Entry to the Stockholm Junior Water Prize 2022

ECO - FILTER

coffee grounds as a resource for the planet

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Index:

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Summary:

One of the most widespread environmental problems in the increasingly industrialised word, is heavy metal pollution. The most common and harmful heavy metals are cadmium, mercury, lead, zinc, and copper.

The exposure of the body to high concentrations of these elements constitutes a great health hazard. These metals cause serious problems in aquatic ecosystems and organisms, with serious repercussions on human health due to bioaccumulation and bio-magnification, harmful effects in the short and long term

Today's methods of water purification from heavy metals involve the use of other substances which in turn produce waste that needs to be treated or disposed of, with great costs and high environmental risk.

There are therefore already several solutions, but while investigating the issue we have found out a cheaper alternative with also a lower ecological imprint.

The idea here is to use spent coffee grounds as a substrate for adsorption of heavy metals from aqueous solution.

For this reason, according to the principles of self-sustainability of the process itself, we have developed ECO-FILTER. We have designed a plant where at every step of the process it is possible to have a complete recovery of the by-products, with a view to a future circular economy.

Adsorption on spent coffee grounds of aqueous solutions and wastewater, containing heavy metals, accumulation, desorption and recovery of metals, develop in the cycle of the prototype chemical plant designed by us. Recycled waste material is used to solve an environmental problem, in a cycle that involves the reuse of coffee grounds and the recovery of metals as fundamental steps of a self sustainable process.

To develop our idea we realized a series of experimental tests for the evaluation of the steps of preparation of coffee grounds, of the processes of adsorption and desorption of metals. These tests have allowed us to clarify the fundamental processes for conceiving and designing the treatment plant.

Introduction:

In an industrializing world, the production plants of different sectors, such as the plants of metal plating, fertilizer industries, mining and equipment usage technology are always expanding more; as a result, in recent years the discharge of metals heavy in the environment has increased dramatically, particularly, but not limited to, in developing countries development that makes the most of the systems we initially talked about.

Unlike other contaminants, heavy metals are not readily biodegradable, and they tend to accumulate in living organisms, causing various diseases and ailments [1], for this reason treatments of wastewater containing these elements became necessary before their unload.

It is by analyzing this problem that we students at the Enrico Fermi Institute of Mantua have wanted to develop a project that can remedy this situation, focusing on a method of eco-sustainable adsorption of heavy metals and adopting a scheme based on principles of the Circular Economy.

The idea is to use used coffee grounds as a substrate for the adsorption of metals heavy from aqueous solutions (at low concentrations); this method has already been studied and tested in several research, [2], [3], but the potential of this process has been underestimated and neglected.

Looking at the data that the STATISTA website provides us today (in the world) about 9997800 tons of coffee per year [4] which inevitably generate large amounts of non-waste recyclable, destined to make our planet more and more irreparable.

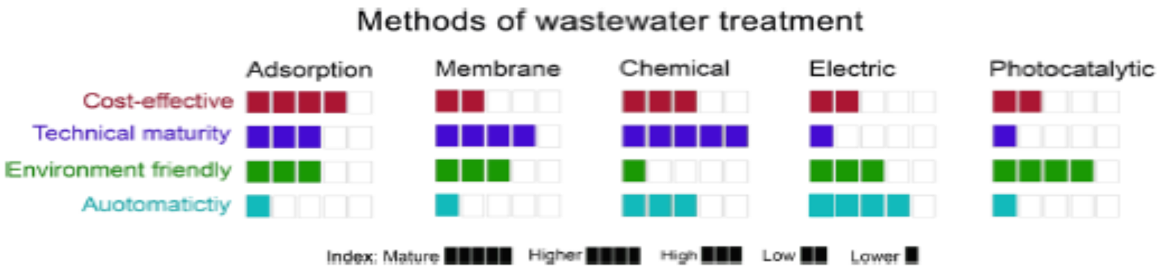
For this reason, the goal of our idea is to be able to give this a second life
material, which thanks to its low cost and high availability can be used as an adsorbent for the removal of heavy metals.

hypothesis and initial research

Our interest in research stems from the need to find an eco-sustainable and low-cost method
cost of absorbing heavy metals from water.

Among the most widespread and harmful heavy metals, we find cadmium, mercury, lead, zinc, and copper. These elements accumulate in the body without being able to be eliminated, causing harmful effects in the short term and long term, different depending on the metal. In fact, they can cause damage to the kidneys, to the system
nervous and immune systems, cardiovascular, reproductive, endocrine systems and in some cases have carcinogenic effects.

For several years now the studies and applications for the solution of this problem have led the development of many techniques, including adsorption on mineral or organic materials, the membrane filtration techniques, chemical methods of precipitation and complexation, techniques electrolytic and the most current photocatalytic techniques [5].



Methods of wastewater treatment

	Adsorption	Membrane	Chemical	Electric	Photocatalytic
Cost-effective	■■■■□	■■□□□	■■■□□	■■□□□	■■□□□
Technical maturity	■■■□□	■■■■□	■■■■■	■□□□□	■□□□□
Environment friendly	■■■□□	■■■□□	■□□□□	■■■□□	■■■■□
Auotomatictiy	■□□□□	■□□□□	■■■□□	■■■■□	■□□□□

Index: Mature ■■■■■ Higher ■■■■ High ■■■ Low ■■ Lower ■

Figure 1. Removal methods: comparison. Source [5]

In Figure 1 a comparison of the most popular methods with respect to costs in relation to maturity efficiency technique, environmental impact, and degree of automation.

One of the most used methods nowadays to reduce its concentrations in water is adsorption with activated carbon [6], this operation is based on the capacity of the activated carbon to adsorb, thanks to its porosity, also most of the organic substances. However, its use is often limited, sometimes absent due to the high costs that are proposed for this service. By continuing to accumulate substances on the surface of activated carbon, we have in addition, the gradual loss of adsorbing power. At this point it is necessary to intervene with a regeneration or replacement of coal. During this operation we have the formation of countless hazardous waste, which must be properly treated. The same spent coal is a dangerous waste and as such must be properly disposed of. There are also widespread studies and applications on nano porous materials related to activated carbons and silicas functionalized and combined and the introduction of carbon nanotubes in removal systems. The processes related to the preparation of the removal substrates lead to excellent results, however expensive and not always easy to replicate on a large scale [5], [6]. Some examples are given in Figure 2.

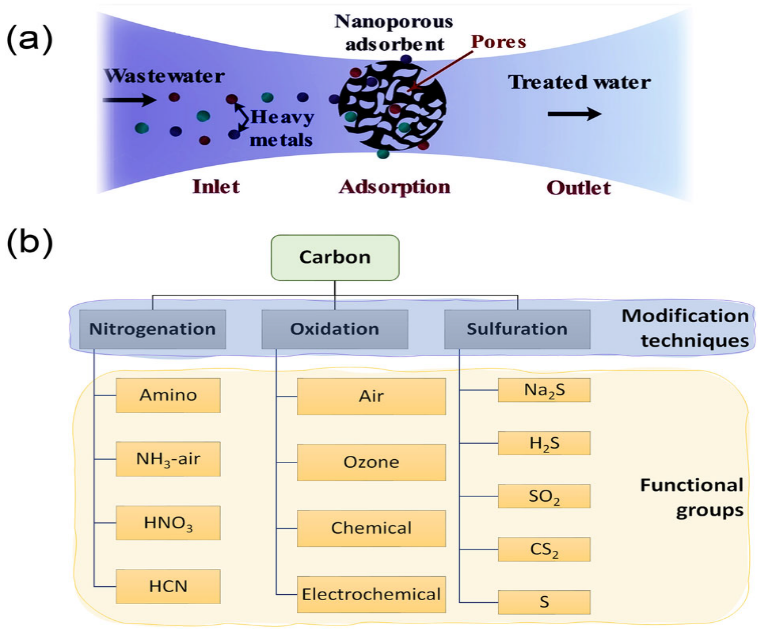


Figure 2. Some absorption processes used for water treatment. Source: [5].

Methods linked to bio absorption techniques are assuming an increasingly topical role and bioinertization, linked to the ability of some microbial species to resist and harden metals inertization for example in the form of sulphides. However, bioremediation techniques do not lead to a real degradation and show their potential with excellent results above allapplied to organic pollutants.

There are also already ideas for developing methods that start from recycled materials, such as filters a sand and rust from ferrous materials, which however still have some critical issues including numerous dangerous substances contained in ferrous waste (residues of pigments, paints, processing oils, plastic, and in turn heavy metals) [7].

Figure 2: Some absorption processes used for water treatment. Source: [5].

Several studies [2], [3] have shown that filtration using coffee grounds for the elimination of heavy metals or their use as soil improvers is a valid alternative to traditional process just outlined.

The treatment we propose, as well as the life cycle and method of use, are like that activated carbon. For this reason, a future process of replacing the two methods in a perspective environmentally sustainable industry is extremely facilitated.

In addition to this, our system appears to have numerous advantages in fundamental points of the process, the first of which are the lower costs of raw materials and a minimal ecological footprint.

A second point in favor lies in the regeneration phase, in fact, the funds can be regenerated through the desorption of metal ions with the use of dilute solutions of nitric acid, which in turn can be recovered after metal precipitation.

Compared to the traditional regeneration of activated carbon, in this case, processes are used easy recovery of desorbed ions. Entering specifically the metal ions form a solution of nitrates, which through the use of a precipitating agent could allow the recovery of the metal in the form of an insoluble salt, thus producing a recoverable product with a acquired value.

In addition to the advantages just analyzed with an overall look, it can be appreciated as in everyone step of the process it is possible to have a complete recovery of the by-products, in view of the circular economy.

Our last goal is to develop a scalable plant prototype aimed at purification of water containing metal cations (Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}), using funds of coffee as adsorbent substrates.

Our route

To better organise the work, we divided it into two phases:
1. Experimental tests: realisation and discussion of a series of experimental tests for the evaluation of the steps of preparation of coffee grounds, the processes of adsorption and desorption of metals;
2. Design and design of the plant.

Step 1. Experimental tests; materials and methods

Before proceeding with the tests, we collected 1kg of coffe grounds from the school bar. We put them to preliminary leaching treatments in an acid and basic environment with diluted solution, in order to stabilize the product and avoid interference in adsorption and release of dyes and organic substances in purified water, also trying to assess the possibility of recovering at the same time natural dyes that could be used in a circular economy perspective.

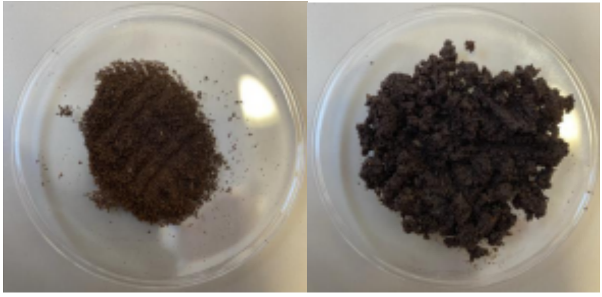


Figure 3. Coffee grounds before and after treatment

First we washed the coffe grounds with distilled water and filtered them with a Buchner funnel to remove coarse impurities (everything they could contain that wasn't purely exhausted coffe); subsequentely we subjected them to several leaching cycles with Buchner funnel, short and with small volumes of solution (test from 1 to 20 cycles) with NaOH 0,01M at room temperature. We also carried out hot tests and and noticed that heating NaOH to about 100°C we got the desired result faster (fewer leaching cycles were needed for coffe ground cleaning), but in order to set up an industrial plant this solution would require a greater energy loss. We then put the coffe grounds in a beaker with HNO3 0,01M for about 4 days, we filtered again and washed them with distilled water until a pH close to 6 is reached, finally we dried them in the stove at 100°C for 1h. These two washes, with NaOH and HNO3, have the function of making unwanted molecules more soluble and therefore more easily extractable from coffe ground. In this way the unwanted molecules do not interfere with the following steps and go to offset the recovery of metals. The treatment also has the purpose of verify that the water is transparent, colourless and without impurities due to funds once subjected to adsorption.

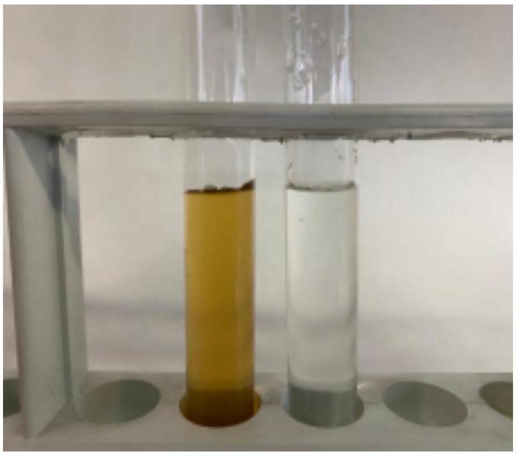


Figure 3. waste water after adsorbtion with untreated coffe grounds (left)
And with leached coffe grounds (right)

Adsorbtion

Adsorption is a phenomenon whereby the surface of a solid substance, called adsorbent, collects molecules from a gas or liquid phase with which it is placed in contact (the surface is both the outer and the 'internal' one such as capillaries or fractures etc…). Since a molecule adsorbing itself, that is by binding to a surface, decreases its degrees of freedom (because it has less possibility of movement), the phenomenon is accompanied by a decrease in entropy, so to increase its efficiency it can be favored under the right conditions.

We can observe two different types of adsorption: physical and chemical. The first one takes place when molecular attraction forces (Van der Waals forces, London forces) come into play etc.) or primary bonds (covalent bonds, ionic bondsSince physical forces do not depend on the specific nature of the substances in contact, physical adsorption always takes place, while chemical adsorption overlaps with the previous one only when binding interactions occur. In our study case we hypothesized that physical adsorption may be predominant, although chemical interactions are not to be excluded on organic support. However, we do not currently have experimental verifications.

Operationally

We have prepared two solutions containing heavy metals at known concentrations to simulate wastewater. The first (Sol.1) it was prepared by dissolving 0,025g of $CuSO_4 \bullet 5H_2O$ in 1l of distilled water obtaining a concentration of 0,0001M; the second (Sol.2) it was prepared by dissolving 0,0169g of $CuCl_2 \bullet 2H_2O$, 0,0201g of $CdCl_2$, 0,0379g of $Pb(CH_3COO)_2$ of 0,0136g of $ZnCl_2$ in 1l of distilled water obtaining a concentration of 0,0001M for each metal.

Five adsorption tests were performed by changing some variables, such as the amount of coffee, the solution of heavy metals, time and continuous mixing.

Below we find schematized the test 1 and 2, the coffe grounds were in contact with solution 1. The only variable between them is the amount of funds used. After treatment the solutions were filtered on Buchner and collected for subsequent tests.

Variables	Test 1a	Test 2a
Amount of coffe grounds used (g)	0,85 g	1,08 g
Volume of Cu^{2+} solution (ml) used	175 ml	175 ml
Contact time between solution and coffe grounds	4 days	4 days

Table 1. Adsorbtion tests Cu^{2+} solution

Coffee grounds at this point theoretically rich in heavy metals achieve the desorbtion phase.

Qualitative test with the use of diphenylcarbazide

We performed a quick qualitative test to verify the adsorption of coffe grounds. We have exploited the formation of complexes, as solutions of this type are colored in the presence of certain metals. We put the Sol.1 and the filtrate in two tubes and added a little of diphenylcarbazide [Fig. 5] in each.

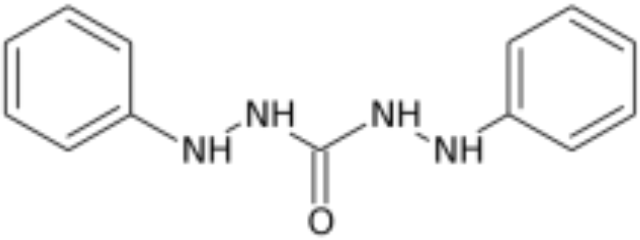


Figure 5. diphenylcarbazide

We noticed that the Slz.1 was colored a bright pink while the filtered of a softer pink, almost transparent, indicating the lower amount of copper. [Fig.6]

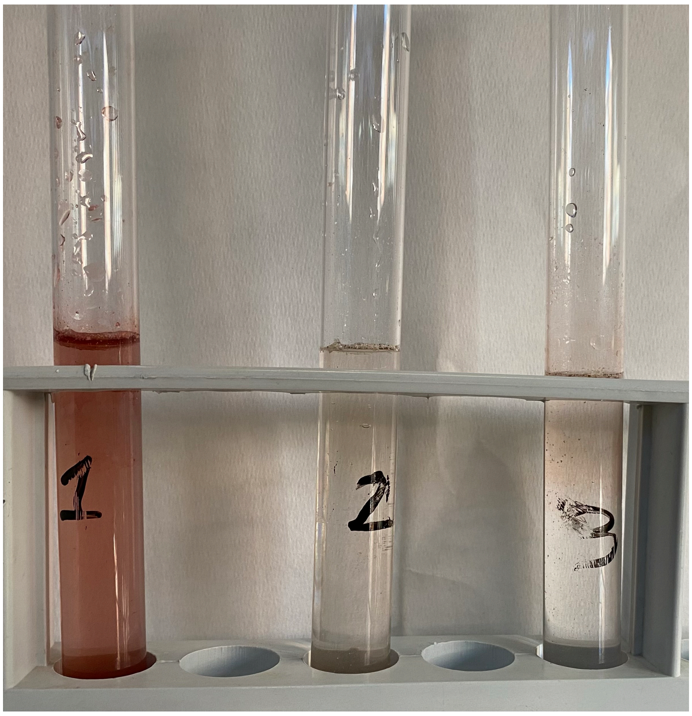


Figure 6. Test with diphenylcarbazide (test tube number 1 starting solution of CuSO4, test tube 2 filtered test 1a, test tube three filtered test 2a.

The next 3 tests (tests 3, 4 and 5) were in contact with solution 2 (multi-element). In these tests the amount of grams of adsorbent is constant (1g) while they have two other variables: the contact time between solution and coffe grounds and the movement of the solution by stir bar and magnetic stirring

Also in this case we subsequently performed the filtration with Buchner and recovered the treated solutions and the coffe grounds.

Table 2. adsorbtion tests multi-element solution

Variables	Test 3a	Test 4a	Test 5a
Amount of coffe grounds used (g)	1,00 g	1,00 g	1,00 g
Volume of Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+} solution (ml) used	175 ml	175 ml	175 ml
Contact time between solution and coffe grounds	4 days	1 h	1 h
Magnetic stirring	No	No	yes

Figure 7. Photographic sequence of the process of treatment.

Data discussion

To verify and increase the reliability of the adsorption tests we collected and sent the samples related to our tests to an external laboratory for the determination of quantities of residual metals through instrumental analysis with official method.

Below we find the data relating to the starting solutions and the five samples referred to the adsorption tests.

concentration of metal ions µg/l	Starting solution 1 Cu^{2+} (0,0001 M)	Test 1a	Test 2a	Method
Copper	7135 µg/l	65 µg/l ± 8	71 µg/l ± 9	UNI EN ISO 11885:2009

Table 3. Cu^{2+} solution analysis report.

For the first two tests, the results indicate a clear adsorption by the coffe grounds. Both solutions were in contact with the coffe grounds for 4 days.

The difference between the two samples is the amount of coffee used, as described above in the adsorption tests. Test 1a gave better results despite the smaller amount, 0.85g, demonstrating an adsorbent power of 99.01%. Test 2a considering the uncertainty gave a very similar result, despite the greater amount 1.08g, demonstrating an adsorbent power of 99 It is very likely that such a small variation in the initial mass of coffee will not lead to great advantages. It will therefore be important to conduct in a future research experiments that consider a larger variation of the starting mass.

Concentration of metal ions µg/l	Starting solution 2 Pb^{2+}, Cd^{2+}, Cu^{2+},Zn^{2+} (0,0001 M)	Test 3a	Test 4a	Test 5a	Method
Lead	20893 µg/l	1042 µg/l ± 823	3703 µg/l ± 1224	1304 µg/l ± 439	UNI EN ISO 11885:2009
Cadmium	11941 µg/l	4509 µg/l ± 732	5757 µg/l ± 934	5434 µg/l ± 882	UNI EN ISO 11885:2009
Copper	6537 µg/l	694 µg/l ± 86	1776 µg/l ± 219	660 µg/l ± 82	UNI EN ISO 11885:2009
Zinc	6734 µg/l	2732 µg/l ± 1405	4708 µg/l ± 4809	2849 µg/l ± 1548	UNI EN ISO 11885:2009

Table 4. Multi-element solution analysis report.

In these three tests the amount of coffe grounds remained constant, what varied was the adsorption time, 4 days in the 3a test, 1h in the 4a and 1h in the 5a, but with a constant stirring in the last test. Among the tests carried out with the solution containing more metals, the best result is found in test 3a. With the following percentages of adsorption per metal: Pb^{2+} -95,01%, Cd^{2+} -62,24%, Cu^{2+} -89,38%, Zn^{2+} -59,43%.
Test 4a was the worst, suggesting that 1h is not a long enough time for effective adsorption, below are the percentages of adsorbtion: Pb^{2+} -82,28%, Cd^{2+} -51,79%, Cu^{2+} -72,83%, Zn^{2+} -30,09%.
Test 5a went better than test 4a approaching the results of test 3a, overcoming them in copper adsorbtion.
The continuous stirring therefore can help to have a better adsorbtion.
Below are the adsorption rates: Pb^{2+} -93,76%, Cd^{2+} -54,49%, Cu^{2+} -89,9%, Zn^{2+} -57,69%. Considering all the adsorption tests, we can say that we have obtained good results. The best results were obtained with copper and with the lead.
Another consideration that may catch the eye when comparing the data from tests 1a and 2a is that the percentages of adsorption of copper were higher when it is in the solution alone which confirms competitive effects in the phenomenon of adsorbtion between the different metals: the adsorbing power could therefore decrease if more metals are present in the same solution..

Desorbption

Desorption is a necessary step to aim for a sustainability of this project; in fact, the goal is to "detach" the metals from the coffe grounds that have undergone the adsorption process, we can regenerate the coffe grounds and reuse them several times.

To perform the desorption tests we took some coffee grounds that had already passed the adsorption part, resulting rich in heavy metals, we performed three tests on three different coffe grounds as per Table 5.

Variables	**Test 1d**	**Test 2d**	**Test 3d**
Coffe grounds from the test	2a	3a	4a
Acid used	Hydrochloric	Hydrochloric	Nitric
Acid concentration	0,10 M	0,10 M	1, 00 M
Contact time between acid and coffe grounds	1 h	2 weeks	1 h

Table 5. desorption test operating scheme

At the end of the tests we should have obtained three solutions rich in heavy metals, so we decided to perform a test again with diphenylcarbazide to check the presence of the metals. All three tests were negative (index of non-desorption of metals from coffee); as for the 1d and 2d test, the water was not colored, while the 3d test, initially negative, was further investigated.

We performed a test on the 3d solution: we added NaOH 1N to the solution already containing diphenylcarbazide up to get pH about 6, at this point in fact, the solution began to color, indicating that the metals had actually desorbed from the coffe grounds, signal that in the previous tests we had not obtained. [Fig. 6]

After this result we carried out research, and indeed, as reported in the study called "Diphenylcarbazide" [8] Different metals form complexes with the diphenylcarbazide at different pH, such as copper that needs pH 9, we must therefore evaluate the pH regulation at a time second of the metals we want to complex.

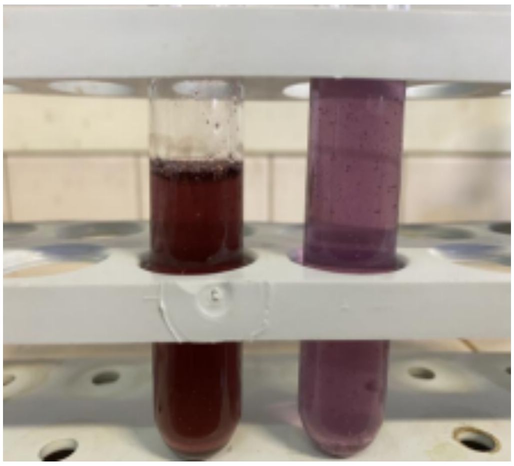


Figure 8. Test with -diphenylcarbazide at ph 6 on the 3d solution to verify the desorption of metal.

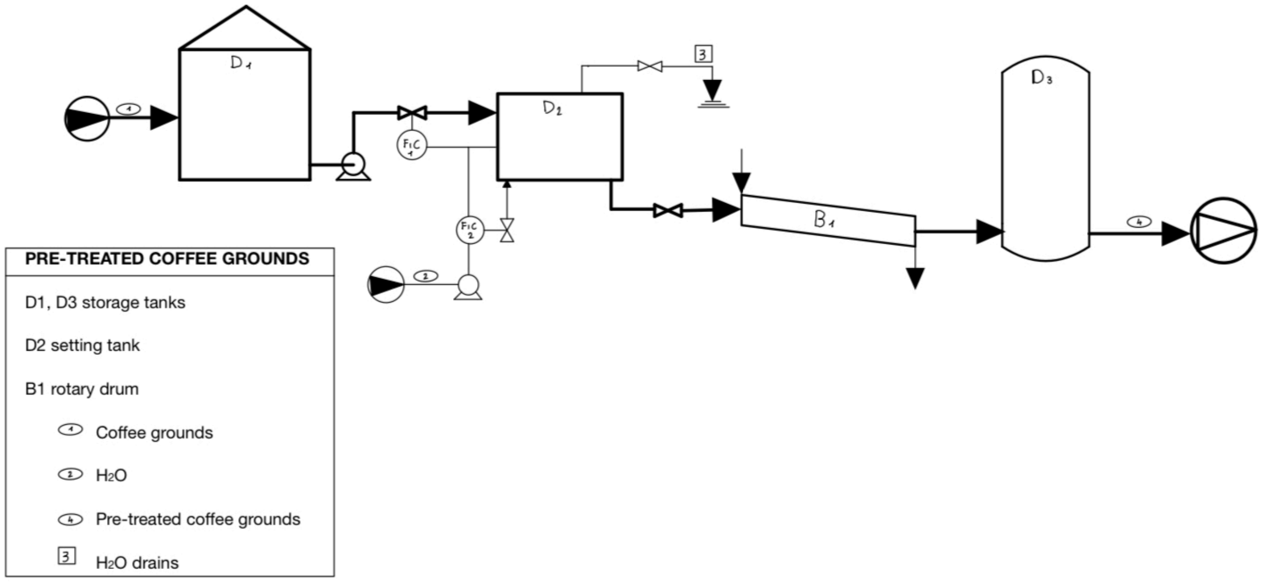
Due to lack of time it was not possible re-perform the 1d and 2d tests, and the related qualitative tests by correcting the pH, we then refer to a subsequent study in which a method will be validated that involves the addition of solutions to bring the pH to neutrality in order to verify immediately whether the desorption has taken place or not. Surely it will be our priority in the future to be able to better develop this side of the project. Considering that the desorption method used had not given satisfactory results in the first two tests, we tried to carry out tests of incineration of the coffe grounds: We inserted coffee grounds used in previous adsorption tests into the muffle at a temperature of 1000C° for about 20min. The method that involved the use of the muffle was discarded not being an eco-sustainable process, due to the energy used and the and the carbon dioxide produced.

Step 2. Design and development of a plant

Thanks to the various experimental tests carried out, we were able to design a system for the treatment of coffee grounds as efficient as possible and with the lowest ecological footprint.
Since we decided to study a system that could relate to industries, we would need large quantities of treated coffee funds and a small laboratory would not be able to produce enough of them; consequently we decided to design our own plant to carry out the development processes on a full scale. Our plant is divided into two parts: the first where the coffee grounds are pretreated and the second where the real process of preparing them takes place. Finally, after undergoing both treatments, the funds are placed inside a reactor in which the adsorption phase of heavy metals takes place, this reactor will be placed at the beginning of the purifier.

Step1. Pretreatment of coffee grounds

At this stage, after being raised by the various local bars, the coffee grounds undergo a pretreatment process, which in turn is divided into four phases:



Storage:

During the storage phase, coffee grounds, being solid material, are stored inside a tank.

Decantation:

At this stage the funds undergo a settling process. Settling is a technique that allows you to separate two substances of a mixture by means of the force of gravity.
In our case, the coffee grounds will pass inside a settling tank, in the first there is a liquid with a higher density than the coffee grounds so as to lead the spent coffee to the bottom and the remaining impurities at the top in order to easily separate the latter and eliminate them.

Drying:

At this stage the bottoms are dried with the help of a rotating drum, so as to avoid the formation of mould that would damage the result. Thanks to the septa inside the rotating drum it is possible to choose the grain size that our coffee bottom will take on.

Step 2. Coffee grounds treatment

In this last phase the funds are placed inside an elliptical tank waiting for the next process.
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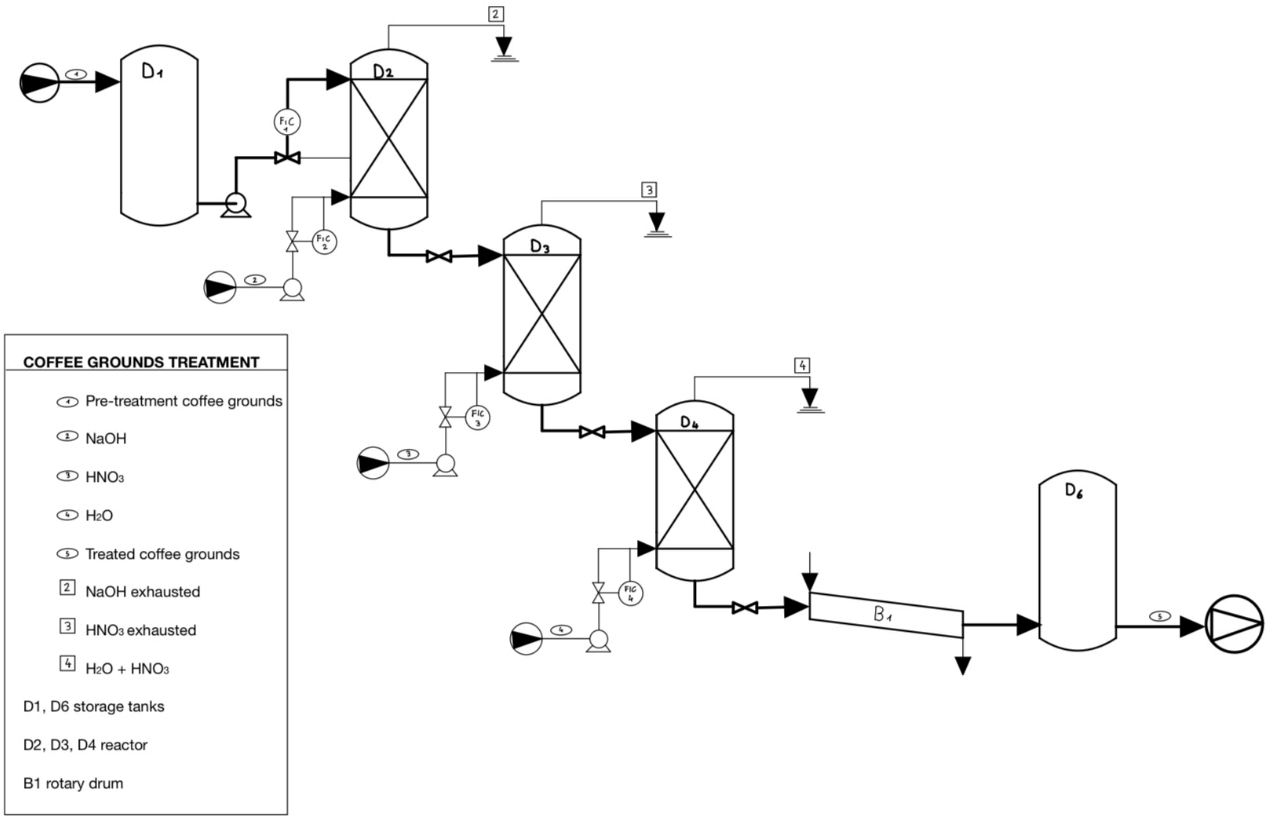

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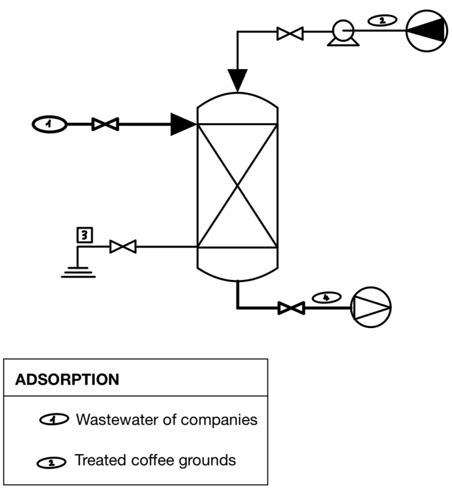
In this last phase the funds are placed inside an elliptical tank waiting for the next process.

Step3. Adsorption

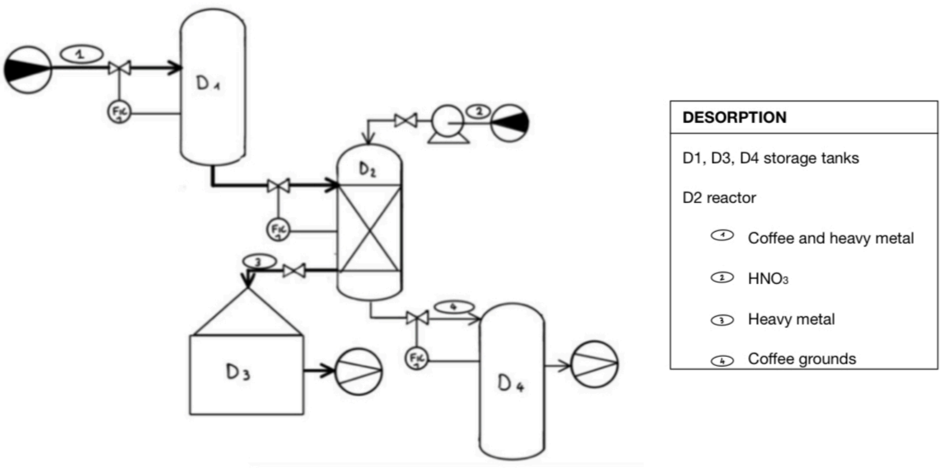
This part of the plant will have to be positioned just after the purifier present in every industry and is the fundamental step for the removal of heavy metals from waste water.



Step 4. Desorption

Our process for desorption is characterised by a single phase, namely the introduction of low-concentration HNO_3 into our reactor.

Our desorption plant starts from the coffee grounds that are taken from the adsorption phase, transported to a new tank. They then pass into the reactor where HNO_3 is added. Outgoing we will find the desorbed coffee grounds or without any presence of heavy metals, ready for a new adsorption cycle.



Future developments:

Future developments

Regarding the future developments of our project, we wanted to collect everything that due to lack of time, equipment and knowledge we could not carry out in the best possible way and validate. Here are some key points that we will try to develop.

Process and plant optimisations

It is essential for us to develop the processes hypothesised in our plant to minimise the consumption of resources (materials, reagents, energy) and use the least amount of chemicals at all stages, recovering them at every stage and steps, and simplify the plant and operation as much as possible in order to spread a possible future scaled model.

Reuse of coffee grounds after adsorption

A key step for the sustainability of our plant is that of re-use. We don't want to stop at the simple reuse of spent coffee grounds, but get to reuse them again: after all the adsorption-desorption cycle, putting them back into the cycle at the beginning of the plant may be able to adsorb other traces of heavy metals again. From here you can make quantifications on the actual durability of a spent coffee primer as an adsorbent.

Recovery of metals after desorption

Moreover, there is the question of the cost-effectiveness of the process: the idea is to obtain solid metals at the end of the plant. A hypothesis under scrutiny could be to use ammonium carbonate, adding it to the solution with a low concentration of nitric acid, containing the metals after desorption, thus making the metals insoluble, and subsequently evaporate everything thus obtaining them in the form of carbonates. We will also study electrochemical methods, such as electroplating.

Design and printing of a 3D model of the plant prototype

Last but not least, we are designing a 3D modelling of our plant so that it can be used as a support for developments and as a test of some phases.

Recovery of other value-added substances

As mentioned in the pretreatment phases of coffee grounds, we are studying the recovery of natural dyes present in coffee for environmentally friendly applications.

Conclusion:

With our project we present an innovative methodology in terms of circularity of processes, for the adsorption of heavy metals, this is made possible thanks to the adsorbent capabilities of coffee grounds.

The project also required considerable commitment from the point of view of creating a plant with the lowest possible environmental impact.

Based on the principles of the circular economy, we have proposed possible uses for all the by-products of the process, such as the possibility of recovering metals in their solid form through electroplating, or the possibility of regenerating the funds themselves.

We can be satisfied with the resolutions obtained: in fact, after strictly applying the scientific method, we came to effective conclusions, which paved the way for new ideas and developments.

Our group has set itself the objective of the continuous improvement of the production plant, such as the desorption of funds; therefore, there is still a long way to go; however, we are strongly convinced of the innovative and eco-sustainable component of our project, to which we will continue to devote a considerable effort.

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