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SOIL DECONTAMINATION BY SUPERCRITICAL EXTRACTION

Teresa Castelo-Grande[(1)] and Domingos Barbosa [(2)]

([1,2]) CBQF – Pólo FEUP – DEQ – University of Porto, Portugal – mea02005@fe.up.pt[(1)] and dbarbosa@ fe.up.pt[(2)]

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Waste management, soil decontamination, supercritical extraction, pesticides, groundwater, atrazine

ABSTRACT

Some of the existing techniques for soil decontamination are reviewed, giving particular emphasis to supercritical extraction (SCE), an environmental friendly technique whose applications to the treatment of effluents and soil remediation are only emerging now. The experimental apparatus and analytical technique used in our laboratory to study the extraction of atrazine from contaminated soil by SCE with carbon dioxide is described.

INTRODUCTION

Nowadays society is becoming more and more aware of the problems that pollution is causing to our planet; man is polluting the water, the air and the soil. A new generation that has "environmental awareness" is growing up. There is a particular concern with the quality of the water and the air but we must not forget that the soil is an essential support for the biosphere, and plays an important role in the food chain - Castelo-Grande and Barbosa (2003). The soil contributes to the hydrological cycle through its capacities of transformation, filtration and buffer effect, and it is in the soil that the resources of potable water are stored. The original characteristics of the soil can be more or less changed depending on the action of the man, which is frequently inadequate and irresponsible – Direcção Geral do Ambiente (1999). Some of these actions are the deposition of degraded material, liquid effluents, solid residues, and the salinization of the underground water by over exploring the aquifers or the abusive use of fertilizers and herbicides.

The action of this last class of chemicals is very important because their retention time in soil is some times very high – Spadoto (2002), and can pollute the underground water - Gish (1998), Smith (1993) due to their characteristics: high drainage potential, high persistence in soils, slow hydrolysis, low vapor pressure, low to moderate solubility in water, moderate absorption by organic matter and clay – Hance (1988). An example of this type of compounds is atrazine, which was chosen to carry out our studies on the removal of herbicides from contaminated soils by supercritical extraction (SCE), due to the fact that this is one of the most widely used herbicides in farming, such as corn, sorghum and sugarcane plantations - WSSA (1994), that acts by inhibiting the photosynthesis - Meister (1998), and is dangerous for man causing cancer - Sathiakumar (1997), and damage to the nervous system and mammary gland - Wiklund (1994). This herbicide has been used in large scale around the world, in countries such as USA, Brazil, New Zealand, Germany, Portugal and other European countries - Algzaga (1996), Batista (2002), Cerdeira (1998), Close (1991), Leistra (1989), Pucarevic (2002), Tappe (2002). Its widespread used and its atmospheric dispersion led to the discovery of atrazine even in isolated areas of the globe – TompkinsCounty (2002). Therefore, the remediation of soil contaminated with atrazine is an important and challenging problem.

SOIL DECONTAMINATION TECHNIQUES

The soil is a structure that is stratified. The upper layer is the unsaturated zone (or infiltrating zone), below which we have the saturated zone. There are many characteristics of the soil that influence the transport of contaminants, such as: density, porosity, humidity and permeability. This phenomena is also influenced by some properties of the contaminants, such as vapor pressure and chemical nature - Norris (1993). After identifying the type of soil and the nature of the contaminants, a suitable remediation technique must be chosen, and the effectiveness of the decontamination process evaluated.

The existing methods for soil decontamination may be divided in - Fiúza (2002): “in situ” techniques, “ex situ” techniques, and the confining/isolation of the contaminated area, which is a temporary solution. These methods can be further divided in biological and non-biological methods. The non-biological methods are subdivided in physical-chemical methods, thermal methods and others methods (e.g., supercritical extraction and electrokinetic). In tables 1 and 2 some of the existing decontamination techniques are summarized, and some of their advantages and disadvantages given.

Table 1- Advantages and disadvantages of some biological technologies used in soil remediation.

	Advantages	Disadvantages
Landfarming	-Relative simple design and implementation; -Short treatment times (six months to two years under optimal conditions).	-Reductions of concentration greater than 95% and concentrations lower than 0.1 ppm are difficult to achieve; -The required area is high; -Dust and vapor generation during landfarming aeration may cause some air quality problems.
Bioventing	-Uses readily available equipment, easy to install; - Creates minimal disturbance to the treatment site; -May not require costly off gas treatment; -Easily combinable with other technologies (e.g., air sparging, groundwater extraction).	-The high concentrations may be toxic for microorganisms; -Not applicable for certain site conditions (e.g., low soil permeability); -Sometimes requires nutrients and air injection wells; -Only treats unsaturated zones of soils, and needs other methods to treat saturated zones of soils and groundwater.
Natural attenuation	-The generation of less remediation waste, and less impact on the environment; -Ease to use when combined with other technologies; -No equipment down time.	-The public may not perceive the effectiveness of the process correctly; -Site characterization can be more costly and complex; - Due to monitoring, active remediation may be more economical; -The potential exists for continued migration.
Phytoremediation	-Is much less expensive than conventional options.	-Is a technology that is seasonal; - Only applicable to low profundity.
Biosparging	-Readily available equipment; -Cost competitive; -Requires no removal, treatment, storage or discharge of groundwater.	-Some interactions among complex chemical, and physical and biological processes are not well understood; -Potential for inducing migration of constituents.
Bio – Rehabilitation in-situ	-Degradation of material dissolved in infiltrated and saturated zone; -Equipment easily available.	-The hole can be obstructed by biomass or precipitation; -Continuous monitoring and maintenance.

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Table 2 - Advantages and disadvantages of some non-biological technologies used in soil remediation.

	Advantages	Disadvantages
Vitrification (Thermal)	-Ex situ vitrification is a well developed technology; -The mobility of contaminants is reduced/eliminated; -The vitrified mass resists leaching for geologic periods of time.	-The process requires intensive energy and high temperatures up to near 2000 K; -Water in soil affects operation and increases the total costs of the process; -Off gases must be collected and treated before release; -In situ vitrification is in pilot scale development.
Incineration (Thermal)	-Contaminant toxicity, as well as volume reduction is addressed by this technology. This is specially true for organic contaminants; -Widely used and available commercially.	-Metals are not destroyed and end up in the flue gases or in the ashes; -Community resistance to incineration is often present; -Certain types of soils such as clay soils or soils containing rocks may need screening.
Soil Washing (Physical-Chemical)	-Reduces the volume of contaminant, therefore, further treatment or disposal is less problematic; -Commercially available.	-Contaminant toxicity is unchanged, although volume is reduced; -Less effective when soil contains a high percentage of silt and clay; -Costs associated with the disposal of the subsequent waste streams must be considered.
Soil Vapor Extraction (physical-chemical)	- Proven performance, readily available equipment, easy to install; - Minimal disturbance to site operations; -Short treatment times (6-48 months).	-Concentration reductions greater than 90% are difficult to achieve; -Effectiveness decreases when applied to sites with low permeability; -Only treats the unsaturated zone; -May require costly treatment for atmospheric discharge of the extracted vapor.
Electrokinetic (others)	-In situ technology that has small impact on environment (soil removal is not required). -Metals are actually removed from soil unlike stabilization, that leaves the metals in the soil.	-Alkaline soils reduce the effectiveness of the process; -Requires soil moisture.

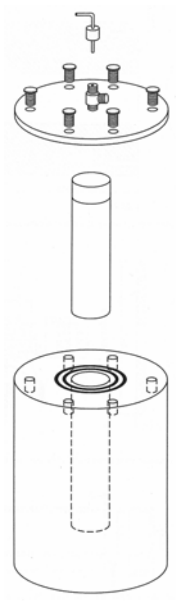
SUPERCRITICAL EXTRACTION APPLIED TO DESCONTAMINATION OF SOIL

The supercritical extraction (SCE) is a technology that is yet in an embryonic state of development for the decontamination of soils. SCE is an extraction process in which the solvent is a supercritical fluid (SCF), which is any substance when used above its critical pressure and temperature. SCF have densities typical of liquids, viscosities close to those of gases, diffusion coefficients that are between those of liquids and gases, and surface tension equal to zero. These properties make SCF particularly good solvents to extract solutes from solid matrices. Due to their high compressibility near the critical point, it is possible to change the solvating power of a SCF between that of a liquid and that of a gas by tuning the pressure of the fluid – Martinez de la Ossa (1990), thus allowing the fractional extraction and separation of solutes and the complete recovery of the solvent by simple pressure reduction - Medina (1998). The mechanisms of decontamination of soil by SCE are similar to the techniques based in solvent extraction, however, due to the transport properties of SCF, SCE is usually more efficient, requires smaller extraction times, is less energy intensive, and does not leave solvent residues in the soil - Bretti (2002).

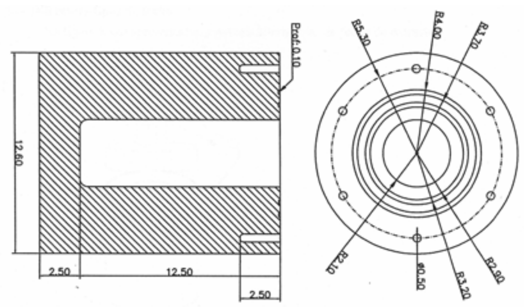
The most widely used SCF is carbon dioxide because of its favorable properties: is nontoxic, nonflammable, not corrosive, inexpensive, does not create additional impact in the environment, does not affect significantly the organic structure of the soil, and has critical properties easy to attain technologically (Pc=7.4 MPa, Tc= 304.2 K) – Glen (1998). The application of SCE allows the extraction of the contaminants, which can then be destroyed by combustion or biodegradation (when possible) - Ghonasgi (1991). SCE has been suggested for the removal of toxins from soils and groundwater – Ghonasgi (1991), and the remediation of soils contaminated by polychlorinated biphenyls (PBCs) – Markowz (1996), polycyclic aromatic hydrocarbons (PAHs) – Tavlarides (2000), pesticides –Yarita (1996), among many other compounds. A new application of SCE has been proposed by researchers at the INEEL (Idaho National Engineering and Environmental Laboratory) for treating soils contaminated with radioactive elements, such as plutonium – ENN (2001). There are also other more futuristic applications of SCE, as the possibility of using the CO2 that exists in the atmosphere around Mars to dissolve and extract minerals, water and others substances from Martian dust –Vanderbilt - School of Engineering (2002). It seems clear that we are only at the beginning of using all the advantages that SCF offer to help improving our environment.

SUPERCRITICAL FLUID EXTACTOR

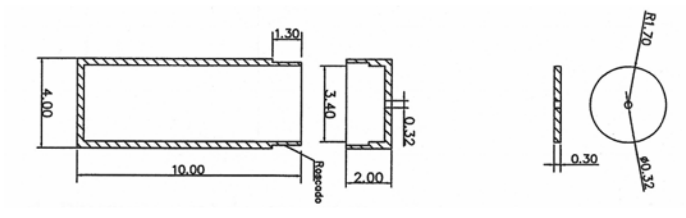
In the supercritical extraction process the contaminated soil contacts continuously with the supercritical fluid in an extractor. In Figure 1, the project of the extractor that is going to be used in this project is shown. The fluid is previously compressed up to a pressure and temperature above its critical point (e.g., in a syringe bomb), and after contacting with the contaminated soil is depressurized precipitating the dissolved contaminants. The gas may then be compressed and fed again to the extractor.



a) The extractor.

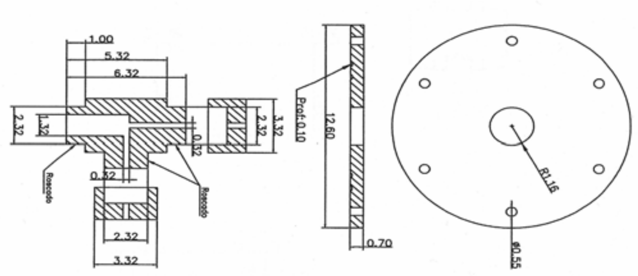


b) Cross sectional cut of the extractor.



c) Cross sectional cut of the extractor body.

Figure 1 –Schematic representation of the extractor



d) Cross sectional cut of the closing

Figure 1 –Schematic Representation of the Extractor *(cont.)*.

ANALYTICAL TECHNIQUE

The extract obtained by SCE must be quantified and characterized by using an appropriate analytical technique. In this research the extract will by characterized by using High Performance Liquid Chromatography (HPLC) carried out in a HP1050. This is the most used technique for analyzing pesticides – Trajkovska (2001), particularly for polar pesticides such as atrazine, because it allows the use of ambient temperatures avoiding the risk of decomposition and is less time-consuming and labor-intensive than GC for this type of analysis - Hewlett Packard (1993). Since in our preliminary studies we will only analyzed the extraction of a single pesticide, the isocratic elution method will be the choice for carrying out the analysis.

CONCLUSIONS

The soil is a complex living system, and the success of its decontamination and the choice of the remediation technique depend on its characteristics and the type of contaminants - Laittinen (1994). However, supercritical extraction with CO2 is emerging as a promising technique for decontamination of soils because it has low impact in the soil structure and on the ambient. By tuning the density of the SCF (by pressure changes) it is possible to extract many classes of compounds ranging from polar to apolar species.

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