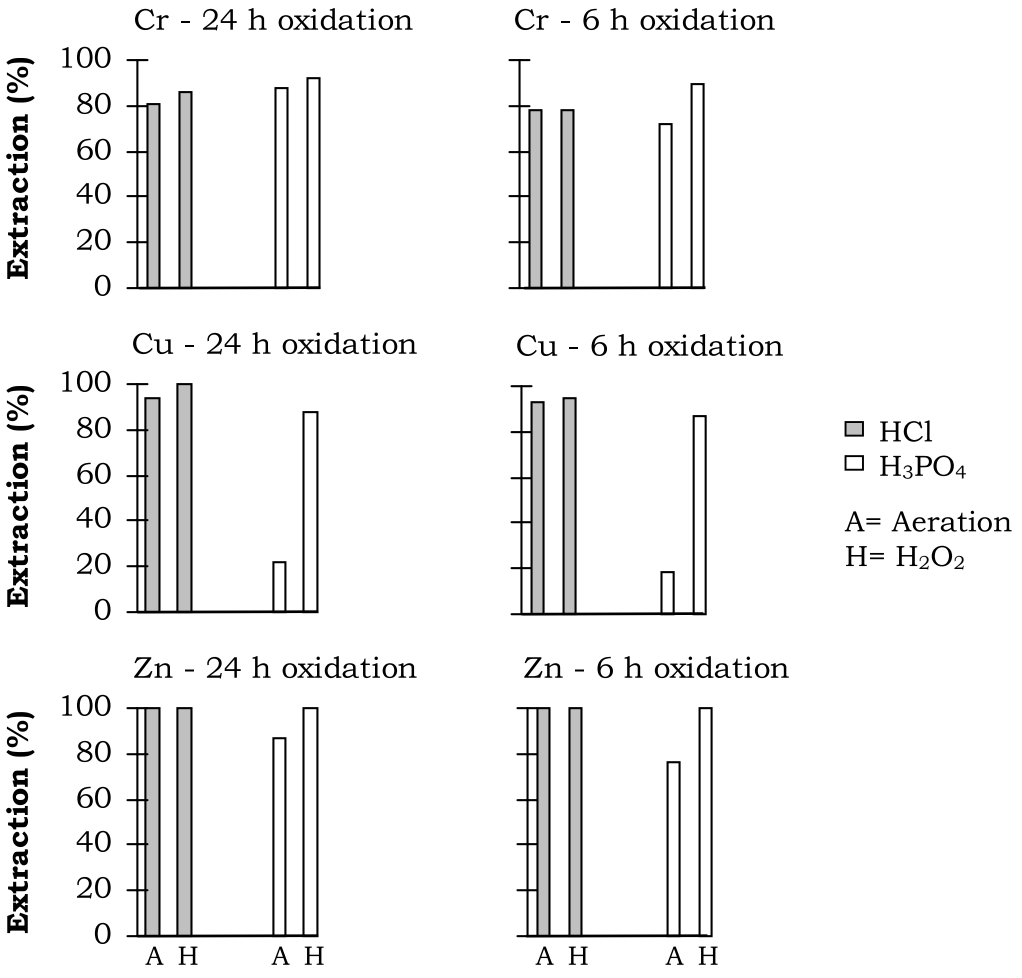

Figure 3.13 - Heavy metals extraction as function of aeration, H_2O_2 and acidification with HCl and H_3PO_4
(Initial concentrations in mg/L: Cu= 26.5, Cr= 13.3, Zn= 52.5)

The maximum differences in the extraction efficiencies due to the different oxidation times were around 5 % for Cu. Comparing HCl and H_3PO_4, the first acid provided better extraction yields for Cu than the second acid, in all situations. As observed for Cr, the effect of the H_2O_2 was superior to the effect of aeration in Cu extraction. Again, there is coherence with the SCE schemes (see Chapter 2). Copper was extracted mainly in the step that included H_2O_2 as reagent in the Tessier (1979) and Veeken (1998) schemes. Differently from Cr, however, the combination of H_3PO_4 and aeration was ineffective to solubilize more than 20 % of Cu, suggesting that H_3PO_4 was only effective in Cu extraction when this acid was combined with H_2O_2. According to the SCE schemes (Chapter 2), Cu is mainly bound or incorporated in the organic matter fraction and precipitated as Cu_2S, as emphasized by Hayes and Theis (1978). This suggests that the H_2O_2 added reacted with the Fe-compounds of the sludge, forming the highly oxidizing hydroxyl radicals, which were perhaps able to oxidize the organic matter and the Cu_2S faster than aeration.

An explanation for the difference in the extraction efficiencies of Cu achieved by the combination of aeration with H_3PO_4 or HCl, however, is still difficult. It cannot be suggested by the SCE schemes or by comparing the critical stability constants of the most likely stable Cu-chloro complex, e.g., $CuCl^+$ (log K_o= 0.4) or Cu-phosphate complex, e.g., $CuH_2PO_4^+$ (log K_o= 1.5). These constants indicate that the Cu-phosphate complex is more stable than the Cu-chloro complex. Although the phosphate solution has a higher extraction capacity for Cu than the chloride solution, even at the pH value around 1.6, HCl showed to be superior to H_3PO_4 in Cu extraction.

When H_3PO_4 is added at a pH value of around 1.6, the form H_3PO_4 (pK_1= 2.12) prevails, whereas about 30 % of phosphoric acid is present as $H_2PO_4^-$. This is an indication that at this pH value, about the same amount of phosphate species are available to complexate with Cu, compared to chloride, when HCl is applied. This is because the H_3PO_4 dosage is about 3 times higher than the HCl dosage required to achieve a pH value of 1.6.

The presence of calcium in the sludge might exert a strong influence on Cu extraction. Speciation calculations with Ecosat (Keizer and van Riemsdijk, 2002) showed that Ca could form stable complexes with phosphate species, e.g., $CaH_2PO_4^+$ (log K_o= 1.4), rather than with chloride. In addition to the competition of Ca^{2+}, Cu^{2+} also competes with H^+ in the phosphate-complexes formation. Speciation calculations with Ecosat (Keizer and van Riemsdijk, 2002) demonstrated, however, that the extraction capacity of the phosphate solution is still high enough. These calculations also confirmed that the formation of calcium phosphate minerals is unlikely to occur at such a low pH value, eliminating the hypothesis of coprecipitation of Cu^{2+} with these crystals.

Additionally to these hypothesis and according to the soil science (Kincheloe, 2003), phosphates and sulfates are adsorbed more strongly than nitrates and chlorides to soil particles. Then it might occur that, parallel to soil material, the phosphate species have a high affinity for binding to the positively charged sites of the solid fraction of the sludge and therefore it would not be available to form complexes with Cu^{2+} as chloride would. But the amount of phosphate added to the sludge is at least three times more than the dry matter content in the sludge. Thus, there would be enough phosphate species available. In this way, the only remaining hypothesis is whether the Cu-phosphate complexes have affinity to bind to organic matter/other solid sites or not. But this is a hypothesis and its consistency should be verified with additional experiments and/or modeling.

The only conditions where Zn extraction was affected by the oxidation time were those when H_3PO_4 and aeration were applied. The other situations were equally effective to solubilize about 100 % of this metal. As observed for Cu, but in less proportion for Zn, the combination of H_3PO_4 and aeration was not as efficient as the other situations to solubilize this metal.

Selection of method

To ease the comparison of the different leaching methods applied in this research, the results are summarized in Table 3.4.

From Table 3.4 it is clear that an oxidative step with either aeration or hydrogen peroxide favors the extraction of the heavy metals, especially Cu. When hydrochloric acid was applied without the oxidation step, Cu extraction efficiency for the dried sludge was better than that for the liquid sludge.

Another point highlighted in Table 3.4 is that, particularly for Cu, the use of nitric acid requires prolonged extraction times (about 5 days) to achieve similar extraction efficiencies as obtained with hydrochloric acid at the same pH value (around 1). Citric acid was advantageous only for Cr.

Table 3.4 - Heavy metals extraction efficiency (%) from anaerobically digested sludge using different methods

Method	pH	Cr		Cu		Pb		Zn	
		%	Days	%	Days	%	Days	%	Days
HCl[a]	1	72	1	49	1	96	1	89	1
Aeration + HCl[a]	1.4	81	1+1[c]	94	1+1[c]	100	1+1[c]	100	1+1[c]
H_2O_2 + HCl[a]	1.6	86	1+1[c]	100	1+1[c]	100	1+1[c]	100	1+1[c]
H_2O_2 + H_3PO_4[a]	1.6	92	1+1[c]	87.5	1+1[c]	100	1+1[c]	100	1+1[c]
HNO_3[b]	1	72	1	56	1	87	1	66	1
HNO_3[b]	1	81	5	74	5	90	5	77	5
HCl[b]	1	68	1	79	1	94	1	84	1
Citric acid[b]	3	90	7	31	5	60	5	85	7

[a] Liquid sludge; [b] Dried and crushed sludge; [c] Oxidation time + acidification time; [d] Negligible.

Both hydrochloric and phosphoric acids were able to solubilize high percentages of heavy metals when applied in combination with hydrogen peroxide (Table 3.4). However, the dosage of phosphoric acid (in mol/L) needed to decrease the pH to a proper value is at least 2 times more than the dosage of hydrochloric acid.

According to Table 3.4, the application of hydrochloric acid (pH around 1, during 24 hours) with previous application of aeration or hydrogen peroxide (with initial pH value of 3, during 24 hours) is able to promote the highest extraction efficiencies of most heavy metals.

Considering that the highest difference between duplicates was 6 %, yet there might be some metal content remaining in the sludge particles, especially Cr. Depending on the final destination of this sludge it is necessary to evaluate whether the remaining heavy metal amount will respect the local management policy. Besides the total concentration of the remaining heavy metals in the sludge it is also important to evaluate the speciation and mobility of these metals. In the case of Cr, it is unlikely that its hexavalent form occurs in anaerobically digested sludges. To avoid the conversion of Cr^{6+} to Cr^{3+} requires an oxidation-reduction potential (ORP) of +1100 mV under standard conditions (Weast, 1979). Under the oxidation conditions applied in the present research, the ORP value of the sludge was raised till the maximum value of +780 mV.

CONCLUSIONS

The results showed that the option including chemical oxidation with either aeration or hydrogen peroxide followed by acidification resulted in the highest extraction percentages of most heavy metals. The extraction yield is very sensitive to the type of acid used. HCl was superior to other acids like HNO_3 and H_3PO_4. Copper extraction was highly influenced by oxidation. The best results achieved were: Cr: 85 % with H_2O_2, Cu: 100 % with H_2O_2, Pb: 100 % with aeration and H_2O_2, and Zn: 100 % with aeration and H_2O_2.

Chapter 4

Bioleaching of heavy metals

Abstract

In the present work, the practical application of bioleaching in the solubilization of Cr, Cu, Pb and Zn from anaerobically digested sludge is evaluated. Bioleaching using elemental sulfur and ferrous iron and chemical leaching with H_2SO_4 were applied. The results were compared with those found in the literature and in previous leaching experiments with HCl. Bioleaching can be a feasible alternative to promote Zn and Cu solubilizations, especially when ferrous iron is added as substrate. Under this condition, the maximum extraction yield achieved for Zn was 80.8 % with a pH value of 2.7. For Cu it was 65.5 % with the pH value of 2.5. Cr solubilization was possible when pH was around 2.5 and Pb was not detected in solution. Chemical leaching with HCl at pH value of 1 solubilized almost 100 % of Pb and also provided the best extraction yield for Cr (around 72 %). At the same pH value, HCl is more effective than H_2SO_4 to solubilize all the metals studied.

Marchioretto M.M., Bruning H., Hien N.T.P. and Rulkens W.H. Presented at Biosolids 2003, Wastewater Sludge as a Resource. Trondheim, Norway. June, 2003.

INTRODUCTION

A safe use of sewage sludge as soil conditioner requires sewage sludge with low heavy metal content. The sludge application rate is governed by the cumulative metal loading of the soil (Sreekrishnan *et al.*, 1993). Reduction of heavy metals in sewage sludge can be achieved either by source control of discharge to sewer systems or by removing the metals from the sludge. As the major difficulty in source control is in identifying the sources, the only possible practical solution is to remove the heavy metals from the sludge (Sreekrishnan *et al.*, 1993).

Heavy metals cannot be removed by a physical separation process without being previously solubilized. Chemical leaching with acids or complexing agents is an effective option to promote metals solubilization. A drawback of this alternative is the large consumption of chemical agents (see Chapter 3). Besides, its application becomes attractive only at high plant capacities (Sreekrishnan and Tyagi, 1996). Biological leaching (bioleaching) can be a feasible and sustainable alternative to reduce de costs of the chemical leaching method.

The principle of bioleaching is the microbial production of sulfuric acid and subsequent solubilization of heavy metals. Tichý (1998) defines bioleaching as a process mediated by specific acidophilic bacteria capable of acid production. Since many of these microbes belong to the genus *Thiobacillus,* they are called thiobacilli-like organisms. Thiobacilli are able to oxidize reduced sulfur or ferrous iron and thus produce the acidity (Tichý, 1998). The main types of bacteria used in bioleaching are *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans.* They occur widely in terrestrial and aquatic habitats wherever inorganic sulfur and iron are present, such as in sewage systems, estuaries and acid mine drainage (Lombardi and Garcia Jr., 1999).

The bioleaching process aims at especially the solubilization of heavy metals but it also causes a reduction of pathogenic organisms. This is the result of the extreme pH conditions introduced by Thiobacilli during the bioleaching process operation. Thus, ideally the sludge coming out from a bioleaching system would present reduced amounts of both toxic metals and pathogenic organisms (Lombardi and Garcia, 1999).

Despite the positive aspects of bioleaching and its numerous studies over the last two decades (e.g., Wong *et al.*, 2002; Couillard and Zhu, 1992;

Hayes *et al.*, 1980), these techniques, applied in the solubilization of heavy metals from sewage sludge, still prevail under laboratory and pilot plant scale. The aim of the present paper was to get more insights into the practical application of bioleaching to solubilize heavy metals (Cr, Cu, Pb and Zn) from anaerobically digested sludge, its advantages and shortcomings. Bioleaching using elemental sulfur and ferrous iron as substrates was investigated and compared with chemical leaching with sulfuric acid. Finally, these results were compared with those found in the literature and in the previous chemical leaching experiments with hydrochloric acid described in Chapter 3.

EXPERIMENTAL

Anaerobically digested sludge

The origin and main characteristics of the sludge as well as the chemical and physical distribution of heavy metals in the sludge applied in this research are described in detail in Chapter 2.

Analysis

The procedures and equipments for heavy metals, pH and oxidation-reduction potential (ORP) analysis are described in Chapter 2. Heavy metal extraction efficiency was calculated as the ratio between the solubilized metal in the sludge after the extraction and the non-solubilized metal in the sludge before the extraction.

Chemical leaching experiments

Ten 1-L glass bottles were filled with 400-ml of sludge, continuously agitated (125 rpm) at 30 °C and simultaneously exposed to intense aeration for 24 hours before and during the acidification. The effect of aeration in the heavy metals solubilization of the present sludge was demonstrated in Chapter 3.

Aeration applied before acidification increases the ORP of the sludge, promoting the oxidation of the non-soluble metal forms to precipitate forms that would be dissolved at low pH. Here, aeration was not only applied before, but also during acidification. This was to ensure that the heavy metals solubilization was carried out at optimal conditions.

Acidification with sulfuric acid was applied for each bottle to achieve initial pH values of 5 (38 mM H_2SO_4/L sludge), 3 (64 mM H_2SO_4/L sludge), 2 (101 mM H_2SO_4/L sludge), and 1 (429 mM H_2SO_4/L sludge). The remaining bottles were preserved with the natural pH (original pH of the sludge). Samples in duplicates of 15 ml sludge were collected after acidification times of 0, 5 hours, 7 hours, 9 hours, 1 day, 2 days, 4 days, and 5 days (see scheme in Figure 4.1).

The ORP and the pH were measured at each time a sample was collected. After collection, the samples were centrifuged at 4000 rpm during 20 minutes. The supernatant was filtered by paper filter S&S black ribbon (12-25 μm) and subsequently analyzed for its terms of heavy metal (Cr, Cu, Pb and Zn) content by ICP-MS (see description in Chapter 2).

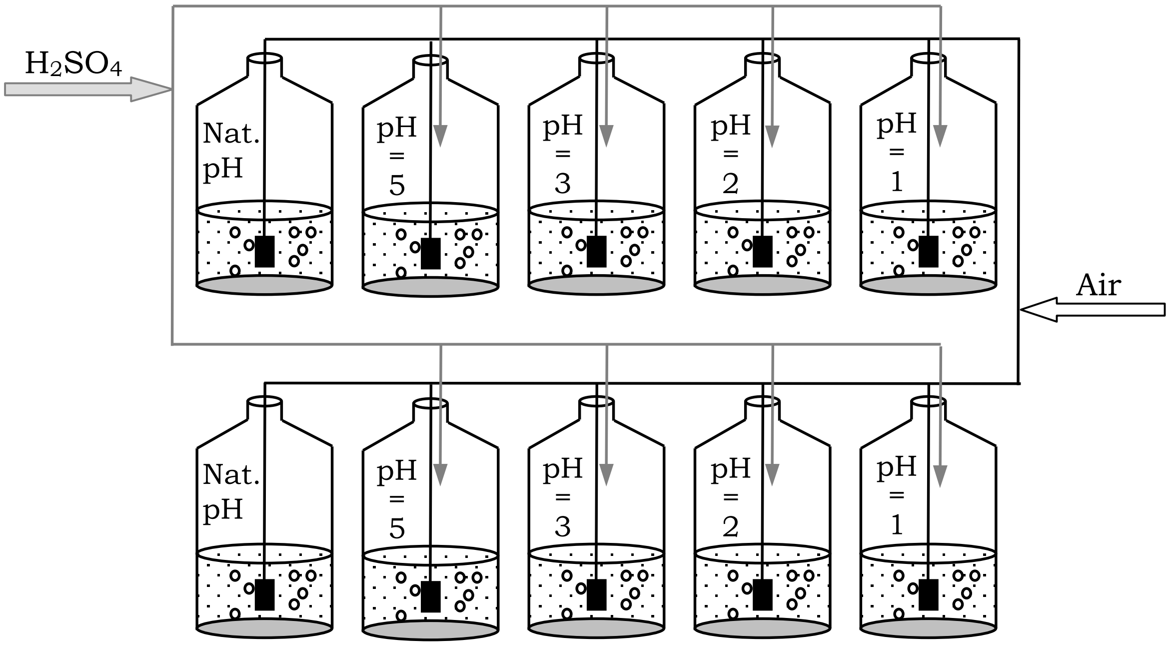

Figure 4.1 - Chemical leaching scheme

Bioleaching experiments

All the sludge bottles were continuously agitated (125 rpm) at 30°C and simultaneously exposed to aeration for 24 hours before and during the bioleaching step, with a total running time of 15 days. Carbon dioxide was applied as carbon source for the autotrophic bacterial growth. The pH was measured every day and samples in duplicate of 15-ml sludge were collected only when the pH value was stable (pH around 3-4, after 9 days). The samples preparation for heavy metals analysis followed the same procedure applied in the chemical leaching experiments.

With addition of elemental sulfur

Four 1-L glass bottles were filled with 400 ml of sludge and amended with elemental sulfur microbiologically produced by a pilot plant treating sulfide-rich paper mill wastewater in Eerbeek, The Netherlands (see Figure 4.2). In order to check the necessity of acid addition, the pH of two bottles was adjusted to 5 by sulfuric acid (38 mM H_2SO_4/L sludge) and the remaining bottles were preserved with the natural pH (original pH of the sludge). The amount of elemental sulfur added to the bottles was determined according to reaction 1 (Couillard and Zhu, 1992) and to the amount of sulfuric acid required to achieve pH value of 1 on the chemical leaching experiments.

$$S^0 + 1.5O_2 + H_2O \longrightarrow H_2SO_4 \quad (1)$$

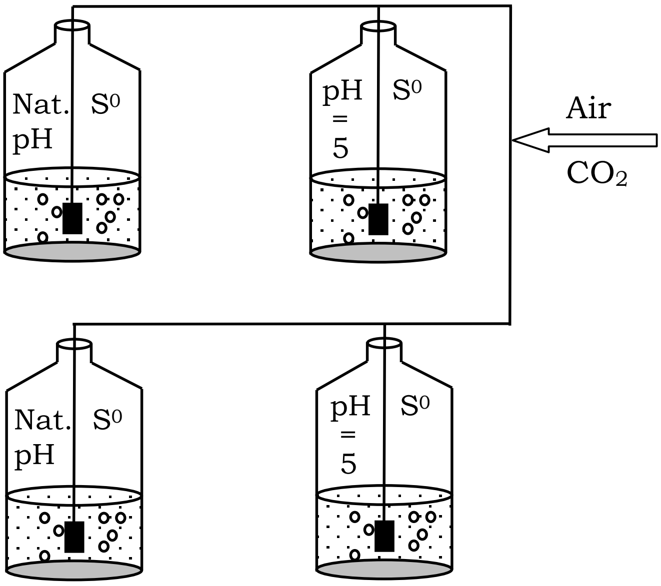

Figure 4.2 - Scheme of bioleaching with addition of elemental sulfur

With addition of ferrous iron

Eight 1-L glass bottles were filled with 400 ml of sludge and amended with ferrous iron substrate in the form of $FeSO_4.7H_2O$ (see reaction 2). The pH of four bottles was adjusted to 5 by sulfuric acid and the remaining bottles were preserved with the natural pH. A culture of growing bacteria (*T. ferrooxidans*) was added to two pre-acidified bottles and to two non-acidified bottles.

The amount of ferrous iron added to the bottles was determined according to stoichiometry of the reactions 2 (Couillard and Zhu, 1992) and 3 (Chartier and Couillard, 1997) and the amount of sulfuric acid required to achieve pH value of 5 in the chemical leaching experiments.

$$2FeSO_4 + 0.5O_2 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + H_2O \quad (2)$$

$$Fe_2(SO_4)_3 + 6H_2O \longrightarrow 2Fe(OH)_3 + 3H_2SO_4 \quad (3)$$

An exceeding amount of 5 g of $FeSO_4.7H_2O$ was applied in order to be sure that the substrate was not limiting.

With addition of a mixed substrate

These experiments were identical to those applied for bioleaching with ferrous iron as substrate. But instead of ferrous iron solely, a mixture of elemental sulfur and ferrous iron was applied.

RESULTS AND DISCUSSIONS

Chemical leaching experiments

pH and oxidation-reduction potential (ORP)

Figure 4.4 shows the curves of the pH and ORP of the sludge during the chemical leaching with sulfuric acid as functions of time. The pH and ORP values of sludge under aeration and acidification did not vary considerably with time.

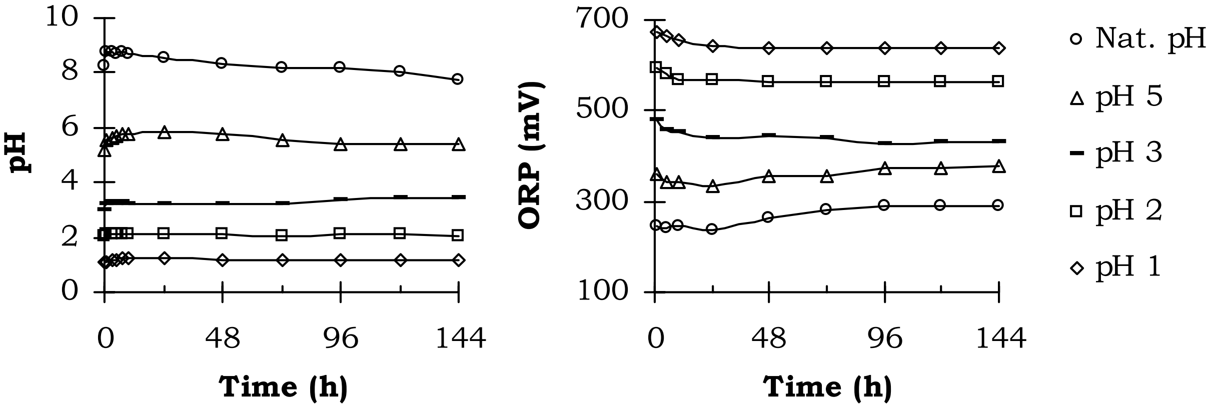

Figure 4.3 - pH and ORP variations during the simultaneous aeration/acidification, after 24 hours of aeration
(Before previous aeration: natural pH= 7.9 and ORP= -90 mV)

The pH values gradually increased during the first 10 hours. This might be due to sorption processes, including physical adsorption, chemical adsorption and sorption based on ion exchange (Tichý *et al.*, 1998). After 10 and 48 hours respectively, the natural pH (initially 7.9) and the initial pH value of 5 decreased more than the other pH values, but they could not reach the value of 4, which is the threshold value for satisfactory mobilization of heavy metals (Lake, 1987). The decrease in the pH values might be the result of chemical and microbial oxidation of reduced sulfur compounds in sludge. The chemical oxidation was caused by aeration and the microbial oxidation by the indigenous bacteria.

Similarly to the changes in the pH values, the ORP of the sludge varied during the first 10 hours and became almost stable after that period. The initial ORP value of -90 mV was high compared with the -300 mV to -520 mV values established by Hayes and Theis (1978) for anaerobically digested sludges. The unavoidable aeration of the sludge during the collection at the sewage plant and the manipulation of the sludge during the experiments might be reasons for this difference. Previous aeration made the ORP value increase considerably. Solubilization strategy requires optimum adjustment of pH and ORP of the sludge so that the chemical equilibria will be shifted in favor of dissolved metallic ion formation (Tyagi *et al.*, 1988).

Heavy metals solubilization

The extraction efficiencies of Cr, Cu, Pb and Zn as functions of time are shown in Figure 4.4. Duplicate values differed from the mean by 3.5 % at most. Zinc solubilization occurred at pH value of 3 or below, whereas the other metals were only solubilized at pH value of 2 or below (see Figure 4.4).

There was a definite lag time of Cu extraction before measurable solubilization. This was also observed by Hayes *et al.* (1980). The low solubility of Cu in the beginning might be due to organic complexation because Cu tends to form complexes with the organic matter in sludges (Chen and Lin, 2000). The affinity of Cu to organic matter was suggested by the speciation schemes presented in Chapter 2. Therefore, Cu extraction needs prolonged time and low pH value (around 2) conditions. According to Figure 4.4, the highest extraction efficiency observed for Cu (67.7 %) was achieved after 96 hours at a pH value of 1. At a pH value of 2, the maximum Cu extraction was 63.2 % after 120 hours.

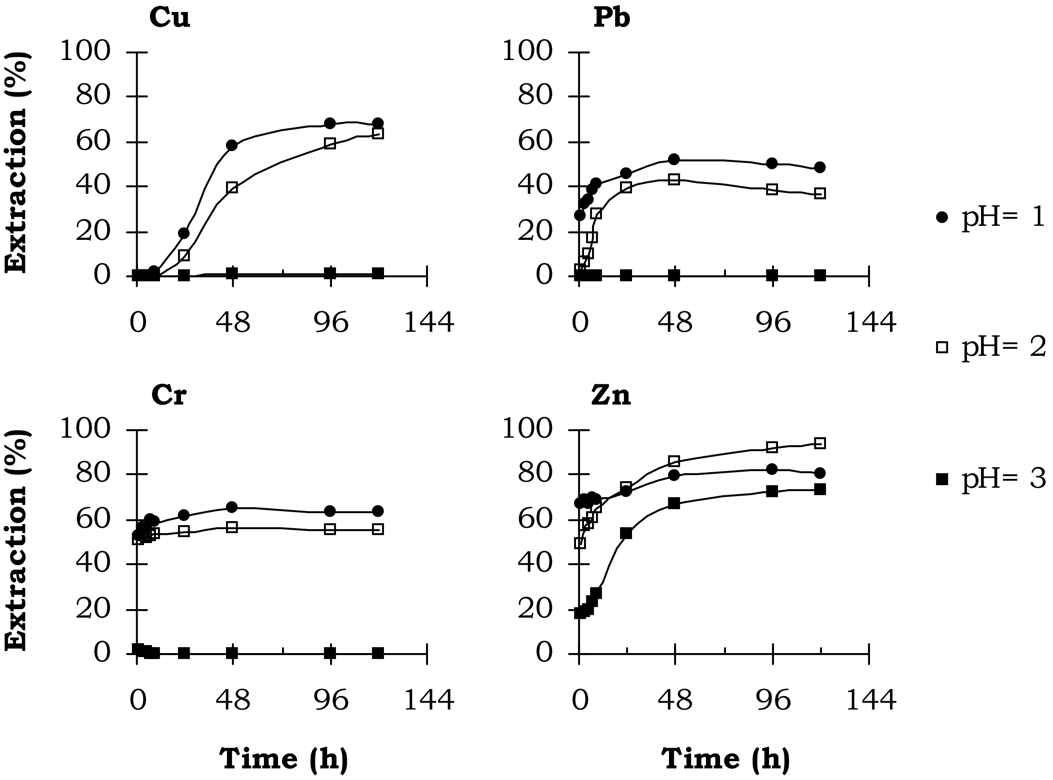

Figure 4.4 - Heavy metals extractions as functions of time during chemical leaching
(Initial concentrations in mg/L: Cu= 25.7, Pb= 5.3, Cr= 11.7, Zn= 51.9)

From Figure 4.4, the time necessary to approach the maximum Pb extraction was 48 hours, at a pH value of 1. As reported by Wozniak and Huang (1982), the initial removal of Pb (and Cu) usually represents less than 10 % of the maximum value under given pH conditions. In the present research about 51.5 % of Pb was extracted. This value, however, was very low when compared with Pb solubilization by HCl (see further discussion). This indicates that some mechanism, such as the formation of a low soluble precipitate ($PbSO_4$) was preventing lead solubilization. This was also observed by Chen and Lin (2001a;b), Chartier and Couillard (1997), and Mercier *et al.* (1996). At a pH value of 2, the maximum Pb extraction was 42.8 %, after 48 hours. No Pb solubilization was observed at a pH value of 3. This is in agreement with Kiekens and Cottenie (1984), who reported that the threshold of pH value for Pb mobilization is near to 2.

Chromium solubilization was not highly affected by the treatment time as shown in Figure 4.4. This is consistent with the results obtained in the experiments with application of different acids described in Chapter 3. The maximum value (64.8 %) was achieved after 48 hours at a pH value of 1.

Zinc presented the highest solubilization of all the heavy metals studied. Even at a pH value of 3 a relatively high concentration of Zn was observed in the liquid. These results agree with the previous leaching experiments shown in Chapter 3. Wozniak and Huang (1982) also concluded that Zn was extracted in large amounts immediately after acidification. The best extraction yield for Zn was 93.5 %, at a pH value of 1 after 120 hours. A further discussion about Zn, as well as Cu, Cr and Pb solubilizations is presented later.

Bioleaching experiments

pH

Figure 4.5 shows the pH variation during the bioleaching experiments as function of time at various conditions of substrate application. After about 8 days, the pH values became stable or decreased slowly.

The lowest pH value of 1.9 occurred in the sample with the addition of S^0/Fe^{2+}/Acid/Culture after 15 days. *T. ferrooxidans* were cultured under acidic conditions and the sulfur compounds might have been produced from the elemental sulfur added. On the other hand, apparently *T. ferrooxidans* oxidized elemental sulfur to generate sulfuric acid but this process occurred more slowly than the oxidation of ferrous iron.

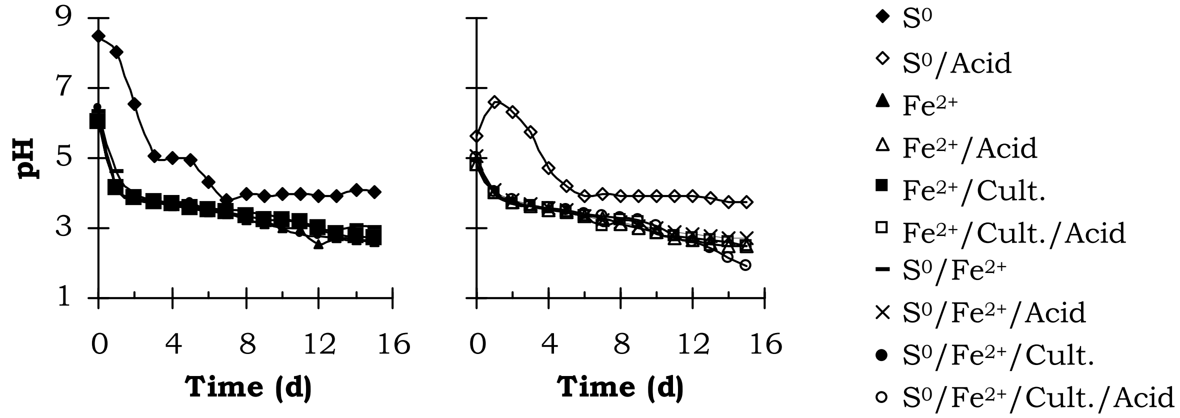

Figure 4.5 - Variation in the pH value during the bioleaching tests (before previous aeration: natural pH= 8.0)

During the first 4 days, the pH values of the samples without the addition of acid decreased more than those of the samples with the addition of acid. All samples reached a pH value around 4 after one day. This was a result of the higher initial pH values of the samples without the addition of acid. A redbrown precipitate in these samples was observed after the ferrous iron addition. It indicated the existence of ferric iron (Fe^{3+}) in form of ferric hydroxide, which was microbiologically or chemically oxidized from ferrous iron. As the product of this reaction, hydrogen ions were generated and the acidity increased. Ferric iron has a high oxidative power and is not able to remain as an ion in the solution at the pH value above 4.5 (Evangelou and Zhang, 1995), due to the reaction:

$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ \qquad (4)$$

Below the value of 4, the decrease in the pH was very slow. Probably ferric hydroxide was reversely solubilized into the solution and no more hydrogen ions were produced. During the experiment, a part of ferrous substrate was lost because of this behaviour. Therefore, the addition of acid to reach the initial pH value of 5 was needed.

The increase in the pH value of the sample with addition of S^0/Acid in the first day might have been caused by the absorption of hydrogen ions to the solid particles and the microbial oxidation rate of elemental sulfur was not fast enough to compensate the amount of hydrogen ions lost. After 9 days the pH became approximately stable at the value of 4. This reduction could be attributed to the action of *T. ferrooxidans*, which oxidizes elemental sulfur to generate sulfuric acid.

Heavy metals solubilization

The concentration of heavy metals was measured after 9 days, when the pH values were relatively stable or slowly decreasing (see Figure 4.5). Figure 4.6 represents the variations of Zn, Cu and Cr extractions and pH (from Figure 4.5) over time for different bioleaching conditions. Duplicate values differed from the mean by 5.8 % at most. Lead extraction was negligible and is not shown. Figure 4.6 shows that bioleaching was well able to mobilize Zn and Cu, but not Cr, even at the lowest pH (1.9) achieved after 15 days.

Zinc showed the highest solubilization of all the heavy metals studied. Its maximum extraction yield was 86.3 %, in the situation with addition of elemental sulfur and ferrous iron as substrates, at pH value of 3.4 after 9 days. The curves of Zn show that its extraction yield could be even higher than the 86.3 % at a shorter period of time, for all the situations studied, with exception of the one with ferrous iron and acid addition. The second highest extraction percentage achieved for Zn was 80.8 % with addition of ferrous iron and acid at a pH value of 2.7 after11 days.

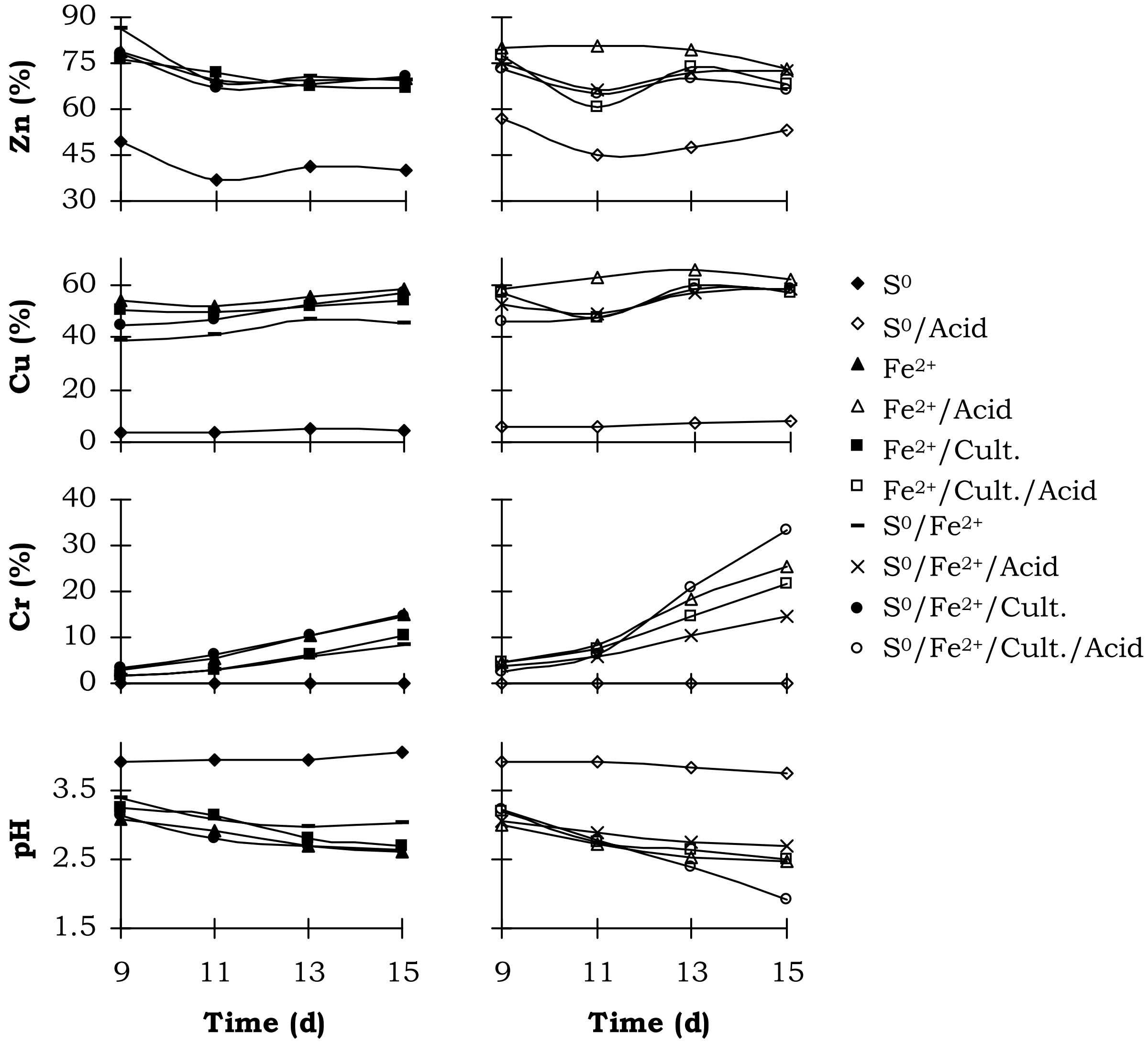

Figure 4.6 - Heavy metals extraction as function of time during the bioleaching experiments
(Initial concentrations in mg/L: Zn= 51.9, Cu= 25.7, Cr= 11.7)

Copper achieved its maximum extraction yield (65.5 %) in the sample with addition of ferrous iron and acid, at pH value of 2.5 after 13 days. As observed for Zn, it was not necessary to reach the lowest pH value of 1.9 for Cu solubilization by bioleaching. At this minimum pH value, both metals extractions were not strongly varied, since they were almost equivalent to the maximum extraction yields achieved with pH 3.4 (Zn) and 2.5 (Cu).

Figure 4.6 shows that Cr extraction was considerably affected by the pH. The maximum extraction percentage of this metal (33.5 %) was found from the sample with the addition of elemental sulfur, ferrous iron, acid, and culture. It matched to the lowest pH value of 1.9 achieved in the 15th day. Chromium speciation in the sludge might explain its low solubility achieved by bioleaching, since this metal was found almost equally distributed in the organic and inorganic fractions, as suggested by the speciation schemes results shown in Chapter 2.

Lead speciation (see Chapter 2) might be also the reason for the absence of this metal in solution when bioleaching was applied, because 80 % of this metal could be distributed in the inorganic matter and/or inorganic precipitates. In another scheme, about 45 % of Pb was found in the residual fraction, in which minerals may hold metals in their crystal structure. This makes lead extraction possible only at very low pH values. But as explained before, the formation of $PbSO_4$ during the bioleaching tests might be the great cause of the negligible Pb solubilization.

Effect of substrates on heavy metals solubilization

Figure 4.6 shows that the addition of elemental sulfur resulted in less effective heavy metals solubilization compared to the other substrate conditions. As the samples with addition of elemental sulfur and acid were comparable to those with sulfur only, the acid addition became unnecessary. Although there was a response of bacteria, the decrease of the pH values could not go further than 4. It was probably a result from the lack of *T. thiooxidans*, which primarily use elemental sulfur as their substrate. But there are other factors that probably affected the bioleaching process, such as the difficulty to dissolve the elemental sulfur, the effectiveness of the aeration system and the metals speciation in the sludge. The distribution of metals between their specific forms depends especially on the characteristics of the sludge (origin, pH, total solids content, particle size), and the chemical properties of these metals.

Villar and Garcia Jr. (2002) could achieve lower pH value (around 1) for an anaerobically digested sludge by using only elemental sulfur as the substrate in the bioleaching. With this minimum pH, the extraction efficiencies of Zn, Cu and Cr were considerably better than those at a pH value of 4.

Comparing the ferrous iron and acid containing samples with and without addition of *T. ferrooxidans* culture, there is no advantage from the culture added. Probably the microorganisms did not adapt to the new medium or there were not enough sulfides available in the sludge to produce hydrogen ions.

The addition of both ferrous iron and elemental sulfur did not provide a real improvement in the extraction of the heavy metals, except for Cr at pH 1.9. At higher pH values (2.5-3.5) Zn and Cu already achieved their highest extraction yields. In this way, there is no need to add the two substrates and the situation with addition of ferrous iron and acid is considered as the most effective here.

Solids content of the sludge

The solids concentration of the sludge was not varied in this research. As mentioned in Chapter 2, the total solids content of the sludge is around 25 g/L and the organic matter represents 60 % of this amount. Sreekrishnan *et al.* (1993), reported that an increased concentration of solids in the sewage sludge intensifies the buffering capacity, nutrient concentration and organic matter content in the sludge. Consequently, an increase in the buffering capacity of the sludge will lead to a smoother and more gradual decrease in the pH of the reactor. As a conclusion, the sludge solids concentrations do not interfere directly in the metal solubilization process, but affect by controlling the rate at which the sludge is acidified. In other words, the total solids concentration might interfere in the initial acidification process, but not in the final result of heavy metals solubilization.

According to Villar and Garcia Jr. (2002), the establishment of solubilization patterns independent of the sludge solids concentration can be of great usefulness when predicting the efficiency of bioleaching systems based on pH measurements. From this point of view, the present research was carried out. In practice, however, the total solids concentration might play an important role in the amounts of substrate and acid required. In the cases of chemical leaching and bioleaching with ferrous iron substrate the acid amount must increase with an increase in the total solids concentration. On the other hand, the possibility of metal extraction at higher sludge solids concentration can reduce the process costs, by reducing the reactor volume (Sreekrishnan and Tyagi, 1996). However, a dilution of the sludge, which is produced in high amounts, will lead to serious operational problems for a possible scale-up of the process (Lombardi and Garcia Jr., 2002).

Comparison between chemical leaching and bioleaching

Although the pH values achieved with bioleaching were higher than the pH value of 1 in the chemical leaching with sulfuric acid, Zn and Cu extraction yields were not so different between the two methods. This is a positive aspect of bioleaching, since it might reduce the costs of sludge treatment after the metals solubilization. In contrast, there was almost no Pb and only a small amount of Cr solubilized by bioleaching.

To easily compare the two leaching methods, the results of the experiments are summarized in Table 4.1. From bioleaching, only the data referring to the addition of ferrous iron and acid is shown. Extraction yields of Cr, Cu, Pb and Zn found in the literature of bioleaching and in previous experiments with HCl (see Chapter 3) are also included. The table shows the minimum percentages of heavy metals that should be extracted (considering further metals removal of 100 %) from the sludge to be under the Dutch standard for sludge disposal on agricultural soils (SDU, 1991). The values were calculated based on the initial heavy metals concentration in the sludge. To allow a comparison of all the methods exposed in Table 4.1, one should assume that all the sludges are similar, especially in terms of heavy metals content, speciation, and total solids concentration

Table 4.1 - Heavy metals extraction (%) from sewage sludge

Method	pH	Cu		Zn		Cr		Pb	
		%	days	%	days	%	days	%	days
H_2SO_4 (this study)[a]	1	67.7	4	93.5	5	64.8	2	51.5	2
HCl with 24 h of previous aeration (see Chapter 3)[a]	1	94	1	97.9	1	80.7	1	100	1
HCl (see Chapter 3)[a]	1	49.0	1	89.0	1	72.1	1	96.1	1
Bioleaching with Fe^{2+}/Acid (this study)[a]	2.5	65.5	13	80.8	11	25.5	15	[c]	
Bioleaching with S^0 - Villar & Garcia Jr. (2002) (approximated values)[a]	1	85	[d]	97	[d]	56	[d]		
Bioleaching with Fe^{2+}/Acid - Xiang *et al.* (2000)[a]	2	92	10	83	10	55	10	16	10
Simultaneous sludge digestion and metal leaching (with S^0), SSDML - Tyagi *et al.* (1997)[b]	2	75	10	86	10	6	10	6	10
BOOM (SDU, 1991)		92.3		87.6		83		55.8	

[a] Anaerobically digested sludge; [b] Aerobically digested sludge; [c] Negligible; [d] Not mentioned.

Just lowering the pH value of the sludge to 1 is not enough to solubilize Cu under the Dutch standard. The only situation where Cu extraction achieves the required value is when HCl is added in combination with previous aeration of the sludge. Copper might be predominantly incorporated in the organic fraction of the sludge, which makes its solubilization difficult. Besides this predominant form, in anaerobic digestion Cu can be present as Cu_2S (solubility product: K_{sp}= 2.5 x 10^{-48}), which is an insoluble precipitate. This form can be oxidized by three different reactions, solubilizing the Cu (Madigan *et al.*, 2003):

$$Cu_2S + \tfrac{1}{2}O_2 + 2H^+ \xrightarrow{\qquad} CuS + Cu^{2+} + H_2O \qquad (4)$$

$$CuS + 2O_2 \xrightarrow{\qquad} Cu^{2+} + SO_4^{2-} \qquad (5)$$

$$CuS + 8Fe^{3+} + 4H_2O \xrightarrow{T.\ ferrooxidans} Cu^{2+} + 8Fe^{2+} + SO_4^{2-} + 8H^+ \qquad (6)$$

From the reactions 4 and 5 it is clear the interference of aeration in the solubilization of Cu. Reaction 6 shows the effect of the *T. ferrooxidans* in Cu extraction. Speciation calculations with Ecosat (Keizer and Van Riemsdijk, 2002) show that when the pH value of the sludge is decreased to 1 with HCl, soluble Cu-chloro compounds are formed, e.g., $CuCl^+$ (stability constant K_o= 2.5). On the other hand, when H_2SO_4 is added to the sludge to achieve the pH value of 1, the very soluble form $CuSO_4$ (K_o= 250) can be generated, but in a lower proportion than the Cu-chloro compounds formed when HCl is added. At a low pH value, however, HSO_4^- (K_o= 95) might be formed and, therefore, SO_4^{2-} is not available to the formation of $CuSO_4$.

The extraction percentages of Zn achieved by chemical leaching with H_2SO_4, HCl, and bioleaching with S^0 (from Villar and Garcia Jr., 2002) are below the value required by the Dutch standard. These situations correspond to those with pH value of 1, leading to the conclusion that Zn solubilization is more related to the pH than to the conditions of which the pH is achieved, no matter whether it is by biological or chemical ways.

Although chemical leaching with HCl provides the best value for Cr solubilization, this extraction value is still higher than the required one. It was demonstrated that Cr requires a prolonged time at low pH value to be solubilized by bioleaching. Due to the reducing conditions prevailing in anaerobic sludges, it is likely that Cr predominates as the trivalent hydroxide at neutral pH (Hayes *et al.*, 1980; Olver *et al.*, 1975). This is consistent with speciation calculations with Ecosat (Keizer and Van Riemsdijk, 2002). In this way, the low solubility product of $Cr(OH)_3$ (K_{sp}= 1 x

10^{-30}) might explain the small Cr release. The low mobility observed for Cr also suggests that the adsorption strength of this metal to distinct fractions present in the sludge is not easily overcome by the acid and oxidative environment of the bioleaching (Villar and Garcia Jr., 2002).

Lead extraction satisfies the Dutch standard only when HCl is applied to the sludge, independently on the aeration process. The elevated concentration of sulfate is a limitation factor to Pb solubilization. The solubility product of $PbSO_4$ is very low (K_{sp}= 1.6 x 10^{-8}) and it explains that if the sulfate concentration is increased, then the concentration of Pb^{2+} will decrease accordingly (Mercier *et al.*, 1996). If the concentration of sulfate is reduced, however, it might increase the solubility of Pb, especially if sulfate ions are replaced by chloride ions, which form soluble Pb-chloro complexes (Mercier *et al.*, 1996), e.g., $PbCl_2$ (K_o= 126).

Differences in metals solubilization obtained by the several methods are due to the different sources of sludge, metals content and speciation, total solids concentration, and experimental conditions. Despite these factors, it is possible to conclude which are the best solutions to mobilize Cr, Cu, Pb and Zn, and their bottlenecks. Even when a more tolerable standard than the Dutch one is used as reference, one should have in mind that only satisfying the limits required is not a safe condition for metals disposal in the environment. Heavy metals removal should be always recommended since the accumulation of the metal load to a disposal site constitutes a serious threat to the environment. In addition, the presence of toxic heavy metals in the sludge is problematic, concerning its further use, leading to low quality products (Naoum *et al.*, 2001).

Bioleaching is not able to solubilize Pb and, in lower proportion Cr. But there are advantages to apply this technique in heavy metals removal from sewage sludge. A combined treatment consisting of bioleaching as a previous acidification step, and chemical leaching with HCl as a second acidification step should be investigated. In this way, the costs of the acid addition with the solely chemical leaching would be reduced. Especially if elemental sulfur is chosen as substrate, since Villar and Garcia Jr. (2002) showed attractive results. In addition, the drawback due to the costs of the elemental sulfur can be surpassed by the use of biological elemental sulfur produced in micro-aerated reactors. In these reactors, sulfide, the most reduced sulfur compound (produced in anaerobic reactors), is partially oxidized into elemental sulfur (Janssen *et al.*, 1998). In fact, elemental sulfur producing reactors is a mature technology and already marketed in northern Europe (Janssen *et al.*, 2000).

CONCLUSIONS

The present research demonstrated that the bioleaching process can be a feasible alternative to promote Zn and Cu solubilizations at moderate pH values, especially when ferrous iron is added as substrate. Under this condition, the maximum extraction yields obtained for Zn was 80.8 % with pH value of 2.7, after 11 days and for Cu it was 65.5 % with pH value of 2.5, after 13 days. Chromium solubilization improved when the pH was below 2.5 and the residence time increased over 11 days. Lead was not released by bioleaching. From these results it is possible to conclude that bioleaching optimization requires especial attention with the substrate addition for the adequate growth of the bacteria, temperature, and aeration conditions. Yet the results showed that the indigenous microflora of the sludge might be enough to promote the heavy metals solubilization. Therefore, bioleaching efficiency depends on how to find the best conditions for these bacteria to act.

Chapter 5

Heavy metals removal from the leachate

Abstract

After solubilization of heavy metals by chemical leaching with previous aeration, the next step was the separation of the sludge solids from the metal-rich acidic liquid (leachate) by centrifugation and filtration. Afterwards, the filtered leachate was submitted to the application of hydroxide precipitation with NaOH and sulfide precipitation with Na_2S, separately and in combination, followed by filtration. The results showed that when iron and aluminium are present in the leachate, adsorption and/or coprecipitation of Cr, Pb and Zn with $Fe(OH)_3$ and $Al(OH)_3$ might occur at increasing pH conditions. The combination of hydroxide and sulfide precipitation was able to promote an effective removal of heavy metals from leachate. Applying NaOH at a pH value of 4-5 as a first precipitation step, followed by filtration and further addition of Na_2S to the filtered liquid at pH values of 7-8 as a second precipitation step, decreased considerably the dosage of the second precipitant, compared to when it was solely applied. The best removal efficiencies obtained were: Pb: ~100%, Cr: 99.9%, Cu: 99.7%, and Zn: 99.9%.

Marchioretto M.M., Bruning H. and Rulkens W.H. Presented at the XXVIII Interamerican Congress of Sanitary and Environmental Engineering. Cancún, Mexico. October, 2002.

INTRODUCTION

General

Heavy metals concentrations in sewage sludges vary from one site to another, depending on the contribution of domestic and industrial input into the sewerage system. Heavy metals are usually so tightly bound or incorporated in organic solids and minerals (see Chapter 2) that a mere physical separation of the major fractions of these metals would be difficult. Prior to the separation process, a treatment focused on the dissolving heavy metals is necessary.

To solubilize heavy metals from the sludge solids into the sludge liquid, an acidification process must be applied (see Chapters 3 and 4). The liquid containing the solubilized metals is then separated from the suspended solids fraction by a physical separation step, e.g., centrifugation. The soluble metallic ions can be ideally converted to insoluble metallic forms by chemical precipitation. The precipitate formed is subsequently removed from the liquid by a physical separation process, e.g. sedimentation, flotation, or membrane filtration. Some bottlenecks of the heavy metals precipitation process may include (Freeman and Harris, 1995):

- Reagent addition must be carefully controlled to prevent unacceptable concentrations in treatment effluent;
- Efficiency of the system relies on adequate solids separation techniques;
- Process generates heavy metals containing sludge, which requires proper disposal;
- Process can be costly depending on reagents used, required system controls, and required operator involvement in system operation;
- In some cases, chemical precipitation has to be performed in conjunction with coagulation/flocculation processes to facilitate the agglomeration of suspended and colloidal material (U.S.EPA, 1998).

Relevant aspects

Precipitation and solubility

The heavy metals precipitation step involves the addition of chemical reagents to adjust the pH of the liquid. The desired pH is one in which the metals exhibit low (or minimum) solubilities in water and therefore precipitate. This ideal pH is dependent on the specific metal-reagent combination (Freeman and Harris, 1995).

Common reagents used include alkalis, such as lime, magnesia, NaOH, $NaHCO_3$, Na_2CO_3, $(NH_4)_2CO_3$, and NH_4OH. Heavy metals like Cr, Cu, Pb and Zn do not precipitate at a pH value below 7, permitting some possibility for separation from ferric iron (Lee *et al.*, 2002; Martínez and McBride, 1998; Brooks, 1991) and aluminium (Lee *et al.*, 2002; Martínez and McBride, 2000), which precipitate at a pH value below 6.5.

The association of heavy metal ions with a ferric or aluminium hydroxide precipitate is controlled by adsorption or coprecipitation. Adsorption implies the two-dimensional accumulation of a metal ion at the interface between a preformed solid and the aqueous phase. Coprecipitation implies the simultaneous removal of a metal ion during the formation of the primary metal precipitates (Lee *et al.*, 2002). Due to the potential for adsorption, coprecipitation and the ion exchange characteristics of the colloidal hydroxide precipitates, even clear differences in pH for hydroxide formation are no guarantee of avoiding mixed precipitates when metal mixtures are in solution (Brooks, 1991).

Sulfides such as Na_2S, H_2S, NaHS, or FeS can be used to precipitate metals and have been applied frequently for metal removal from waste effluents to achieve emission standard limitations (Brooks, 1991; Peters and Ku, 1988). The lower solubility of metal sulfides in the acid region below pH value of 7 permits reduction of metal solubility to values that are orders of magnitude lower than are attainable by hydroxide precipitation (Brooks, 1991). Other advantages of sulfide over hydroxide precipitation are shown later.

To illustrate the solubilities of heavy metals (Al, Cr, Cu, Fe, Pb and Zn) hydroxides and sulfides as functions of the pH, a diagram is shown in Figure 5.1. The curves of metals hydroxides and sulfides were calculated on the basis of the stability constants of the metals complexes and solubility products of minerals involved, considering ionic strength value below 0.1 M (Stumm and Morgan, 1996; Smith and Martell, 1981). In this way, according to Moore (1976), the effect of the ionic strength on the solubility could be considered negligible in the calculations of the equilibrium relationships of all the species. As convenient here, the diagram was determined based on the heavy metals of interest, present in the liquid under investigation.

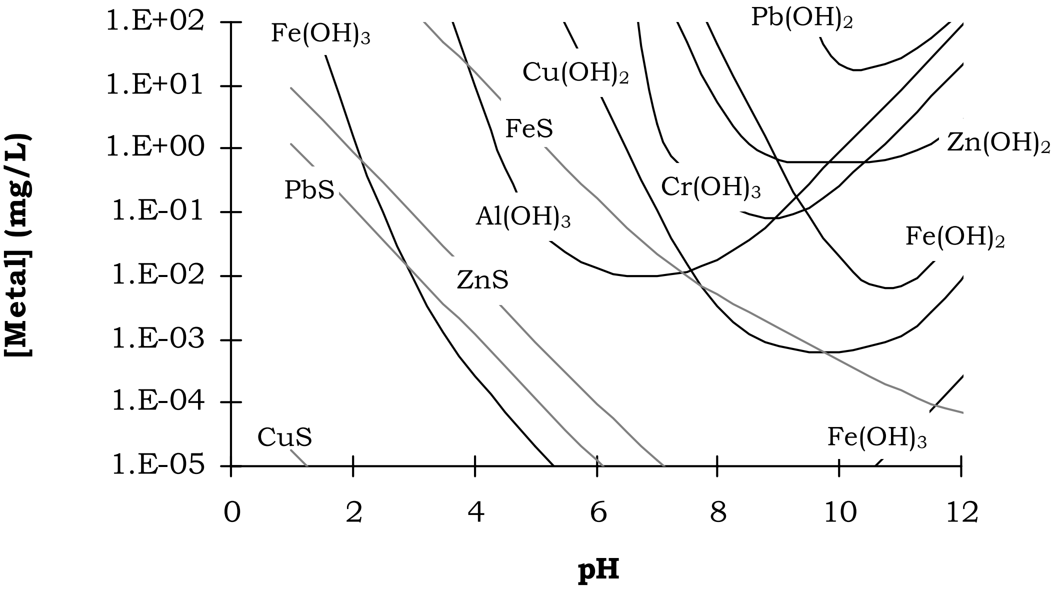

Figure 5.1 - Solubilities of metal hydroxides and metal sulfides as functions of pH (calculated for the present research)

Advantages and limitations of sulfide and hydroxide precipitation

The most relevant advantages and limitations of hydroxide and sulfide processes are included in Table 5.1 (Moore, 1998; Freeman and Harris, 1995; Peters and Ku, 1984):

Table 5.1 - Main advantages and limitations of precipitation methods

Hydroxide precipitation	Sulfide precipitation
Advantages	Advantages
▪ Low capital and operating costs; ▪ Fewer safety-related problems in the treatment than when sulfide is used.	▪ Lower pH is required for efficient removal compared to hydroxide; ▪ Smaller sludge volume than hydroxide; ▪ Sludge exhibits better thickening and dewatering characteristics than hydroxide sludges; ▪ Removes chromates and dichromates without previous reduction of chromium to its trivalent state; ▪ The influence of complexing agents (when present) in the precipitation of metals is less strong than in hydroxide precipitation; ▪ More complete heavy metals removal than hydroxide.
Limitations	Limitations
▪ Tendency of resolubilization if the solution pH is changed; ▪ The minimum solubilities for different metals occur at different pH values; ▪ Greater sludge volume than sulfide; ▪ Sludge may be difficult to dewater; ▪ Hexavalent chromium is not precipitated; ▪ Complexing agents (EDTA, NTA, soluble organic matter, tartrate, etc.) may have an adverse effect on metal precipitation; ▪ Will not achieve removal efficiency as high as with sulfide.	▪ Higher capital and operating costs than hydroxide; ▪ Potential for toxic hydrogen sulfide gas and residual sulfide in treated effluent.

Nowadays, a combination of hydroxide and sulfide precipitation for optimal metals removal is being considered (U.S.EPA, 1998). A common configuration is a two-stage process in which hydroxide precipitation is pursued by sulfide precipitation with each stage followed by a separate solids removal step. This will produce the high quality effluent of the sulfide precipitation process. Moreover, it will reduce the consumption of sulfide reagents, which are more expensive than hydroxide reagents (e.g., lime and caustic), and will result in a smaller amount of sludge compared to the hydroxide precipitation process alone (U.S.EPA, 1998).

Residues of the precipitation process

Chemical precipitation can remove heavy metals from the contaminated liquid. But a factor that negatively affects the ranking of the technology is that metal containing sludges are produced during the process. The disposal of metal hydroxides and metal sulfides sludges will have to attend to regulations. In some cases, the sludge may be dewatered to the maximum extent possible, drummed and disposed of in a secure landfill (Freeman and Harris, 1995). A process of metals recovery from the sludge in order to reuse them as metal ore should be also evaluated. The water phase including high concentration of sodium chloride, due to the use of HCl for metals solubilization, and NaOH combined with Na_2S for metals precipitation, should be correctly discharged or reused in a proper way. In addition, dissolved organics are also likely to be present in this liquid, as a result of the acidification process.

Despite its bottleneck, chemical precipitation is still one of the most effective alternatives to remove heavy metals from contaminated liquids. In case of sewage sludges containing high amount of heavy metals, it is a promising technique to separate mobilized heavy metals. Chemical precipitation is able to remove the heavy metals from a huge fraction, e.g., sewage sludge, producing a smaller amount of a metal rich sludge.

Normally, recovery and reuse of metals separated from metal rich sludges will not be economical, unless the commercial value of the metals is high enough to justify the costs of separating these metals from the sludge and from the other metals in the sludge. In general, for sewage sludge or wastewater contaminated with multiple metals, which have been previously mobilized, a series of selective precipitation treatment steps using different pH values and/or different treatment chemicals is being well considered

(U.S.EPA, 1998). This alternative, however, might be only applicable if the purpose is the recovery and sale of the high purity metal precipitates, as demonstrated by Tabak and Govind (2002) for acid mine water. Each precipitation step needs to be followed by a solids separation step in order to prevent the resolubilization of metal precipitates during the subsequent treatment step (U.S.EPA, 1998).

Nowadays, an interesting alternative to the use of chemically produced sulfide compounds is the application of the biogenic hydrogen sulfide formed from sulfate reduction by hydrogen consuming sulfate-reducing bacteria (Gilbert *et al.*, 2002; Tabak and Govind, 2002). Biogenic sulfide precipitation has been investigated for treatment of acid mine drainage and industrial wastewaters (Tabak and Govind, 2002; Foucher *et al.*, 2001). This option is also very promising in the treatment of sewage sludges aiming at heavy metals removal. Especially when metals sulfate are present in the leachate, which is a result, for instance, of the sludge acidification with sulfuric acid produced by bioleaching process. This treatment possibility would prevent the generation of the liquid containing high concentration of sodium chloride (see detailed discussion in the next chapter).

Particle size of precipitates

The particle size of precipitates is an important factor in the present work, as it will be demonstrated later. According to Veeken *et al.* (2003), the particle size of precipitates depends on the competition between nucleation and crystal growth. When the nucleation rate dominates the crystal growth rate, colloidal particles (< 0.05 μm) will result. If the initial concentration of the reactant is high, consequently increasing the concentration of the precipitate, which has a low solubility, the resulting high supersaturation leads to high rates of a primary nucleation (Mersmann, 1999). Primary nucleation occurs with formation of clusters of molecules at the sub-micrometer level. If a coarse product is desired, the supersaturation must be kept low by using low concentration of the reactants (perhaps by dilution), appropriate micromixing in the entire precipitator, and seeding by high recycling rates of slurry to decrease local supersaturation peaks by crystal growth (Mersmann, 1999).

When a mixture of heavy metals is present in the liquid to be treated, it is likely that each metal precipitate particle size evolutes differently from the others. Therefore, in practice, it might be difficult to find an optimal crystal growth rate for all the metals studied. This point is discussed later.

Scope of the study

This chapter deals with the precipitation of heavy metals from the leachate, which is separated from the sludge particles by centrifugation and filtration, after the solubilization of the heavy metals. The objective is to gain insight in the feasibility of the process, regarding the type of chemicals to be used, and the required dosages. On the basis of literature, hydroxide precipitation with NaOH and sulfide precipitation with Na_2S are investigated here. Both precipitating agents are applied solely and in combination, followed by a filtration step. The chemicals are dosed according to pH values varying from 4 to 11 and the occurrence of adsorption and coprecipitation is considered.

EXPERIMENTAL

Anaerobically digested sludge

The origin and main characteristics of the sludge applied in this research as well as the chemical and physical distribution of heavy metals in the sludge are presented in detail in Chapter 2.

Analysis

The procedures and equipments for heavy metals and pH analysis are described in Chapter 2.

Heavy metals solubilization

To achieve the best conditions for heavy metals solubilization (see the complete study in Chapter 3), samples of 1 L of the sludge were subjected to previous aeration, followed by acidification, centrifugation and filtration. Both aeration and acidification were applied during 24 hours, with continuous shaking (150 rpm), at 20 °C. During aeration the air flow rate was 1.5 L/h. Acidification with 13.9 g/L (380 mM/L) of hydrochloric acid was applied to decrease the initial pH value of the original sludge (around 8) to 1.

The acidified samples were centrifuged at 4000 rpm during 30 minutes. The acidic supernatant containing the dissolved heavy metals (leachate) was filtered by paper filter S&S black ribbon (12-25 µm) to remove residual small particles and the resulting liquid was used in the heavy metals precipitation experiments. The heavy metals concentration in this filtered leachate and in the original sludge is shown in Table 5.2. In this table, the concentrations of aluminium and iron in the sludge and in the leachate are also shown in order to facilitate further discussion.

Table 5.2 - Heavy metals content of the original sludge and the leachate applied in the precipitation experiments

Fraction	Heavy metals content in mg/L [% OS][a]					
	Al	Cr	Cu	Fe	Pb	Zn
Original Sludge (OS) (pH= 8)	680	9.2	19.8	500	4.9	35
Leachate (pH= 1)	578 [85]	7.2 [78.3]	18.4 [92.9]	450 [90]	4.8 [99.7]	34 [97]

[a] Percentage of heavy metals in the leachate related to the total heavy metals content in the sludge.

Precipitation experiments

The precipitation experiments were carried out in three phases. In the first phase hydroxide precipitation was studied with NaOH application in such doses to increase the original pH value of the liquid from 1 till 5, 7, 9 and 11. In the second phase, sulfide precipitation with Na_2S was applied at the same pH values used in the first phase. In the third phase of the experiments a combination of hydroxide and sulfide precipitation was investigated. Initially, NaOH was added to the liquid till the pH values of 4 and 5 were both achieved. These pH values were determined according to the results of the previous phases. After NaOH addition the liquids were filtered and submitted to Na_2S addition in such dosage to reach the pH values of 5, 5.5, 6, 7, and 8. The chemical dosages are shown in Table 5.3 and expressed in gram and millimol per litre of leachate.

After each experiment the liquid was filtered by paper filter S&S black ribbon (12-25 µm) and two samples were collected and analyzed for their heavy metals (Cr, Cu, Pb, and Zn) content. All the experiments were performed in duplicates, with continuous shaking (100 rpm) during 60 minutes. Figures 5.2 to 5.4 show the schemes of the precipitation experiments and the previous heavy metals solubilization procedure.

Table 5.3 - Chemical dosages applied in the experiments

Type of	NaOH			Na_2S		
experiment	pH	g/L	mM/L	pH	g/L	mM/L
Single precipitation	5	10.7	270	5	11.6	150
	7	11.4	290	7	18.6	240
	9	13.2	330	9	26.3	340
	11	16.4	410	11	35.5	460
Combined precipitation I	4	10.3	260	5	0.042	0.54
				5.5	0.046	0.59
				6	0.049	0.63
				7	0.063	0.81
				8	0.095	1.2
Combined precipitation II	5	10.7	270	5.5	0.003	0.038
				6	0.004	0.051
				7	0.014	0.18
				8	0.056	0.72

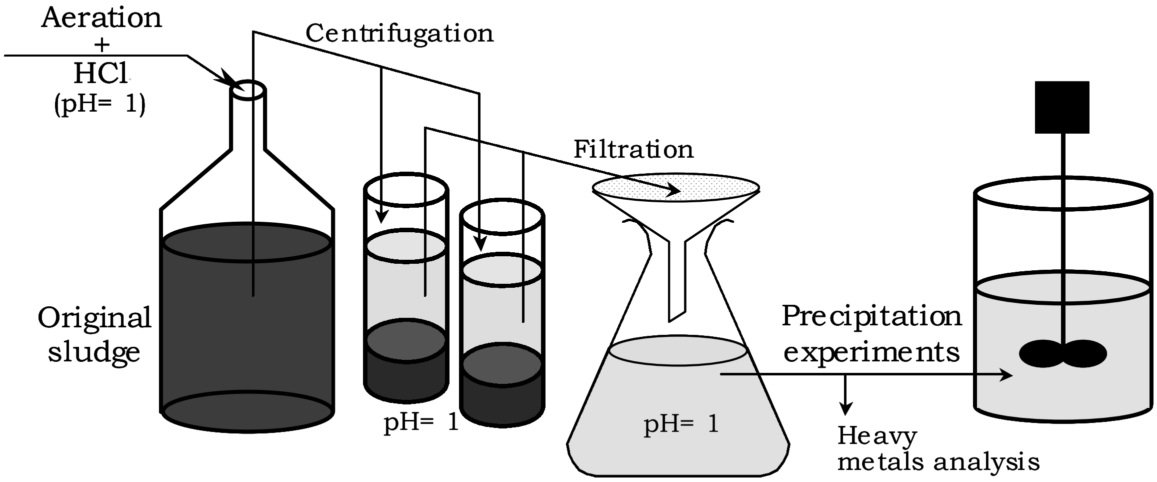

Figure 5.2 - Scheme of the heavy metals solubilization experiments

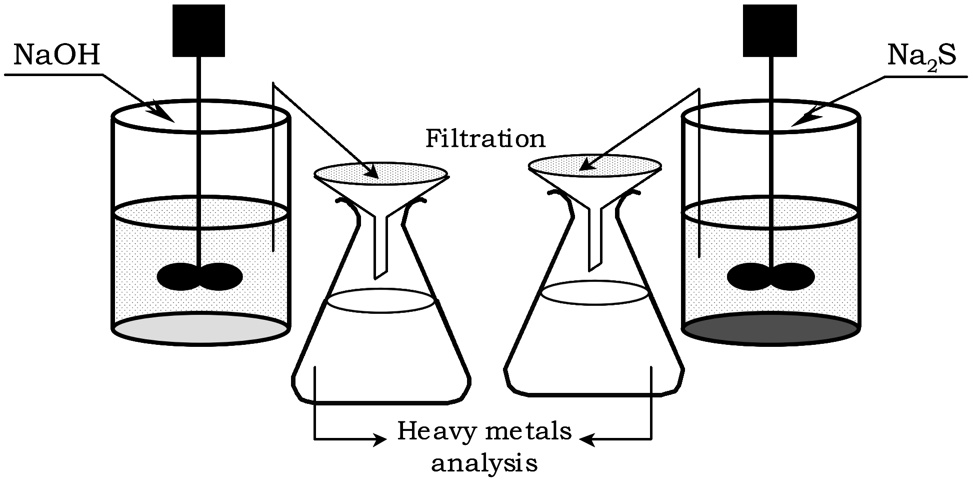

Figure 5.3 - Scheme of the single precipitation experiments

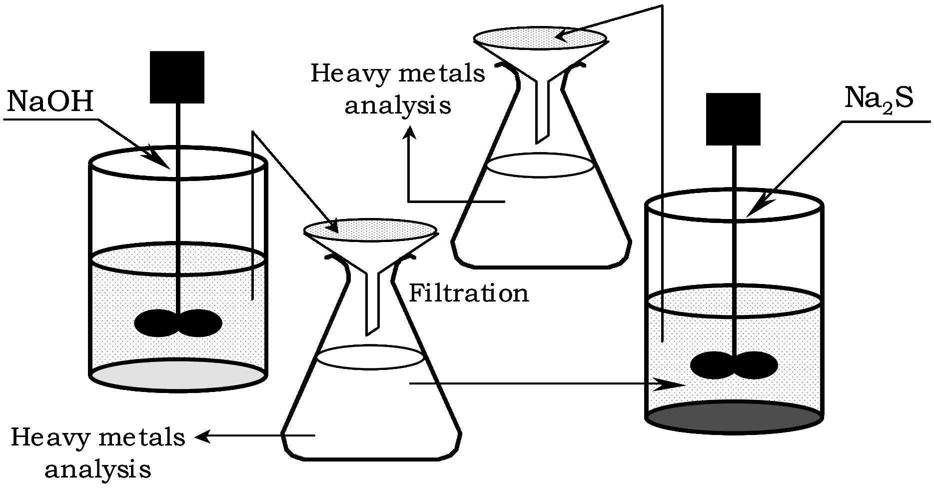

Figure 5.4 - Scheme of the combined precipitation experiments

RESULTS AND DISCUSSIONS

Single precipitation

Figure 5.5 shows the percentage of the remaining heavy metals concentration in the filtered liquids resulted from the precipitation experiments, at different pH values. The duplicate values differed from the mean by 4.5 % at most. When hydroxide precipitation was applied, Cu removal was very low, independently on the range of the investigated pH. At a pH value of 5, Zn removal was similar to Cu removal, but at higher pH values it improved. In general, sulfide precipitation was more effective in removing all the metals together even at pH value of 5.

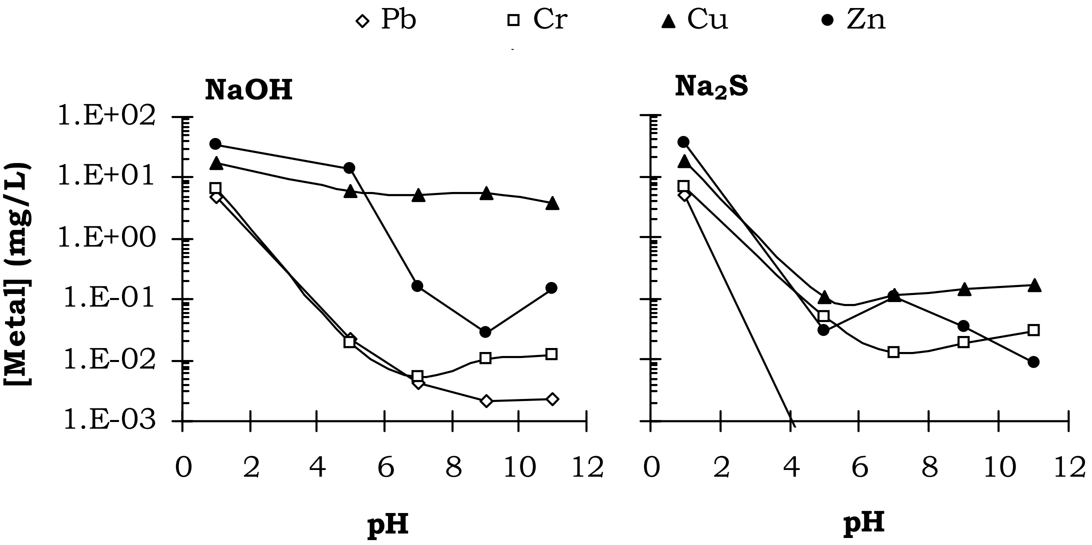

Figure 5.5 - Heavy metals content in the remaining liquid after hydroxide and sulfide precipitation followed by filtration (at pH= 1: initial metals concentration in the leachate)

Before explaining the results exposed in Figure 5.5, it is convenient to observe Figure 5.6, which was plotted on basis of Figure 5.1. The diagrams of metal sulfides and hydroxides are shown separately and the initial metals concentration in the leachate is indicated in the curve of the correspondent metal precipitate. The initial concentration of Pb is below the curve of $Pb(OH)_2$ and it appears only in the PbS curve. The initial Cu concentration is above the CuS curve and it is not shown either.

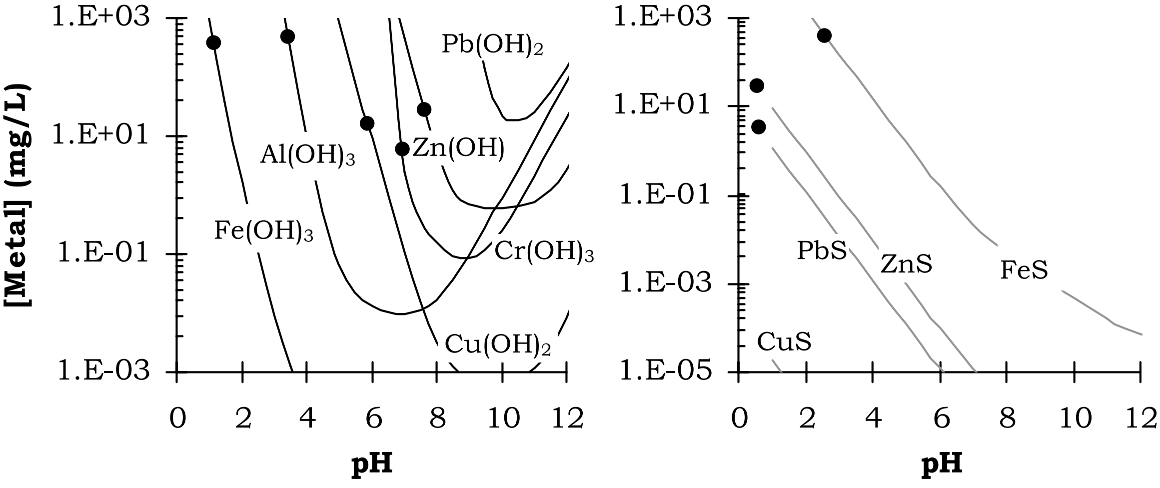

Figure 5.6 - Solubilities of metal hydroxides and metal sulfides as functions of pH
(● Initial metals concentration)

Hydroxide precipitation

From Figure 5.6, it is clear that Cu, Cr, Zn, and Pb were not able to form hydroxide precipitates at pH values below 6 (Cu), 7.2 (Cr), and 7.5 (Zn). Figure 5.5 shows, however, that more than 99 % of Cr and Pb were already removed at pH value of 5. When the pH value was higher than 5, Zn started to be removed and when the pH achieved the value of 7.5, more than 99 % of this metal was already removed. At the pH value of 9 Zn achieved its best removal efficiency and this was close to the value obtained in Figure 5.6.

As exposed in Table 5.2 and Figure 5.6, Fe and Al are abundant in the sludge and in the acidified liquid, comparing to the other metals. Figure 5.6 shows that Fe(III) and Al can start forming hydroxide precipitates at pH values of 1.3 (Fe) and 3.5 (Al). These curves suggest that adsorption and/or coprecipitation of Cr, Pb and Zn with $Fe(OH)_3$ and $Al(OH)_3$ were taking place as the dominant factors in the removal of these metals. In this way, the removals of Cr, Pb and Zn depend on the precipitation of Fe and Al, which act as sorbents (Lee *et al.*, 2002) and coprecipitants.

From Figure 5.6, it is observed that $Cu(OH)_2$ has the lowest solubility among Cu, Cr, Pb, and Zn hydroxides. This contradicts the extremely low removal achieved for Cu. On the other hand, when the precipitate has low solubility products, supersaturation is favored and consequently the nucleation rate increases, as the particle sizes decrease (Veeken *et al.*, 2003; Mersmann, 1999). In fact, after filtration, the liquid was a bit turbid and this is an indication of the high nucleation rate. This might be a strong reason for the low retention of Cu hydroxide (co)precipitate in the paper filter.

The low Cu removal by coprecipitation with Al and Fe obtained in the present experiments are not in accordance with Lee *et al.* (2002) and Martínez and McBride (2000) who found more promising results for waters contaminated with acid mine drainage and a synthetic water, respectively. Such differences might be due to the presence of soluble organic matter (SOM) in the leachate (which was probably not present in the waters used by those authors). The affinity of Cu to organic matter is discussed in Chapter 2. According to Fletcher and Beckett (1987a;b), at a pH value over 7, there is less competition between Cu and other protons for sites on the SOM and thus a high concentration of Cu is likely to be bound to the SOM. These Cu-SOM complexes formed were probably at the colloidal range, which was probably smaller than the filter pore size (12-25 μm) that was used.

Sulfide precipitation

When Na_2S was applied at a pH value of 5, all the metals were removed at a level of 99 %, (see Figure 5.5). Figure 5.6 confirms that at pH value below 5, ZnS, PbS and CuS precipitates already started to form. But still, adsorption and coprecipitation with Fe and Al might also occur also when Na_2S is applied. Lead showed the highest removal efficiency of all the metals. Figure 5.5 suggests that, at a pH value below 5, PbS was already almost totally removed. Zinc sulfide removal was less efficient at a pH value of 7 than at a pH value of 5. Perhaps the threshold for increasing the solubility of ZnS is at this pH range. However, this explanation cannot be confirmed by Figure 5.6. The residual concentrations of Zn (around 0.05 mg/L) and Cu (around 0.1 mg/L) at pH value of 8 were identical to those obtained by Bhattacharyya *et al.* (1979).

According to Figure 5.6, CuS should present the highest removal efficiency of all the other metal sulfides. But this is not observed in Figure 5.5. Despite the relatively high range of removal, there might be some factors affecting its increase. A possible explanation is the fact that CuS has a very low solubility comparing with ZnS and PbS. As explained before, the low solubility product favors the decrease in the particle sizes (Veeken *et al.*, 2003; Mersmann, 1999). This was confirmed by the experiments, because the filtrated liquid was somewhat dark turbid. In addition, in the case of sulfide precipitation, it is not possible to affirm that the formation of Cu-SOM complexes would occur when the pH value was up to 7. Moreover, the slight decrease in CuS removal at a pH value over 6, as shown in Figure 5.5, could be due to the change in the solubility of CuS at this pH. However, this explanation cannot be confirmed by Figure 5.6.

Chromium (III) sulfide is not likely to occur here, because in water this is a very unstable form (Weast, 1979). When Na_2S was applied, it seems that Cr was still being removed by adsorption and coprecipitation with $Fe(OH)_3$ and $Al(OH)_3$ that might be present in the liquid as long as the pH value increases. Comparing both graphs of NaOH and Na_2S in Figure 5.5, Cr removal was better when NaOH was applied, since $Fe(OH)_3$ and $Al(OH)_3$ might be formed in larger extend than when Na_2S is used.

Combined precipitation

Figure 5.7 shows the percentage of the remaining heavy metals in the filtered liquids resulted from a precipitation process consisting of previous application of NaOH to achieve pH values of 4 and 5, followed by Na_2S dosing. After each precipitation step, the liquids were filtered. The initial pH values of 4 and 5 were chosen because according to the Figure 5.5, sulfide precipitation was already efficient at pH value of 5. The duplicate values differed from the mean by 3.5 % at most.

With initial pH value of 4, obtained after precipitation with NaOH, metals were removed at lower pH with Na_2S than when the initial pH value was 5. At the highest initial pH value, the removal of metals by the subsequent sulfide precipitation was more difficult, especially for Cu and Zn.

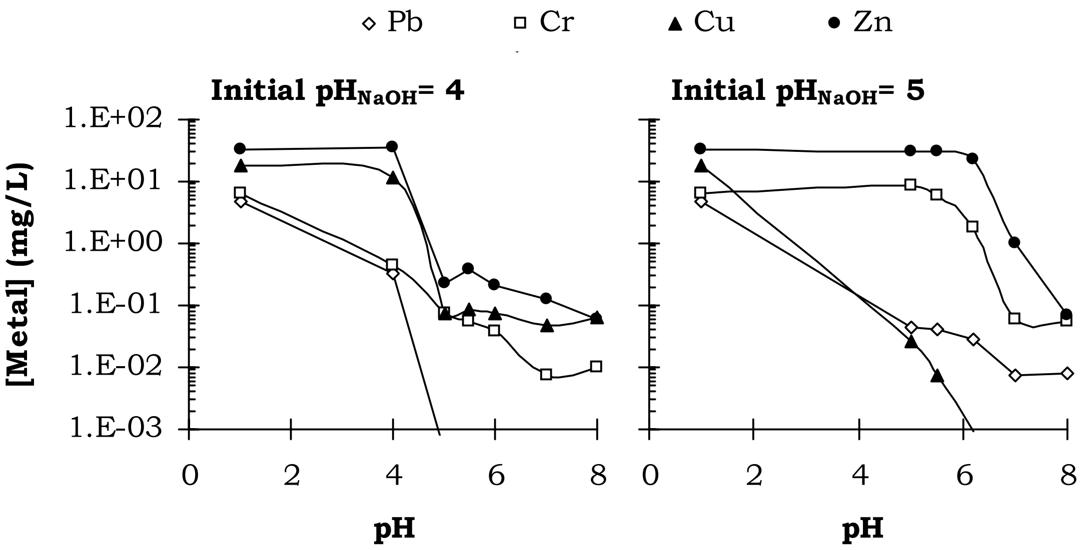

Figure 5.7 - Heavy metals content in the remaining liquid after combined hydroxide and sulfide precipitation followed by filtration (at pH= 1: initial metals concentration in the leachate)

Before explaining the results shown in Figure 5.7, it is important to understand what happened with the heavy metals when NaOH was previously applied. From the results of single precipitation (see Figure 5.6), all the metals, with exception of Cu, were probably adsorbed and/or coprecipitated with $Fe(OH)_3$ and $Al(OH)_3$ at pH value over 5 (Zn) or below 5 (Cr and Pb). Figure 5.7 shows that at pH value of 5 Cr and Pb were better removed than at pH value of 4. This might be due to the fact that at the higher pH value, $Fe(OH)_3$ and $Al(OH)_3$ were better formed, as presented in Figure 5.6. As observed before, Cr achieved its best removal efficiency at a pH value of 7.

From Figure 5.7, when more Na_2S was applied, as in the case when the initial pH value was 4 (Na_2S and NaOH doses are shown in Table 5.3), the formation of Zn and Cu sulfide precipitates occurred at a lower pH value than when less Na_2S was applied (when the initial pH value was 5).

Comparing Figure 5.5 and Figure 5.7 with Na_2S addition, it is observed that a high removal of ZnS can be obtained at a high pH value, since in all the three graphs the curve of ZnS is still going down at the last pH value measured.

When Na_2S was solely applied, the highest removal of Cu occurred at a pH value of 5, whereas in the combined precipitation (with both initial pH values of 4 and 5) the same removal efficiency was achieved only at a pH value of 7. These differences are due to the low initial Cu removal obtained when NaOH was applied. As mentioned before, although Cu achieved a high removal efficiency, in theory (see Figure 5.6) this value should be even higher. The formation of Cu-SOM complexes and the low solubility of $Cu(OH)_2$ and CuS are the probable reasons for this fact.

Furthermore, from Figure 5.7, when the pH value is raised to 4 or 5 by NaOH, it should be increased another 3 pH-units by Na_2S to obtain the highest metals removal. The option with less Na_2S dosage seems to be advantageous since this chemical is at least 4 times more expensive than NaOH (per mol) and more toxic. Comparing the chemical doses required for single sulfide precipitation and the amount of Na_2S needed for the combined precipitation, in the second case much less precipitant is needed to achieve the same metals removal. This can be observed in Table 5.4, where the highest removal efficiencies obtained are displayed.

Table 5.4 - Highest heavy metal removal efficiencies achieved at different process conditions

Situation	pH		Dosage (mM/L)		Heavy metal			
	NaOH	Na_2S	NaOH	Na_2S	Cu	Cr	Pb	Zn
Na_2S	-	5	-	150				
Removal (%)					99.4	99.2	100	99.9
[Metal] (mg/L)[a]					0.1	0.05	0	0.03
NaOH + Na_2S	4	7	260	0.81				
Removal (%)					99.7	99.9	100	99.7
[Metal] (mg/L)[a]					0.05	0.007	0	0.1
NaOH + Na_2S	5	8	270	0.72				
Removal (%)					99.7	99.9	100	99.9
[Metal] (mg/L)[a]					0	0.06	0.008	0.07

[a] Heavy metal concentration remaining in the leachate after precipitation and filtration.

From Table 5.4 it is clear the advantage of the combined hydroxide and sulfide precipitation over the single sulfide precipitation, in terms of Na_2S dosage and removals of Cu and Cr. In accordance with Charerntanyarak (1999) and Bhattacharyya *et al.* (1980), the results show that a combination of hydroxide and sulfide precipitation is an effective alternative to remove heavy metals from sewage sludges leachate or wastewaters.

For the main goal of this research it is appropriate to find the lowest cost solution, where the heavy metals are removed to acceptable concentrations, enabling the discharge of the liquid. As mentioned before, proper destination for the metal concentrated sludge must be attended and the possibilities of heavy metals recovery from this sludge should be also evaluated. In that respect, the presence of aluminium and iron in the sludge leachate is a relevant fact.

CONCLUSIONS

With the combination of hydroxide and sulfide precipitation followed by a separation process, highly effective separation of heavy metals from the metal-rich acidic liquid (leachate) is obtained. The leachate is resulted from the separation with the sludge solids by centrifugation and filtration. Before the separation step, the sludge is previously aerated and acidified in order to promote heavy metals solubilization.

The dissolved heavy metals present in the leachate are precipitated. The combination of NaOH (pH equal to 4 and 5) and Na_2S (pH equal to 7 and 8 respectively) is able to reduce considerably the dosage of the second precipitant, when it is solely applied.

Moreover, when iron and aluminium are present in the leachate, adsorption and/or coprecipitation of Cr, Pb and Zn with $Fe(OH)_3$ and $Al(OH)_3$ might occur at increasing pH conditions.

Chapter 6

General discussion

INTRODUCTION

Despite the numerous studies in the field of heavy metals removal from sewage sludges, soils and sediments over the last three decades, the techniques applied for this purpose still remain in the laboratory and pilot plant scale. In order to get more scientific and practical insights into this topic, a study focusing on the removal of heavy metals from anaerobically digested sewage sludge was performed.

This closing chapter will briefly discuss the relevant aspects found in this research and how they may lead, together with the already available information, to the implementation of techniques for heavy metals removal from sewage sludges. This chapter will discuss the following issues:

Physical-chemical characterization of heavy metals in the sludge:

- Physical distribution of heavy metals in the sludge;
- Chemical speciation of heavy metals using sequential chemical extraction (SCE).

Heavy metals solubilization:

- Chemical leaching of heavy metals;
- Bioleaching of heavy metals.

Heavy metals removal from the leachate:

- Hydroxide and sulfide precipitation.

Technological aspects:

- Conceptual design for a physical-chemical process to remove heavy metals from sewage sludges;
- Conceptual design for a biological-physical-chemical process to remove heavy metals from sewage sludges.

PHYSICAL-CHEMICAL CHARACTERIZATION OF THE SLUDGE

The initial step in the investigation of technologies applied for heavy metals removal from anaerobically digested sludge was a detailed physical-chemical characterization of these metals in the sludge material. First, a physical distribution of the heavy metals in the sludge was carried out, separating the sludge into different particle-sized fractions by a wet-sieving process. The dry matter, organic matter and heavy metals content were determined in each size class and in the total sludge sample. Second, the chemical speciation of the heavy metals in the sludge was investigated by using three different sequential chemical extraction (SCE) schemes.

Physical distribution of heavy metals in the sludge

The results demonstrated that heavy metals were mostly concentrated in the fractions < 0.063 mm, constituting about 70 % of the total sludge mass and contributing 78-85 % of the heavy metals present in the sludge. In all the separated fractions, however, most of the metals concentrations exceeded the Dutch standard (BOOM). This indicates that if land application is considered, then the whole sludge has to be treated, without any previous separation.

A previous physical separation of the sludge can be useful in the case when the heavy metals concentration in a certain fraction exceeds the local limits for land application of the sludge and when the volume of this fraction is quite considerable compared to the total volume of the sludge. Usually, the fraction with the lowest heavy metals content comprehends particles with size larger than 0.5 mm. In the case of the sludge used in this research, this fraction represented only 4-7 % of the total sludge mass, and consisted of more than 80 % of organic matter. Still, depending on the volume of the sludge to be treated, the 4-7 % of the total sludge mass with low heavy metals concentrations could be separated, disposed, and contribute to a decrease in the dimensions of the sludge treatment plant. Moreover, in case that sludge can be separated in a relatively large fraction that is slightly polluted and a small fraction that is strongly polluted, mild process conditions might be sufficient to reduce metals concentration in the larger fraction.

Chemical speciation of heavy metals using SCE (sequential chemical extraction)

Several SCE schemes are applied as a useful assessment tool for evaluating heavy metals mobilization in the sludge matrix and for discussing further results obtained with sludge treatment techniques. Although there are many SCE schemes, it is observed in literature that, in general, researchers apply only one scheme to sludge, soil or sediment materials and use the results as a unique speciation profile. This can be a risky procedure, especially because of the wide variety in the nomenclature proposed for each extraction step of the SCE schemes. For this reason, it is wise to evaluate the SCE schemes according to the type of chemicals used (electrolyte, weak acid, oxidizing agent, chelating agent, reducing agent, strong acid), and not only to the fractions names given by different authors. Moreover, the evaluation of a SCE procedure must be always associated to the experimental conditions applied, with respect to temperature, pH and reaction time.

In the present research, as a tentative to investigate the causes of the differences among the results obtained with three original SCE schemes tested, two modified schemes were developed. In this way, some conditions were slightly altered from original ones. The results of the application of the three original SCE schemes and the two modified SCE schemes showed that different procedures supply different results for the heavy metals speciation. The experiments carried out here demonstrated that although the two modified SCE schemes gave different results from the original schemes, they provided valuable information for interpretation of the differences in the results of the original SCE schemes.

Despite the uncertainty of the SCE method with respect to selectivity (metals bound to more than one phase are solubilized) and specificity (more than one phase is solubilized), it gives useful information concerning the availability of the metals. The SCE results of the investigated sludge revealed that Cr (65 - 67 %) and Cu (65 - 87 %) could be effectively released in an oxidizing environment (85 °C, pH= 2). Zinc (78 - 86 %) could be extracted by a reducing agent (96 °C, pH= 2), whereas Pb (62 - 81 %) could be solubilized at strong acidic conditions at high temperature (150 °C in the microwave oven). Furthermore, a chelating agent (20 °C, pH= 4.5) was able to release considerable amounts of Cr (56 - 57 %), Pb (57 - 78 %) and Zn (50 - 62 %). About 70 % of Cu could be also extracted with application of high pH (12.6) at 20 °C.

HEAVY METALS SOLUBILIZATION

Chemical leaching of heavy metals

In sewage sludges, heavy metals are usually so tightly incorporated or bound to minerals and organic solids, that only at extreme acidic conditions these metals can be sufficiently released to the liquid. Despite the high costs of acid addition in the chemical leaching process, this technique can still be considered as a practical step in the heavy metals removal from sewage sludges. In fact, there is no other feasible alternative, except for bioleaching.

Particularly in the case of anaerobically digested sludges, the highest heavy metals solubilization, especially copper, can be obtained if the oxidation-reduction potential (ORP) of the sludge is increased, before the low pH conditions are applied by acidification. The ORP can be raised either by means of biological or chemical oxidation, which can be achieved through aeration. Chemical oxidation can also occur by the addition of an oxidizing agent like hydrogen peroxide, which in the presence of sludge can lead to Fenton reactions.

This research evaluated the chemical leaching as an applicable technique for the anaerobically digested sewage sludge treatment, aiming at heavy metals removal. For this aim, several acids were tested at different conditions of pH, reaction time and ORP. The effect of acidification was intensively tested for liquid samples of the sludge and briefly tested for dried and crushed samples of the sludge. The influence of the chemical oxidation on the heavy metals solubilization was also investigated by applying aeration or adding hydrogen peroxide.

The results showed that the option including chemical oxidation with either aeration or hydrogen peroxide followed by acidification with hydrochloric acid resulted in the highest extraction yields of almost all heavy metals. Especially copper extraction was highly influenced by oxidation. This might be due to its speciation in the sludge. The SCE schemes suggested that Cu is tightly bound to organic matter and this bond might become less strong when an oxidation step is applied. In anaerobically digested sludges, it is likely that metal sulfides are also present. When the ORP of the sludge is raised, the transition of the very insoluble metal sulfides (e.g., Cu_2S) to the very soluble metal sulfates (e.g., $CuSO_4$) will occur.

The highest extraction efficiencies achieved at different acidification and oxidation situations for all the heavy metals studied are summarized in Table 6.1, which is exposed in the next section.

Bioleaching of heavy metals

Despite the numerous studies on bioleaching over the last two decades, the application of this technique in the solubilization of heavy metals from sewage sludge still prevails under laboratory and pilot plant scale. This study was executed in order to gain more insights into the practical application of bioleaching in the solubilization of heavy metals from anaerobically digested sludge, its advantages and shortcomings. For that, bioleaching using elemental sulfur and ferrous iron as substrates was investigated and compared with chemical leaching with sulfuric acid and aeration.

The results showed that, although the pH values achieved with bioleaching were not as low as in the chemical leaching with sulfuric acid, Zn and Cu extraction efficiencies were not highly different between the two methods. Differently from Cu and Zn, bioleaching was not able to solubilize Pb and only a small amount of Cr was released. The removal efficiencies obtained were lower than those found in the literature (Villar and Garcia Jr., 2002; Xiang *et al.*, 2000) for the same type of sludge and substrate. These differences might be due to the different sources of sludge, metals content and speciation, total solids concentration, pH and experimental conditions.

In the case of the present research, it is possible to conclude that the optimization of the bioleaching process requires especial attention with respect to the substrate addition for the adequate growth of the bacteria, temperature, and aeration conditions. Yet the results showed that the indigenous microflora of the sludge is able to promote the heavy metals solubilization. The bioleaching efficiency depends on how to find the best process conditions for the microbiological activity.

To easily compare the leaching methods applied in this research, the results are summarized in Table 6.1. The table also includes some literature information.

Table 6.1 - Heavy metals extraction efficiency (%) from anaerobically digested sludge using different methods

Method	pH	Cr		Cu		Pb		Zn	
		%	Days	%	Days	%	Days	%	Days
HCl[a]	1	72	1	49	1	96	1	89	1
Aeration + HCl[a]	1.4	81	1+1[c]	94	1+1[c]	100	1+1[c]	100	1+1[c]
H_2O_2 + HCl[a]	1.6	86	1+1[c]	100	1+1[c]	100	1+1[c]	100	1+1[c]
H_2O_2 + H_3PO_4[a]	1.6	92	1+1[c]	87	1+1[c]	100	1+1[c]	100	1+1[c]
Bioleaching with $FeSO_4$ + H_2SO_4[a]	2.5	25.5	15	65.5	13	[d]		81	11
Bioleaching with $FeSO_4$ + H_2SO_4 (Xiang *et al.*, 2000)	2	55	10	92	10	16	10	83	10
Bioleaching with S^o (Villar and Garcia Jr., 2002)	1	56	[e]	85	[e]			97	[e]
Aeration + H_2SO_4[a]	1	65	2	68	4	51.5	2	93.5	5
HNO_3[b]	1	72	1	56	1	87	1	66	1
HNO_3[b]	1	81	5	74	5	90	5	77	5
HCl[b]	1	68	1	79	1	94	1	84	1

[a] Liquid sludge; [b] Dried and crushed sludge; [c] Oxidation time + acidification time; [d] Negligible; [e] Not mentioned.

Table 6.1 highlights that an oxidative step with either aeration or hydrogen peroxide favors the extraction of the heavy metals, especially Cu. When HCl was applied without the oxidation step, the result of Cu extraction for the dried sludge was better than that for the liquid sludge. From a practical and economical point of view, however, the process of drying and crushing the sludge does not seem to be feasible.

Another important aspect shown in Table 6.1 is that, although HNO_3 is an oxidizing agent, it requires, particularly for Cu, prolonged extraction times (about 5 days) to achieve similar extraction efficiencies as obtained with HCl at the same pH value (around 1). Another disadvantage of HNO_3 is its higher costs (per mol) compared to HCl (factor 7). Nevertheless, different from HCl, HNO_3 has the advantage to be biodegradable.

Table 6.1 also shows that, in combination with H_2O_2, both HCl and H_3PO_4 were able to solubilize high percentages of heavy metals. However, the dosage of H_3PO_4 (in mol/L) needed to decrease the pH to a proper value is at least 2 times more than the dosage of HCl. Furthermore, H_3PO_4 costs (per mol) are about 1.5 times more than the costs of HCl.

According to Table 6.1, acidification with H_2SO_4 (chemically or biologically produced) is not the best option to promote the extraction of Pb when this metal is present in high concentrations in the sewage sludge. The formation of the insoluble $PbSO_4$ is the reason for that.

HEAVY METALS REMOVAL FROM THE LEACHATE

Hydroxide and sulfide precipitation

In the present research, the first step in the removal of heavy metals from the sludge was a solubilization by chemical leaching with previous aeration. The next treatment step was a separation of the sludge particles from the metal-rich acidic water phase (leachate) by centrifugation. Thereafter, the leachate was filtered (to remove remaining suspended particles) and sent to a precipitation reactor. Hydroxide precipitation with NaOH and sulfide precipitation with Na_2S were investigated by applying both precipitating agents separately and in combination, followed by filtration.

The results showed that, when iron and aluminium are present in the leachate, adsorption and/or coprecipitation of Cr, Pb and Zn with $Fe(OH)_3$ and $Al(OH)_3$ might occur at low pH conditions, at which the heavy metals hydroxides are still soluble. The results also demonstrated that, with the combination of hydroxide and sulfide precipitation, highly effective removal of heavy metals was obtained. The combination of NaOH and Na_2S was able to reduce considerably the dosage of the second precipitant, compared to when it was solely applied. It is advantageous to reduce the dosage of Na_2S, since this chemical costs (per mol) are at least 4 times more than the costs of NaOH and has a potential to release toxic hydrogen sulfide gas at low pH.

TECHNOLOGICAL ASPECTS

Based on the results obtained, two conceptual designs for heavy metals removal from sewage sludge are presented and discussed. One refers to a physical-chemical treatment (Figure 6.1) and the other to a biological-physical-chemical treatment (Figure 6.2).

Conceptual design for a physical-chemical process to remove heavy metals from anaerobically digested sludges

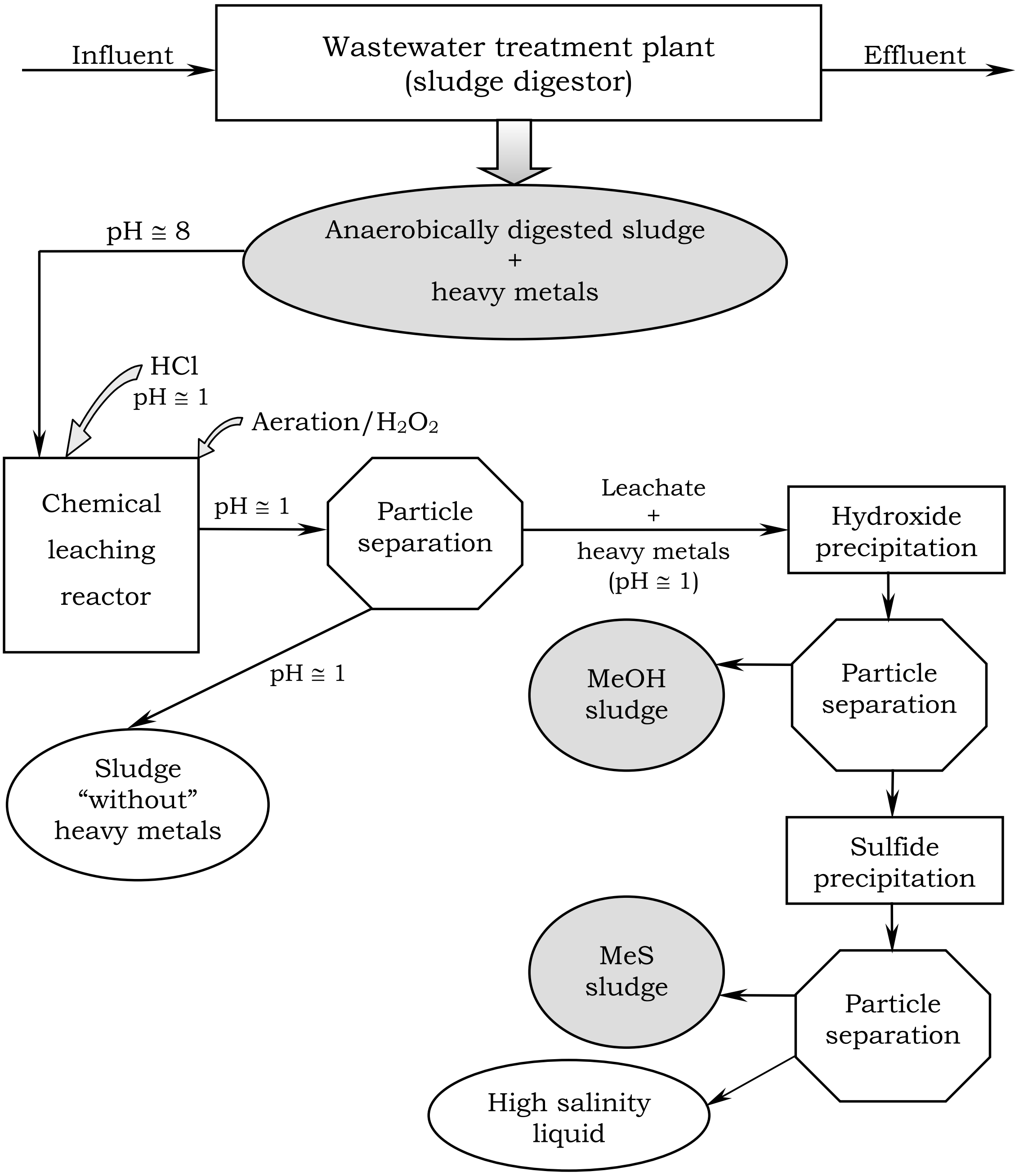

Figure 6.1 - Scheme of a conceptual design for a physical-chemical process to remove heavy metals from anaerobically digested sludge

The first process step consists of heavy metals solubilization by acidification with HCl (pH value around 1) with a previous oxidative pre-treatment (in the same reactor) either by aeration or by H_2O_2.

The second step comprises a separation of the water phase containing the mobilized heavy metals and the sludge particles. The separator might be a hydrocyclone, a centrifuge, a settler, a flotation tank, or a filtration device. The sludge is removed as a concentrated sludge. After the pH correction with lime and dewatering, the sludge can be disposed to land, perhaps used as compost for soil improvement or as part of a material for civil construction. It is important to realize that the quality of this sludge for agricultural purposes might be negatively influenced by the acidification step. As such, nutrients like phosphorus and potassium might be present in the leachate.

The third step is the precipitation of the heavy metals and the application of a separation unit for the removal of the obtained precipitate. The precipitation process is first executed by adding NaOH up to a pH value of 4 to 5. This hydroxide precipitation is followed by a separation step. After removal of the metal hydroxides flocs, a second precipitation step takes place by using Na_2S. The resulted metal sulfides flocs are separated from the water phase in a separator. The concentrated metal hydroxides and metal sulfides sludges should be properly disposed as hazardous waste. A process of metals recovery from the slurry in order to reuse them as metal ore is also possible. It might be, however, complicated and expensive. The water phase including high concentration of NaCl and dissolved organics should be discharged or reused in a proper way. Selective precipitation of nutrients from the leachate should be considered as an option for the treatment.

This conceptual design of a physical-chemical process for heavy metals removal from sewage sludge is very effective in achieving its main goal. However, there are some drawbacks inherent to this option. The costs of the chemicals (HCl, NaOH, Na_2S) and the oxidation process (aeration or H_2O_2) associated to the excess of NaCl in the final effluent constitute the major bottlenecks. One possibility is to redirect this final effluent to the beginning of the wastewater treatment plant, depending on the already existent concentration of NaCl in the influent of this plant. For the costs evaluation the required treatment time must be also considered.

Conceptual design for a biological-physical-chemical process to remove heavy metals from anaerobically digested sludges

A modification of the first conceptual design is presented in Figure 6.2. The idea is to use the benefits of the bioleaching technique, which is mediated by acidophilic bacteria (genus *Thiobacillus*) able to produce acid.

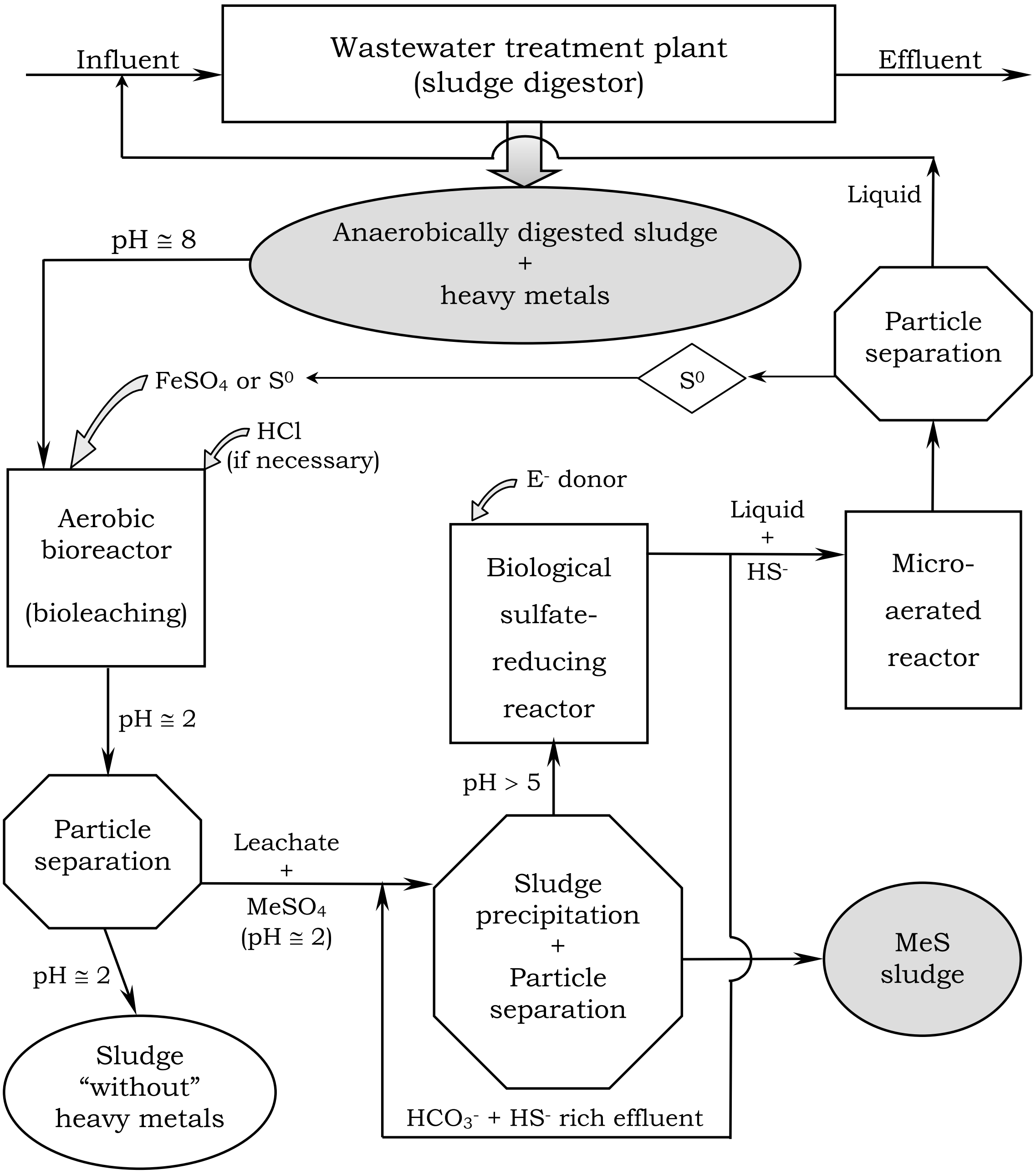

Figure 6.2 - Scheme of a conceptual design for a biological-physical-chemical process to remove heavy metals from sewage sludge

The first step consists of an aerobic bioreactor fed with oxygen and a reduced sulfur source (S^o) or ferrous iron ($FeSO_4$ or FeS) component. These components are oxidized by *Thiobacillus* and converted into sulfuric acid. The required dosage of sulfur or ferrous iron depends on the initial pH of the sludge, the buffering capacity and the desired final pH of the sludge. If lead is present in the sludge, it might be necessary to apply HCl, after the pH is decreased in the bioleaching process. This procedure, however, makes the process more complex and its effectiveness should be investigated.

The second step is identical to that presented in the first proposed scheme. The third step comprises the removal of the heavy metals from the leachate in a two steps precipitation and separation unit. In this way, a sulfur cycle can be introduced into the system (see Figure 6.2).

Due to the inorganic nature of leachate, the addition of an electron donor as substrate in the sulfate reduction process is required. In order to be economically feasible, the electron donor must be cheap and fully degradable, so that no remaining pollution is generated from the biodegradation process. Possible electron donors are: hydrogen (along with carbon dioxide), methanol, ethanol, or acetate. The reduction of oxidized sulfur compounds (SO_4^{2-}) will generate an effluent with dissolved sulfide (HS-) and carbonate (HCO_3^-). Part of this effluent will be mixed with the leachate containing $MeSO_4$, causing the formation of insoluble MeS and a raise of the pH. The effluent of the sulfate-reducing reactor is partially oxidized into elemental sulfur, which can be separated and reused as electron donor for the *Thiobacillus* in the bioleaching process. This will result in the oxidation of elemental sulfur back to sulfate, closing the sulfur cycle inside the treatment system.

There is a necessity of a metal separation unit before the sulfate-reducing reactor because of two reasons. First, there is a need to increase the pH of the leachate before contacting the biomass inside the sulfate-reducing reactor, which is pH sensitive. Second, the formation of metal precipitates inside the sulfate-reducing reactor must be avoided, since it would result in a poor quality metal sludge (rich in biomass). Therefore, if separated in a previous compartment, higher quality metal slurry can be produced. This slurry contains high concentrations of heavy metals and after being dewatered it has to be properly disposed. The liquid fraction that is separated from the elemental sulfur produced in the micro-aerated reactor can be returned to the beginning of the wastewater treatment plant.

From an environmental and economical point of view, the biological-physical-chemical process seems to be more attractive than the physical-chemical process. The final effluent generated in the biological-physical-chemical process can be mixed with the influent of the wastewater treatment plant, dismissing especial post-treatment. In addition, the costs of acid addition are minimized. If elemental sulfur is chosen as substrate, the costs with its addition can be partially surpassed by the use of biological elemental sulfur produced in micro-aerated reactors. Disadvantages of this process include the costs of the energy supply for aeration and the costs of the electron donor (depending on its origin). Moreover, the formation of $PbSO_4$ prevents the solubilization of Pb by bioleaching process. Thus, an additional acidification step with HCl must be considered, when a high concentration of Pb is present in the sludge. This would, of course, make the process more expensive. Another disadvantage is the complexity of the operation and possibly difficult process control.

With respect to the pathogens organisms present in the sludge, it might occur that the extreme acidic conditions applied during the bio(leaching) process causes a considerable reduction in the concentration of such organisms.

The goal of this research was to develop an effective process for removal of heavy metals from sewage sludge to sufficiently low concentrations, at acceptable costs. Definitely in the further development of the process to a practical scale, attention has to be paid to the possibilities of reuse of the heavy metals recovered from the sludge. Furthermore, how to deal with the remaining liquid residues, such as those obtained after an extraction process with HCl must be also considered.

This research was dealing with extreme low pH conditions, in order to attain high heavy metals removal efficiencies from sewage sludges. There might be some cases, however, that the application of milder pH conditions is appropriate to achieve sufficient heavy metals removal efficiencies. Besides, the results of this study may also be of interest for the removal of heavy metals from other type of wastes, such as sediments.

Chapter 7

Summary

Samenvatting

Sumário

SUMMARY

Removal of heavy metals from sewage sludge

Heavy metals can cause serious problems for human beings and ecosystems. As mentioned in Chapter 1, the process of heavy metals removal from sewage sludges is in general only feasible in the case of very strongly polluted sludges. There are advantages of heavy metals removal from this type of sludge. First, the possibility of sludge disposal to landfill with reduced risk of metals being leached to surface and groundwater. Second, sludge can be used as soil improver with less harm. Third, sludge can be applied, with lower costs, as energy source in co-incineration. The off-gas treatment system might be less complex and can operate at milder process conditions than when the sludge is strongly polluted with heavy metals. Finally, dewatered sludge or sludge fly ashes can be applied, with lower environmental risks, as raw material in civil construction materials.

Although numerous studies have appeared in the field of heavy metals removal from sewage sludges, several knowledge gaps still exist, which are the reason for the less attention that has been paid to the implementation of techniques for this purpose. Such techniques still remain in the laboratory and pilot plant scale. The aim of this work is to contribute to the further development of practical application of the technologies, which might be applied in the heavy metals removal from anaerobically digested sludge.

Sludge characterization

In Chapter 2, the materials and main analytical procedures used in the experimental part of the research are described, and the physical and chemical characteristics of the applied sludge are evaluated. The concentration of the heavy metals present in the sludge is emphasized and legal standards for metals disposal on land are shown and discussed.

A physical classification scheme, based on differences in the particle size of sludge was applied in order to determine the heavy metal content of the various fractions of the sludge. The results demonstrated that heavy metals were mostly concentrated in the fractions < 0.063 mm, constituting about 70 % of the total sludge mass and contributing to 78-85 % of the heavy metals present in the sludge. In all the separated fractions, however, most of the metals concentrations exceeded the Dutch standard (BOOM) for land application. This indicates that, if land application is considered, then the whole sludge has to be treated, without any previous separation.

An analytical approach for determining the chemical forms of heavy metals in the sludge based on sequential chemical extraction (SCE) procedures was executed. A sequential chemical extraction procedure consists of the utilization of a series of chemical extractants in a sequence of reagents of increasing harshness. For each extraction step, a specific chemical form of the metal is expected to dissolve. Three sequential chemical extraction schemes were tested in this research: Tessier (1979), Veeken (1998), and Sims & Kline (1991). In addition, modified versions of Veeken and Tessier schemes were applied as a tentative to investigate the causes of the differences between both schemes. In these modified versions, some conditions were slightly altered from the original ones.

Despite the uncertainty of the SCE method with respect to selectivity (metals bound to more than one phase are solubilized) and specificity (more than one phase is solubilized), it gives useful information concerning the availability of the metals. The SCE results of the investigated sludge revealed that Cr (65 - 67 %) and Cu (65 - 87 %) could be effectively released in an oxidizing environment (85 °C, pH= 2). Zinc (78 - 86 %) could be extracted by a reducing agent (96 °C, pH= 2), whereas Pb (62 - 81 %) could be solubilized at strong acidic conditions at high temperature (150 °C in a microwave oven). Furthermore, a chelating agent (20 °C, pH= 4.5) was able to release considerable amounts of Cr (56 - 57 %), Pb (57 - 78 %) and Zn (50 - 62 %). About 70 % of Cu could also be extracted with application of high pH (12.6) at 20 °C. The experiments demonstrated that the two modified schemes provided valuable information for interpretation of the differences in the results of the original schemes.

Chemical leaching of heavy metals

Chapter 3 deals with the chemical leaching process applied in the crucial step of the sludge treatment aimed at heavy metals removal: the metals solubilization step. For this aim, organic acids (citric and oxalic) and inorganic acids (nitric, hydrochloric and phosphoric) were tested at different conditions of pH, reaction time, and oxidation-reduction potential (ORP). The effect of acidification was intensively tested for liquid samples of the sludge and briefly tested for dried and crushed sludge samples.

It is known that a low pH value is not always enough to promote a satisfactory metals release from anaerobic sludge particles to the liquid, unless acidification was preceded by a rise in the sludge ORP. This increase in the ORP of the sludge can occur by chemical oxidation or biological oxidation. In the present work, chemical oxidation with application of aeration or adding hydrogen peroxide were investigated. Especially copper was highly influenced by oxidation. This was due to its speciation in the sludge. As suggested by the SCE schemes, Cu is tightly bound to the organic matter fraction in the sludge. Moreover, in anaerobic sludges the heavy metals are present usually in their most reducible form. Accordingly, Cu predominates as Cu^{1+}. Thus, if this metal is also present as the insoluble Cu_2S in the sludge, to solubilize Cu it is necessary to oxidize Cu^{1+} to the soluble form Cu^{2+}, as $CuSO_4$.

The results showed that the option including chemical oxidation with either aeration or hydrogen peroxide followed by acidification with HCl resulted in the highest extraction yields of most heavy metals. The best results achieved were: Cr: 85 % with H_2O_2, Cu: 100 % with H_2O_2, Pb: 100 % with aeration and H_2O_2, and Zn: 100 % with aeration and H_2O_2.

Bioleaching of heavy metals

In Chapter 4, the effect of bioleaching on the solubilization of Cr, Cu, Pb and Zn from anaerobically digested sludge is discussed. The principle of bioleaching is the production of acid by specific acidophilic bacteria (genus *Thiobacillus*). These bacteria can oxidize reduced sulfur or ferrous iron to sulfuric acid. In this research, bioleaching with elemental sulfur and ferrous iron and chemical leaching with H_2SO_4 were applied.

The results were compared with those found in literature and in previous leaching experiments with HCl. It was found that bioleaching can be a feasible alternative to promote the solubilization of Zn and Cu, especially when ferrous iron is added as substrate. Under this condition, the maximum extraction yield achieved for Zn was 80.8 % with a pH value of 2.7. For Cu it was 65.5 % with a pH value of 2.5. Chromium solubilization was possible when pH was around 2.5. Less than 1 % of Pb was extracted by bioleaching, due to the formation of the insoluble $PbSO_4$. Chemical leaching with HCl at a pH value of 1 solubilized almost 100 % of Pb and also provided the best extraction yield for Cr (around 72 %). At the same pH value, HCl is more effective than H_2SO_4 to solubilize all the metals studied.

Heavy metals removal from the leachate

In the present work, after solubilization of heavy metals by chemical leaching with previous aeration, the next step was the separation of the sludge solids from the metal-rich acidic liquid (leachate) by centrifugation and filtration. In Chapter 5, research into the removal of heavy metals from the leachate was carried out. For that, the obtained filtered leachate was submitted to the application of hydroxide precipitation with NaOH and sulfide precipitation with Na_2S, both separately and in combination. These two types of precipitation processes are the most widely applied and the chemicals, which were chosen, are the most common ones. Each precipitation step was followed by filtration of the precipitate.

The results showed that when iron and aluminium are present in the sludge (as it was the case), adsorption and/or coprecipitation of the heavy metals to a ferric or aluminium hydroxide precipitate might occur. This was especially observed when hydroxide precipitation was solely applied. In addition, Cu was not satisfactorily removed by hydroxide precipitation, despite the fact that $Cu(OH)_2$ has the lowest solubility among Cr, Pb and Zn hydroxides. This phenomenon might be due to the high nucleation rate that occurs when the precipitate has low solubility product. The increase in the nucleation rate favors the particle size decrease. In the present research, the particles passed through the filter pore size and therefore Cu was detected in the liquid.

The combination of hydroxide and sulfide precipitation was able to promote an effective removal of heavy metals from the leachate. Applying NaOH at a pH value of 4-5 as a first precipitation step, followed by filtration and further addition of Na_2S to the filtered liquid at a pH value of 7-8 as a second precipitation step, considerably decreased the dosage of the second precipitant, when it was exclusively applied. The best removal efficiencies obtained were: Pb: 100 %, Cr: 99.9 %, Cu: 99.7 %, and Zn: 99.9 %.

Concluding remarks

Based on the results obtained, two conceptual designs for heavy metals removal from sewage sludge were presented and discussed in Chapter 6. One scheme referred to a physical-chemical treatment and the other to a biological-physical-chemical treatment. The first scheme comprises the use of chemical leaching in the metals solubilization step and addition of NaOH and Na_2S in combination, in the precipitation step. The second scheme substitutes the chemical leaching step by bioleaching and, in the precipitation step, the sulfide produced in a sulfate-reducing reactor is utilized. The reduction of oxidized sulfur compounds (SO_4^{2-}) will generate an effluent with dissolved sulfide (HS-) and carbonate (HCO_3^-). Part of this effluent will be mixed with the leachate containing $MeSO_4$, causing the formation of the insoluble MeS and the raise of the pH. The effluent of the sulfate-reducing reactor is partially oxidized into elemental sulfur, which can be separated and reused as electron donor for the *Thiobacillus* in the bioleaching process.

From an environmental and economical point of view, the biological-physical-chemical process seems to be more attractive than the physical-chemical process. The final effluent generated in the biological-physical-chemical process can be mixed with the influent of the wastewater treatment plant, dismissing the special post-treatment required in the physical-chemical process, as the remaining water in this process contains a high concentration of NaCl. In addition, the costs of acid addition are minimized by bioleaching.

This research had the purpose to develop an effective process for removal of heavy metals from sewage sludge to sufficiently low concentrations, at acceptable costs. In further development of the process to a practical scale, attention has to be paid to the reuse possibilities of heavy metals recovered from the sludge and how to deal with the remaining liquid residues.

Extreme low pH conditions are necessary to achieve high heavy metals removal efficiencies from sewage sludges. Nevertheless there might be some cases that the application of milder pH conditions is suitable to obtain sufficient heavy metals removal efficiencies. Moreover, the results of this study may also be applicable for the removal of heavy metals from other wastes, such as sediments.

SAMENVATTING

Het verwijderen van zware metalen uit zuiveringsslib

Zware metalen kunnen een serieuze bedreiging vormen voor zowel mensen als ecosystemen. In het algemeen is een proces om zware metalen te verwijderen uit zuiveringsslib alleen technisch en economisch haalbaar indien het slib sterk verontreinigd is. Het verwijderen van de zware metalen uit dit soort slib heeft verscheidene voordelen. Ten eerste geeft het de mogelijkheid om het slib na reiniging te storten met slechts een gering risico voor uitlogen van zware metalen naar het grondwater en het oppervlaktewater. Ten tweede is het risico bij het gebruik van het slib als bodemverbeteraar veel minder. Ten derde kan er een besparing optreden bij het verbranden van slib, omdat bij de rookgasreiniging minder rekening gehouden hoeft te worden met de aanwezigheid van zware metalen, zodat een eenvoudigere procesvoering mogelijk is. Tenslotte is het milieurisico kleiner bij toepassing van ontwaterd slib of vliegas in civiele constructies.

Hoewel er op het gebied van zware metalenverwijdering uit rioolwaterslib reeds vele studies verschenen zijn, zijn er nog steeds verscheidene kennisleemtes. Dit is in feite de reden dat er nog weinig aandacht is besteed aan de implementatie van technieken voor het verwijderen van zware metalen. Dergelijke technieken zijn nog steeds in de fase van laboratoriumonderzoek. Het doel van de onderhavige studie is om een bijdrage te leveren aan de verdere ontwikkeling van de praktische toepassing van de technologieën, die toegepast zouden kunnen worden voor de verwijdering van zware metalen uit anaëroob vergist slib.

Slibkarakterisering

De materialen en belangrijkste analytische procedures, welke in het experimentele onderzoek zijn gebruikt, worden beschreven in Hoofdstuk 2. Verder worden in dit hoofdstuk de chemische en fysische karakteristieken van het onderzochte slib beschreven. Met name worden de concentraties aan zware metalen in het slib gegeven, en in een discussie vergeleken met de normen voor toepassing op het land als bodemverbeteraar.

De concentraties aan zware metalen zijn experimenteel bepaald in verschillende deeltjesgroottefracties. Het resultaat toont aan dat de zware metalen met name geconcentreerd zijn in de fractie kleiner dan 0,063 mm, welke ongeveer 70 % van het totale slib uitmaakt en 78-85 % van de zware metalen die aanwezig zijn in het slib bevat. In alle deeltjesgroottefracties zijn de concentraties aan zware metalen dermate hoog, dat ze niet voldoen aan de Nederlandse norm voor toepassing op het land (BOOM). Dit geeft aan dat, indien toepassing op het land wordt overwogen, het gehele slib dient te worden behandeld, zonder voorafgaande deeltjesscheiding.

Verder is een techniek, gebaseerd op sequentiële chemische extractie (SCE), toegepast om de verschillende chemische wijze van voorkomen van de metalen te bepalen. Een SCE bestaat uit een serie van extracties met extractievloeistoffen in oplopende agressiviteit. Bij iedere extractie wordt een specifieke chemische vorm van de metalen in oplossing gebracht. Drie verschillende extractieschema's zijn toegepast in dit onderzoek: Tessier (1979), Veeken (1998) en Sims & Kline (1991). Verder zijn twee aangepaste versies van de schema's van Veeken en Tessier uitgevoerd teneinde de verschillen in resultaten van de beide schema's op te helderen.

Niettegenstaande de onzekerheden in de SCE-methode met betrekking tot selectiviteit (metalen gebonden aan meer dan een fase gaan in oplossing) en specificiteit (meer dan een fase gaat in oplossing), geeft de methode bruikbare informatie over de beschikbaarheid van metalen. De SCE-resultaten van het onderzochte slib geven aan dat chroom (65 - 67 %) en koper (65 - 87 %) in een oxiderend milieu, bij pH= 2 en 85 °C, effectief kunnen worden gemobiliseerd. Zink (78 - 86 %) kon worden geëxtraheerd in een reducerend milieu bij pH= 2 en 96 °C, terwijl lood (62 - 81 %) in oplossing kan worden gebracht onder sterk zure condities bij hoge temperatuur (150 °C in een magnetronoven). Verder was een chelator in staat aanmerkelijke hoeveelheden chroom (56 - 57 %), lood (57 - 78 %) en zink (50 - 62 %) van het slib los te maken. Circa 70 % van het koper kan ook worden geëxtraheerd bij hoge pH (12.6) en 20 °C. De resultaten laten zien dat de aangepaste SCE-schema's waardevolle informatie verschaffen om de verschillen in de originele schema's te verklaren.

Chemische uitloging van zware metalen

Hoofdstuk 3 behandelt het chemische uitlogingsproces dat in de cruciale stap van de slibbehandeling voor zware-metalenverwijdering wordt toegepast, de solubilisatiestap. Voor dit doel werden verschillende organische (citroenzuur en oxaalzuur) en anorganische (salpeterzuur, zoutzuur en fosforzuur) zuren getest onder verschillende condities wat betreft pH, reactietijd en redoxpotentiaal. Het effect van zuurtoediening is uitgebreid getest voor vloeibare monsters van het slib, en beperkt getest voor gedroogde en gemalen monsters.

Het is bekend dat lage pH-waarden niet altijd voldoende zijn om de zware metalen voldoende los te maken van de slibdeeltjes, tenzij de zuurtoediening voorafgegaan wordt door een verhoging van de redoxpotentiaal van het slib. Deze verhoging kan bereikt worden door of een chemische of een biologische oxidatie. In deze studie is chemische oxidatie door middel van beluchting of waterstofperoxidedosering onderzocht. Met name koper is zeer gevoelig voor de redoxpotentiaal. Dit kan worden verklaard uit de speciatie van koper. Volgens de SCE-resultaten is koper vooral gebonden aan de organische fractie. Verder is het zo dat in anaëroob slib metalen doorgaans aanwezig zijn in hun meest gereduceerde vorm. Derhalve is koper aanwezig als Cu^+ in onder andere het onoplosbare C_2S. Het is dus noodzakelijk deze vorm te oxideren tot het oplosbare $CuSO_4$.

De resultaten tonen aan dat chemische oxidatie door hetzij beluchting, hetzij waterstofperoxidedosering, gevolgd door zuurdosering in de vorm van zoutzuur de hoogste extractierendementen opleverde. De beste resultaten zijn gevonden voor chroom (85 %) met H_2O_2, koper (100 %) met H_2O_2, lood (100 %) met zowel beluchting als H_2O_2 en zink (100 %), ook met lucht en H_2O_2.

Biologische uitloging van zware metalen

In Hoofdstuk 4 wordt het effect van biologische uitloging op het oplosbaar maken van chroom, koper , lood en zink uit anaëroob vergist slib behandeld. Het principe van deze uitloging is de productie van zuur door bepaalde acidofiele bacteriën (genus *Thiobacillus*) Deze bacteriën oxideren gereduceerd zwavel of ijzer(II) tot zwavelzuur. Ter vergelijking werd ook chemische uitloging met zwavelzuur toegepast.

De resultaten zijn vergeleken met literatuurgegevens en de resultaten met zoutzuur zoals gevonden in Hoofdstuk 3. Er is gevonden dat biologische uitloging een haalbaar alternatief is voor het oplosbaar maken van zink en koper, met name wanneer Fe(II) als substraat wordt toegevoegd. De maximale extractierendementen die zijn behaald zijn voor zink 80,8 % bij een pH-waarde van 2,7 en voor koper 65,6 % bij een pH-waarde van 2,5. Het oplossen van chroom was gedeeltelijk mogelijk bij een pH van 2,5. Minder dan 1 % van het lood ging in oplossing vanwege de formatie van het onoplosbare loodsulfaat. Chemische uitloging met zoutzuur bij pH= 1 resulteert in een rendement van bijna 100 % voor lood en circa 72 % voor chroom. Bij vergelijkbare pH is zoutzuur veel effectiever dan zwavelzuur in het oplossen van de bestudeerde zware metalen.

Het verwijderen van zware metalen uit de extractievloeistof

De volgende stap in de behandeling van het slib is het afscheiden van de gereinigde slib deeltjes van het extractiemedium door middel van centrifugeren of filtreren. Vervolgens dient de extractievloeistof gereinigd te worden van zware metalen, hetgeen het onderwerp is van Hoofdstuk 5. Hiertoe werd de gefiltreerde extractievloeistof onderworpen aan een precipitatieproces met NaOH en Na_2S, beide zowel separaat als in combinatie. Deze procedure is gebaseerd op een veel toegepaste methode. Iedere precipitatie werd gevolgd door het affiltreren van het precipitaat.

De resultaten gaven een indicatie dat indien ijzer of alumnium aanwezig is, zoals in het gebruikte slib, adsorptie en coprecipitatie van zware metalen en ijzer of aluminiumhydroxide een belangrijk mechanisme is. Dit is met name het geval wanneer de pricipitatie met alleen natronloog wordt uitgevoerd. Verder blijkt dat koper door precipitatie slechts in beperkte mate wordt verwijderd, niettegenstaande het feit dat koperhydroxide in vergelijking met chroom-, lood- en zinkhydroxide de laagste oplosbaarheid heeft. Dit verschijnsel zou verklaard kunnen worden uit het gegeven dat een lage oplosbaarheid gepaard kan gaan met een hoge nucleatiesnelheid. Hierdoor is de deeltjesgrootte van koperhydroxidekristallen zeer klein, en worden ze niet afgescheiden door het filter. Bij de analyse worden ze daardoor in feite gemeten als opgelost koper.

De combinatie van hydroxide- en sulfideprecipitatie leidt tot een effectieve verwijdering van zware metalen uit de extractievloeistof. Door de pH eerst op een waarde van 4-5 te brengen met natronloog en vervolgens tot een waarde van 7-8 met sulfide in een tweede precipitatiestap, kan de dosering van sulfide aanzienlijk gereduceerd worden in vergelijking met het toepassen van sulfide zonder natronloog. De beste verwijderingsrendementen die behaald zijn bij de precipitatie zijn: Pb: 100 %, Cr: 99.9 %, Cu: 99.7 %, en Zn: 99.9 %.

Afsluitende opmerkingen

Uitgaande van de behaalde resultaten zijn twee conceptuele procesontwerpen voor de verwijdering van zware metalen uit zuiveringsslib gemaakt, welke in Hoofdstuk 6 gepresenteerd worden. Eén ontwerp is gebaseerd op een totaal fysisch-chemisch proces, het andere op een biologisch en fysisch-chemisch proces. In het eerste processchema wordt het slib chemisch geëxtraheerd en vervolgens de extractievloeistof van metalen gezuiverd door middel van precipitatie met natronloog en sulfide. In het tweede schema wordt de chemische extractie vervangen door een biologische extractie en wordt voor de precipitatie sulfide gebruikt uit een sulfaat-reducerende bioreactor. De reductie van geoxideerd zwavel (SO_4^{2-}) resulteert in een oplossing van sulfide en carbonaat. Deze oplossing wordt aan de metaalsulfaathoudende extractievloeistof gedoseerd, wat leidt tot de vorming van onoplosbare metaalsulfiden en een pH-verhoging. Het sulfaat zal gedeeltelijk gereduceerd worden tot elementair zwavel, wat gebruikt kan worden als elektrondonor voor de *Thiobacillus* in het biologische extractieproces.

Uit milieu en economisch oogpunt bekeken lijkt het biologisch-fysisch-chemische proces aantrekkelijker dan het fysisch-chemische proces. Het effluent van het biologische proces kan worden toegevoegd aan het influent van de waterzuiveringsinstallatie, waardoor een verdere nabehandeling voor ontzouting achterwege kan blijven. Verder worden in het biologische proces de kosten voor de aanschaf van zuur geminimaliseerd.

Het doel van het onderzoek was om tot een effectief proces te komen voor de verwijdering van zware metalen uit zuiveringsslib, tot voldoende lage concentraties tegen acceptabele kosten. Bij de verdere ontwikkeling van het proces dient aandacht te worden geschonken aan hergebruikmogelijkheden voor de teruggewonnen zware metalen en de verdere behandeling van vloeistofresiduen.

Extreem lage pH-condities zijn noodzakelijk om een goede verwijdering van zware metalen uit zuiveringsslib te bereiken. Nochtans kan het mogelijk zijn dat in geval van andere metaalspeciaties mildere condities voldoende zijn. De resultaten van dit onderzoek zijn mogelijk ook toepasbaar voor andere afvalstromen, zoals baggerspecie.

SUMÁRIO

Remoção de metais pesados de lodo de esgoto

Os metais pesados podem causar sérios danos aos seres humanos e ecossistemas. Conforme mencionado no Capítulo 1, o processo de remoção de metais pesados de lodo de esgoto é, em geral, apenas viável no caso de lodos altamente poluídos. Neste caso, a remoção dos metais pesados pode ser bem vantajosa por várias razões. Em primeiro lugar, existe a possibilidade de dispor o lodo em aterros sanitários com risco reduzido de contaminação do lençol superficial e subterrâneo. Em segundo lugar, o lodo pode ser usado como beneficiador de solos. Em terceiro lugar, o lodo pode ser aplicado, a custos reduzidos, como fonte de energia no processo de co-incineração. O sistema de tratamento do gás gerado neste processo seria menos complexo e poderia operar sob condições mais amenas que no caso de lodos altamente poluídos com metais pesados. Finalmente, o lodo tratado desidratado ou as cinzas do lodo tratado incinerado podem ser utilizados, com menores riscos ambientais, como matéria-prima na fabricação de materiais de construção.

Apesar de existirem inúmeros estudos a respeito da remoção de metais pesados de lodos de esgoto, vários são ainda os pontos não esclarecidos, os quais são a maior razão para a deficiência na implementação das técnicas existentes para este fim. Tais técnicas ainda prevalecem em escala de laboratório e piloto. O objetivo deste trabalho é contribuir para o desenvolvimento da aplicação prática de tecnologias destinadas à remoção de metais pesados de lodos de esgoto, com ênfase nos lodos anaerobiamente digeridos.

Caracterização do lodo

No Capítulo 2, os materiais e principais procedimentos analíticos utilizados na parte experimental desta pesquisa são descritos e as características físico-químicas do lodo estudado são avaliadas. As concentrações dos metais pesados presentes no lodo, bem como as concentrações dos metais permitida pelos limites legais de disposição de lodos no solo são mostradas e discutidas. Um esquema de classificação física, baseado em diferenças de tamanho de partículas do lodo foi aplicado a fim de se determinar o teor de metais presente nas várias frações do lodo. Os resultados demonstraram que os metais se concentravam principalmente nas frações < 0.063 mm, constituindo cerca de 70 % da massa total do lodo e contribuindo 78-85 % do total de metais presentes no lodo. Em todas as frações, entretanto, a maioria das concentrações dos metais excedia o limite holandês (BOOM) para aplicação do lodo no solo. Isto indica que, se a aplicação do lodo no solo for considerada, então o lodo deve ser tratado por inteiro, sem prévia separação de suas frações.

Para a determinação das formas químicas dos metais pesados (especiação química) no lodo, utilizou-se um método analítico aproximado baseado em esquemas seqüenciais de extração química ("sequential chemical extraction"). Este método consiste em se utilizar uma série de reagentes aplicados seqüencialmente (em ordem progressiva de "força"), tendo por intuito solubilizar uma forma química particular dos metais. Três destes esquemas foram testados nesta pesquisa: Tessier (1979), Veeken (1998), and Sims & Kline (1991). Adicionalmente, versões modificadas dos esquemas Tessier e Veeken foram aplicadas como tentativa de se investigar as causas das diferenças entre ambos os esquemas. Nestas versões modficadas, algumas condições foram ligeiramente alteradas das originais.

Apesar da incerteza dos métodos dos esquemas seqüenciais com respeito a seletividade (metais ligados a mais de uma fase são solubilizados) e especificidade (mais de uma fase é solubilizada), tais métodos fornecem informações úteis no que tange à disponibilidade dos metais no lodo. Os reultados dos esquemas seqüenciais investigados mostraram que o Cr (65 - 67 %) e o Cu (65 - 87 %) podem ser efetivamente solubilizados em condições oxidativas (a 85 °C e pH= 2). O zinco (78 - 86 %) pode ser extraído do lodo por um agente redutor (a 96 °C e pH= 2), ao passo que o Pb (62 - 81 %) pode ser dissolvido sob condições de acidificação extrema (a 150 °C no microondas). Além do mais, um agente quelante (a 20 °C e pH= 4.5) pode ser capaz de solubilizar considerável concentração de Cr (56 - 57 %), Pb (57 - 78 %) and Zn (50 - 62 %). Cerca de 70 % do Cu pode também ser extraído com a aplicação de um alto valor de pH (12.6) a 20 °C. Os experimentos demonstraram que as duas versões modificadas dos esquemas seqüenciais forneceram valiosas informações para a interpretação das diferenças entre os esquemas originais testados.

Lixiviação química dos metais pesados

O Capítulo 3 se refere ao processo de lixiviação química utilizado na fase crucial do tratamento do lodo: a solubilização dos metais. Neste sentido, ácidos orgânicos (cítrico e oxálico) e ácidos inorgânicos (nítrico, clorídrico e fosfórico) foram testados sob diferentes condições de pH, tempo de reação e potencial de oxidação-redução. O efeito da acidificação foi intensamente estudado para amostras de lodo líquidas e brevemente estudado para amostras de lodo secas e trituradas.

Reduzir o valor do pH do lodo nem sempre é condição suficiente para promover uma satisfatória mobilização dos metais da fase sólida para a fase líquida. A menos que esta redução no valor do pH seja precedida de um aumento no valor do potencial de oxidação-redução do lodo, o qual pode ocorrer por oxidação química ou biológica. No presente trabalho, a oxidação química por aeração e por adição de peróxido de hidrogênio foi investigada. Verificou-se que especialmente o Cu foi influenciado pela oxidação. Isto se deve ao fato da especiação deste metal no lodo. Conforme indicado pelos esquemas seqüenciais de extração química, o Cu é fortemente ligado à matéria orgânica do lodo. Ademais, em lodos anaeróbios, os metais estão presentes em suas mais reduzidas formas. Assim, o Cu predomina como Cu^{1+}. Desse modo, se este metal está também presente no lodo como o insolúvel Cu_2S, para solubilizar o Cu é necessário oxidar Cu^{1+} à solúvel forma Cu^{2+}, como $CuSO_4$.

Os resultados mostraram que a opção que inclui a oxidação química com aeração ou peróxido de hidrogênio seguida de acidificação com HCl resultou na mais alta porcentagem de extração da maioria dos metais pesados. Os melhores reultados alcançados foram: Cr: 85 % com H_2O_2, Cu: 100 % com H_2O_2, Pb: 100 % com aeração e H_2O_2, e Zn: 100 % com aeração e H_2O_2. A extração do Cu foi particularmente influenciada pela oxidação.

Biolixiviação (“Bioleaching”) dos metais pesados

No Capítulo 4 é discutida a investigação da biolixiviação na solubilização do Cr, Cu, Pb e Zn presentes no lodo anaeróbio. A biolixiviação tem como princípio a produção de ácido pela bactéria acidofílica específica (genus *Thiobacillus*). Tais bactérias são capazes de oxidar enxofre elementar ou ferro ferroso a ácido sulfúrico. Nesta pesquisa, aplicou-se a biolixiviação com enxofre elementar e ferro ferroso, assim como a lixiviação química com H_2SO_4.

Os resultados foram comparados com os encontrados na literatura e em experimentos anteriores com HCl. Foi observado que a biolixiviação é uma alternativa viável para promover a solubilização do Zn e do Cu, especialmente se o ferro ferroso for adicionado como substrato no processo. Sob estas condições, a máxima porcentagem de extração obtida para o Zn foi de 80.8 % com valor de pH a 2.7. Para o Cu, obteve-se 65.5 % de extração, com valor de pH a 2.5. A solubilização do Cr foi possível somente quando o valor do pH chegou por volta de 2.5. Menos de 1 % do Pb foi extraído pela biolixiviação devido à formação do insolúvel $PbSO_4$. A lixiviação química com HCl a valor de pH por volta de 1 foi capaz de solubilizar quase 100 % do Pb e também propiciou a melhor porcentagem de extração do Cr (ao redor de 72 %). Sob o mesmo valor de pH, o HCl é mais eficiente que o H_2SO_4 para solubilizar todos os metais pesados estudados.

Remoção dos metais pesados do lixiviado

Após a solubilização dos metais pesados por lixiviação química com prévia aeração do lodo, o próximo passo no tratamento do lodo foi a separação física da parte sólida do lodo, do líquido acidificado rico em metais (lixiviado), por centrifugação e filtração. O Capítulo 5 discorre sobre a remoção dos metais pesados do lixiviado. Para tanto, o lixiviado, já filtrado, foi submetido à aplicação separada e combinada da precipitação por hidróxidos com NaOH e da precipitação por sulfetos com Na_2S. Estes dois tipos de precipitação são os mais aplicados atualmente e os químicos utilizados são os mais comuns. Durante os experimentos, cada uma das etapas de precipitação ocorreu seguida de filtração do precipitado.

Os resultados demostraram que, quando Fe e Al estão presentes no lodo (como era o caso), adsorção e/ou coprecipitação dos metais pesados podem ocorrer. Tais fenômenos foram especialmente observados quando a precipitação por hidróxidos foi aplicada unicamente. Adicionalmente, este tipo de precipitação não foi capaz de remover satisfatoriamente o Cu, apesar de o $Cu(OH)_2$ apresentar a mais baixa solubilidade entre os hidróxidos de Cr, Pb e Zn. Este resultado pode ser explicado pela alta taxa de nucleação ("nucleation") que ocorre quando o precipitado possui baixo produto de solubilidade. O aumento na taxa de nucleação favorece a diminuição no tamanho das partículas. Na presente pesquisa, os precipitados formados passaram através do poro do filtro utilizado e, por esta razão, o Cu foi detectado na fase líquida.

A combinação das precipitações por hidróxidos e sulfetos foi capaz de promover uma efetiva remoção dos metais pesados do lixiviado. Primeiro, aplicando-se NaOH a um valor de pH entre 4-5 como primeira etapa de precipitação, seguida de filtração. Depois, adicionando-se Na_2S ao líquido filtrado a um valor de pH entre 7-8 como segunda etapa de precipitação. Tal combinação foi capaz de diminuir consideravelmente a dosagem do Na_2S, em relação à sua dosagem aplicada na precipitação única. As melhores eficiências de remoção obtidas foram: Pb: 100 %, Cr: 99.9 %, Cu: 99.7 %, e Zn: 99.9 %.

Aspectos importantes

Baseando-se nos resultados atingidos, dois esquemas conceituais para a remoção de metais pesados de lodos de esgoto foram apresentados e discutidos no Capítulo 6. Um esquema se refere a tratamento físico-químico e o outro a tratamento biológico-físico-químico. O primeiro deles engloba o uso da lixiviação química dos metais na fase de solubilização destes e adição combinada de NaOH e Na_2S na fase de precipitação metálica. O segundo esquema substitui a lixiviação química pela biolixiviação e, na etapa de precipitação, o sulfeto produzido num reator de redução de sulfato é utilizado. A redução de compostos de enxofre oxidados (SO_4^{2-}) gera um efluente contendo sulfeto dissolvido (HS-) e carbonato (HCO_3^-). Parte deste efluente deve ser misturado com o lixiviado contendo sulfato metálico, causando a formação do insolúvel sulfeto metálico e aumentando o valor do pH. O efluente do reator de redução de sulfato é parcialmente oxidado a enxofre elementar, o qual pode ser separado e reusado como doador de elétrons para o *Thiobacillus* no processo de biolixiviação.

Sob um ponto de vista ambiental e econômico, o processo biológico-físico-químico é mais atraente que o processo físico-químico. O efluente final produzido no processo biológico-físico-químico pode ser misturado ao afluente da estação de tratamento, dispensando o pós-tratamento especial requerido no processo físico-químico. Neste último, o efluente contém alta concentração de NaCl. Além do mais, os custos com a adição de ácido são minimizados na biolixiviação.

Esta pesquisa teve o propósito de desenvolver um processo efetivo para a remoção de metais pesados de lodos de esgoto a concentrações suficientemente baixas, e custos aceitáveis. Em posteriores desenvolvimentos do processo visando a escala prática, atenção especial deve ser dada às possibilidades de reúso dos metais pesados removidos do lodo, assim como ao destino final dos líquidos remanescentes.

Condições baixíssimas de pH são necessárias para se atingir elevadas eficiências de remoção de metais pesados de lodos de esgoto. Entretanto, haverá casos em que a aplicação de condições menos extremas serão adequadas para se obter suficientes eficiências de remoção dos metais. Ademais, é provável que os resultados deste estudo possam ser aplicados à remoção de metais pesados de outros tipos de materiais residuários, como por exemplo, sedimentos.

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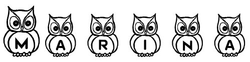

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