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BENTOMET

DESIGN AND CONSTRUCTION OF A BENTONITES RECYCLING LINE FOR THE
PRODUCTION OF A HEAVY METAL ADSORBENT

Deliverable D.6.3.

Visits of potential clients

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PU	Public	✓
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for member of the consortium (including the Commission Services)	

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1. Objective of the market analysis

The main objective of the deliverable D6.3 “Visits of potential clients” is to study, identify and contact with the main interested parties of the products to be developed in the BENTOMET project.

The design and construction of a bentonite recycling line could be very useful for several industries, for example for that which generate bentonite waste in their industrial processes and have to pay for the subproduct treatment to specialized waste management companies, as distilleries.

Furthermore, the obtained product from this recycling line will be very interesting for a wide range of industries, because it will result in an efficient and cheap heavy metal adsorbent.

The market analysis will be focused on four groups:

- Providers of bentonites: wineries, among others.
- Industrial sectors which generate heavy metals
- Potential clients of the product obtained from the bentonite recycling.
- Competitors

2. Bentonites Providers

There is a wide diversity of companies that could provide contaminated bentonites for its recycling, as they are used in a lot of processes as oil, wine and cider clarification.

In the case of this project we have chosen bentonites from wine clarification, and we have contacted with the following wineries:

- **Bodegas Fernández de Arcaya:**

Familiar winery which started its activity in 1990 with the varieties Tempranillo, Cabernet Sauvignon and Merlot in their own vineyards, planted since 1982.

For this purpose, all their buildings were remodeled by installing small stainless steel tanks, which all together have a production capacity up 594 000 litres.

The ageing is completed in American and French oak barrels. The winery makes red and rose wine under the brands “Fernández Arcaya” and “Viña Perguita”.

Bodegas fernández de Arcaya has a clear orientation to the production of quality “Crianza” and “Reserva” red wines, without neglecting the production of young red, rose and white wines. These wines are commercialized with the brands “Fernández de Arcaya” and “Viña Perguita”.

- **Bodega Barón de Ley:**

This winery was designed and founded in 1985 with the objective of building a winery inspired in the “Chateaux” of Medoc, with the objective to manufacture wine as work of art.

So they bought the land of Imas in Mendavia, placed on the left hand of Ebro river, with the best climatic conditions and the best soil composition for an excellent wine.

The first results of this ambitious project came out in 1990, when the first bottles of Barón de Ley were commercialized.

Currently Bodegas Barón de Ley has a winery for the elaboration, ageing and bottling wine of DOC Rioja.

In this winery are elaborated young wines, “Crianza” wines, white and rose wines with the brands:

- Barón de Ley Gran Reserva y Finca Monasterio
- Barón de Ley Reserva.
- Barón de Ley blanco y rosado.

A sign of the quality of these wines are the important prizes they have won.

- **Bodegas Navarsotillo:**

Familiar winery where are elaborated exclusively DOCa Rioja wines, with ecological agriculture certification.

Navarsotillo defends the ecologic agriculture betting for the collection of quality foods through low environmental impact techniques.

All the winery's activity is supported by modern installations. For the wine ageing American and French oak barrels are used and it has adequate bottle rack for the wine ageing, taking care of the tastes of the wines.

This is completed with exhaustive work procedures to assure the final product quality.

A prove of this work are the certifications of quality management systems, environmental management and food safety management. The certification of Navarsotillo is expanded with their certifications of Organic Product for USA (NOP certification) and for Suisse (Bio Suisse).

The current production amount is nearly 700 000 kg of grapes per year. The sales volume is about 400 000 bottles of wine (250 000 of red young wine and 150 000 of "Crianza" wine). For this production, 500 barrels are used (80% American oak – 20% French oak) which are replaced roughly 90 barrels per year.

- **Bodegas San Martín:**

Bodegas San Martín is a Cooperative Society founded in 1914. The winery is placed in the area named as East Middle Navarra, in the village San Martín de Unx.

It produces 3 000 000 litres of wine per year, which are mostly sold in the north of Spain (Navarra and País Vasco) and exported to France, Germany, Netherlands, USA and Venezuela.

Bodegas San Martín dedicates the most of its wine-growing area to autochthone grape varieties as Viura (Macabeo) in white wines and Garncha and Tempranillo in red wines. It has some French varieties as Merlot and Cabernet Sauvignon which complete and expand its wines.

- **Bodegas Aroa:**

In 1998 a business of organic products was established by Laket and Aroa in the same company. Since 1998 the actionists were regrouped and there were founded two societies, Laket Bio which continues with the distribution of organic products and Aroa Bodegas which produce wines.

The wines elaborated in this winery are selected wines, produced with several varieties of red grape: Tempranillo, Cabernet Sauvignon and Merlot, as a result of a impeccable viticulture.

All Aroa's wines are controlled and certified by the CPAEN-NNPEK.

- **Doniene Gorrondona Txakolina:**

Doniene Gorrondona (Bentalde S.L) is a modern winery where txakoli is produced by a professional way.

The winery is placed in the coastal town of Bakio, considered the heart of txakoli in Vizcaya.

The main activities of the winery are:

- Viticulture: they produce all the grapes in the winery.
- Winery: they elaborate about 70 000 litres of txakoli
- Distillery: they distill the residues of the production of txakoli
- Enoturism: they organize visits and wine tasting in the winery

Hondarribi Beltza and Hondarribi Zuri are the identity signs of the winery, autochthones varieties of red and white grapes, which are giving positive results in the several productions they are making.

In addition to the installations for txakoli elaboration, the winery has a distillery constituted by five copper stills where the residues of Hondarribi Zuri and Hondarribi Beltza are distilled.

3. Recycled bentonites sectors of application

The products developed in this recycling line will be mainly destined to the industries which generate heavy metals wastes which are very toxic and their treatment is very difficult.

These wastes, which would afterwards contaminate water or air, could come from natural sources or human activities. Currently, the most important source is, without any doubt, the last one.

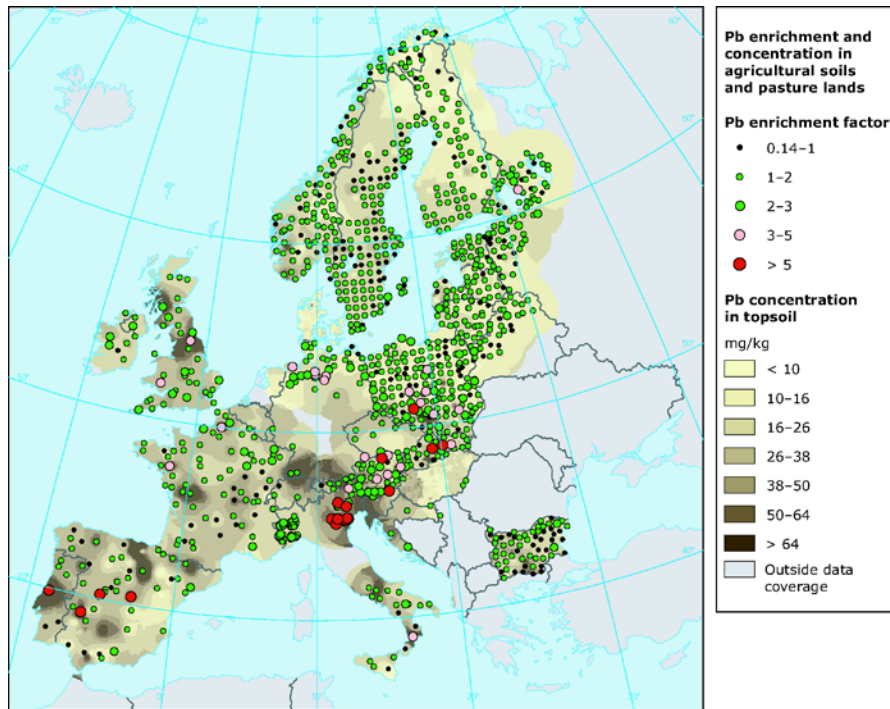
There are two main human pollution focuses which generate great amounts of heavy metals wastes:

1. Urban wastes: Domestic activities mostly generate organic wastes, but the sewage drags all type of substances: cars emissions (hydrocarbons, lead, other metals...), acids, salts, etc.

The required construction of waste treatment plants in towns is cutting down this kind of pollution, but in Spain the waste water treatment is still very poor.

2. Industry: Depending on the type of industry so many types of wastes are produced. Usually, in developed countries, many trades have efficient water purification systems, especially those which generate hazardous pollution as heavy metals. On the other hand, in some non-developed countries the contamination of water due to industrial wastes is very high.

In the following picture it is shown the heavy metals' contaminated soil of Europe:



Lead concentration in Europe's soil

Polluters can be classified in the following way:

Industrial area	Main polluters
Building industry	Solids, heavy metals, pH
Mining industry	Solids, heavy metals, pH, organic matter, cyanides.
Energy industry	Heat, hydrocarbons, chemicals
Textile industry	Chromium, tannines, sulphides, dyes, surfactants, organic solvents, fats, formic and acetic acid, solids...
Automotive industry	Lubricating oils, paints, waste water.
Shipbuilding industry	Oil, chemicals, solvents and pigments.
Steel sector	Metal husk, oil, dissolved metals, acids and bases.
Inorganic chemistry	Hg, P, fluorides, cyanides, amoniac, nitritos, ácido sulfhídrico, F, Mn, Mo, Pb, Ag, Se, Zn, etc. y los compuestos de todos ellos.
Organic chemistry	Organohalogen, organosilicious, carcinogenic compounds and other which affect to oxygen balance
Fertilizers	Nitrates and phosphates

Paper industry	Solids and other which affect to oxygen balance
Pesticides	Organohalogen, organophosphate, carcinogenic compounds, biocides, etc.
Painting and dye industry	Compounds of Zn, Cr, Se, Mo, Ti, Sn, Ba, Co, etc.

The current document would focus on the main industrial sectors which produce heavy metals wastes.

3.1) Textile industry:

The textile industry is chemically intensive, employing different chemicals for every process, from the coating of the fabrics to the printings and finishing processes.

The waste water from these processes is usually toxic and could pollute important rivers. These dangerous discharges could negatively affect human health, wildlife and environment. The heavy metals, such as cadmium, lead and mercury, are used to make some dyes and pigments. Chromium (VI) is commonly employed in some textile processes and in leather tanning.

These metals are accumulated in the organism along the time and are highly toxic with irreversible effects, including nervous system damage (lead and mercury), or in kidneys (cadmium). Cadmium is also associated with cancer.

Chromium (VI) is very hazardous and carcinogenic even in low quantities.

3.2) Steel industry

The steel sector is characterised for having an important social and economic impact. In Spain, approximately 137 000 companies work in this sector, which results in, approximately, a third of the industrial production of Spain.

The steel industry contaminates the soil in several ways:

- By dust and aerosol emissions which are carried by air and placed on the growth and soil.
- By effluents which contaminate soils in floods.
- By landfilling where metals can be corroded and lixiviated to soil. Many heavy metals are used in steels and alloys, so the manufacturing or recycling of these materials can result in environmental pollution.

3.3) Mining industry

Although current techniques of mining and casting are, in general, efficient and the rock pieces have low amounts of heavy metals, during the XIX century, these pieces had great amounts of heavy metals because the inefficient separation processes. In this sense, the waste particles, which could be carried by water or air, were a significant source of heavy metal pollution in soil in regions near mines and casting areas.

Once in the soil, the mineral particles are oxidized and, then, the heavy metals are introduced into the soil.

3.4) Microelectronic industry

A wide range of heavy metals including Cu, Zn, Ag, Au, Pb, Sn, Y, W, Cr, Se, Sm, Ir, In, Ga, Ge, Re, Tb, Co, Mo, Hg, Sb, As and Gd are used in the manufacturing of semiconductors, wires, connections and another electronic components. For that reason, the environmental pollution resulted from the manufacturing as well as any accidental contact of their wastes with soil, could be considered as the main source of contamination of this industry.

3.5) Chemical industry

Another important heavy metal pollution source is the manufacturing or use of batteries, paints, pigments, catalysts, stabiliser polymers, plastics, medical products, additives in oils and lubricants...widely employed in the chemical industry.

3.6) Paint and dye sector

Paints and dyes have synthetic products from petrochemical industry which could affect the environment and human health.

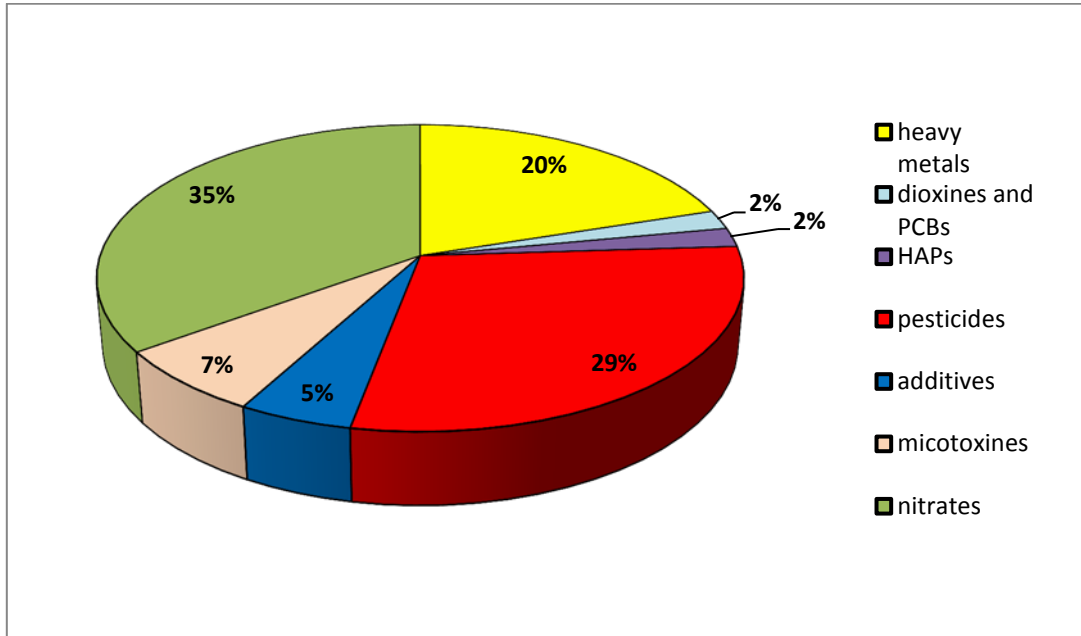
The risks of these products are the presence of heavy metals as lead, cadmium, mercury etc, and organic volatile compounds as xylene, toluene, phenols and formaldehydes, which are emitted by paints and varnishes while they are applied and even weeks later.

3.7) Agricultural Industry

Agricultural practices are another very important source of heavy metals in water and in soils and which affect to most of the world, especially in areas of high activity. The main sources are:

- Impurities in fertilizers: Cd, Cr, Mo, Pb, U, V, Zn
- Waste water and slurries: Cd, Ni, Cu, Pb, Zn...
- Animal dung, mainly birds and pigs, of the intense animal production: Cu, As, Zn

- Pesticides: Cu, As, Hg, Pb, Mn, Zn
- Organic fertilizers waste: Cd, Cu, Ni, Pb, Zn
- Wood preservatives: As, Cu, Cr
- Metallic objects corrosion: Zn, Cd



4. Recycled bentonites potential clients

Basing on the industrial sectors mentioned before, we contacted with the following companies, with the aim of offering them the developed product in this project:

Waste Water Treatment Plants (WWTP):

- **SMSA:**

Servicios de Montejurra (SMSA) is a company in charge of managing and promoting the rational use of water at Montejurra's Mancommunity.

SMSA does this task from an integral perspective because it treats the water in all its phases, from its collection in the river to its discharge.

As the management entity of the integral water cycle, the activity of SMSA covers the processes of:

- Water collection
- Water purifying
- Water distribution
- Sewage treatment
- Water spill

Its main tasks are the treatment of water and urban wastes, but it also develops other actions of great interest social areas.

- **EDAR Tafalla Olite:**

It is the waste water treatment plant of Tafalla and Olite. In this plant several processes are done with the objective of obtain purified water suitable for discharge. These processes are: pre-treatment, physical primary treatment, biological secondary treatment of active slurries.

Furthermore, the slurries produced are sanitized and dehydrated.

This waste water treatment plant discharges water to Cidacos River, this water is the most important fluent volume so its condition needs to be optimal.

- **EDAR Tudela:**

This waste water treatment plant provides service not only to Tudela, also to Murchante, Cascante and Fontellas. It's water treatment tasks are very important because it returns the fluent to the most polluted river in Spain: Ebro river. This river is the second more long in the mainland and it passes through Spain.France and Andorra.

In Navarra there are other waste water treatment plants which release their water to Ebro River for example in Viana, Mendavia, Lodosa-Sartaguda, Azagra, Castejóm. Valtierra-Árguedas and Bajo-Ebro.

- **Navagua:**

Navarre company which designs, builds, installs and maintenances plants and equipment which could treat all kind of water for its use in industries, towns or sanitary water.

Its job goes from defining the best kind of treatment for each circumstance until the installation and maintenance.

Metal industry:

- **Tecnimoem:**

Tecnimoem is a company founded in 1997 in Navarra, which develops, produces and distributes beds and complements for domestic, sanitary and geriatric use.

It has become a leader in the sector thanks to the quality of the developed processes, and they have expanded their products to all Spain and now they are expanding to international market.

- **TEIM:**

Tecnología Electrostática e Industria del Metal (TEIM) is a company founded in 2008 in Marcilla (Navarra) which produces machined metal sheets. They make several processes like cutting, welding, sanding...of metal sheets of several materials like electroplated, iron, aluminum, alloys...

Despite its recent start up, TEIM has a defined market, the major part of their products are destined to industrial clients out of the metal sector, for example: Gamesa Valencia, Jofemar, Faeco, Exkal y Metalcomponentes MB.

Paints and dyes industry:

- **KUPSA:**

KUPSA Coatings is a company founded 40 years ago with a trajectory focused in the production of wood protection products and similar materials.

Nowadays KUPSA has a production capacity of more than 30 000 tonnes per year of products for wood, industrial carpentry, and related products, plastics, etc... That put it at the forefront of the sector in Spain.

- **Barpimo:**

Barpimo is a familiar company founded in Nájera (La Rioja) fifty years ago, which manufactures and commercializes varnishes and paintings for wood, decoration, building and industry.

It has experienced a continuous internationalization process. As a result, Barpimo Group has now more than 5000 clients in the five continents.

- **Pinturas Fierro:**

Is a family company founded more than 100 years ago in Barbastro (Huesca), which manufactures and commercializes paintings.

All its products are properly tested under rigorous certifications made at develop and quality control laboratory, by qualified staff.

The company could work in continuos or discontinuos thanks to its versatile installations.

- **Colorcenter:**

Color Center, S.A. is a chemical company founded in 1978 which has been dedicated since its start to the designing, manufacturing and marketing of dyes and auxiliary products for the textile industry.

The company works in the development, acquisition and formulation of new materials and nano-materials, always by an environmental friendly way.

They have a wide range of products which cover all steps in the textile process and another related, giving products as detergents, softeners, oils, organic emulsions, pigments...and others.

5. Competitors

Traditionally, industrial effluents have been treated with a combination of physical-chemical combination, as flocculation, precipitation and filtration; and biological processes as activated slurries. However, these processes fail because they aren't able to reduce the amount of heavy metals i under the levels permitted by law.

Furthermore, these technologies are not capable to easily differ the composition of the wastes, being difficult to reuse or recycle the subproducts and, as a consequence the obtained slurries are very difficult to treat.

WWTP aren't designed to treat toxic wastes. Metals and its toxicity persist even in the treated slurries, for that reason, they must be removed in the emissive source, in a special designed pre-treatment.

This specific treatment should be characterised for not being too expensive since, in some occasions, large volumes of effluent need to be treated. As a result, research has focused their efforts on developing new materials and techniques capable of adsorbe heavy metals.

Some of the technologies employed in the separation of metals from the effluents for its later recovery are chemical precipitation, recovery with solvents and adsorption and ionic interchange processes based on membrane technology. Hereafter, they are briefly described:

5.1. Chemical precipitation

It is considered the standard treatment for removing metals from all type of waters. The capacity of removing metals depends of two factors:

- The solubility of the most soluble metal specie that can be formed, which depends of the pH and the concentration of the precipitating species.
- The separation of the solid from the aqueous solution. These factors made that precipitation is not very effective when the metal is in low concentration, because a precipitating agent is needed to form a precipitate, and in many cases the solid formed particle hasn't the enough stabilization to separate from the solution.

To overcome this barriers, a co-precipitation treatment is often used, adding iron or aluminium hydroxide with the precipitating agent with the aim of they act as a coagulant or adsorb the non-precipitating metals.

5.2) Recovery with solvents

It is one of the separation technologies more established to remove the heavy metals from industrial effluents. This process is often used at a bigger scale when the concentration of the polluter is higher.

Solvents used are more selective each time, which allow separate the specific molecules from the aqueous phase while the rest are retained. The recovery with solvent has a great commercial application in those cases which a selective separation of metallic ions is required.

This procedure consists in getting in touch an organic apolar solvent with the waste water and the metallic ions are transferred to the organic phase forming a metallic complex insoluble in water. When the organic phase is charged is put in contact again with another aqueous phase and the metallic ions are transferred to this new aqueous solution which is returned to the process again (reextraction)

This technology requires of great amounts of organic extracting agents, which increase the economic costs. When the amounts of polluter are under 5g/L this process is not economically viable.

5.3) Membrane technology

A membrane is a semipermeable barrier in which only can pass through some chemical species.

Historically the membrane technology has had a vast application in treatment and desalinization with the inverse osmosis. In this process a potential difference is used to overcome the osmotic pressure gradient. Under these conditions ions can't pass through the membrane and they are separated from the solvent.

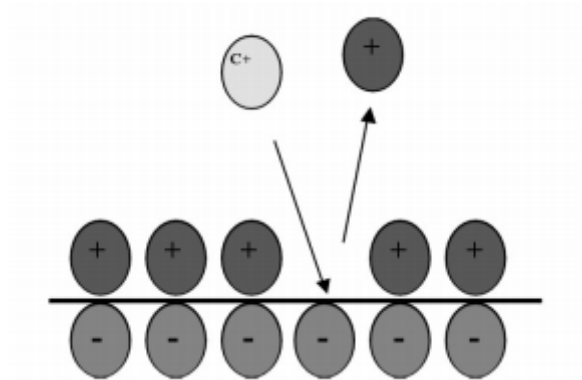
5.4) Ionic interchange:

It's an electrostatic interaction mechanism due to the Coulomb attraction forces which have place when an ion from a solution is interchanged for another ion with the same charge which is bonded to an immobile solid particle. When the concentrations of the metals in effluents are low, the use of membranes or recovery with solvents are inefficient. In this case an alternative technology is required: the ionic interchange.

Most of the geologic materials have a negative charge on its surface so the interaction is mainly with the cations present in the solution.

Usually, it is a fast and reversible process that depends on the water ionic force. When the ionic force is high, it is a big competition between soluble cations for the interchange places on the solid's surface.

The following picture shows how the cationic interchange between two species is produced:



As it has been mentioned before, the main problem of the current treatments for this task is or the low effectivity either the high economical cost.

There is a company which produces bentonites with the aim of employ them as heavy metals adsorbents in water is SEPIOLSA.

SEPIOLSA is a mining company founded in 1986 which extracts and commercialize special clays (sepiolite, bentonite, estevensite-kerolite, atapulgite...) which are used in several industrial applications: adsorbents, animal feed additives, sand for cats, oil and fats clarification, industrial adsorbents for toxic products...

It has a business model with own mine yards in Madrid (sepiolite and bentonite), Toledo (clarifying earths) and Senegal (atapulgite); and processing plants in Guadalajara (Spain), Mbodiene (Senegal) and Ostende (Belgium).

However, the bentontie they produce is pure and not-improved, so its heavy-metal adsorbent capacity is worst.

6. Summary

The market analysis has allowed the consortium to confirm that the recycling of bentonites has a huge interest in different sectors.

On the one hand, there are different companies interested in the recycling process in order to reduce the amount of wastes generated in their processes and the cost of their treatment in specialized centres, as wineries.

On the other hand, there are companies interested in the recycled material to incorporate it in the depuration of their industrial waste waters, rich in heavy metals.

However, it is very important to optimize the project as much as it's possible with the objective to develop a competitive product with high performances and, thus, be capable to easily incorporate it in the market.