



Treball Final de Grau

Use of industrial by-products as sorbents for the removal of lanthanides in contaminated waters.

Ús de subproductes industrials com a sorbents per a l'eliminació de lantànids en aigües contaminades.

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*Lo más incomprensible acerca de este mundo es
que sea comprensible.*

Albert Einstein

Aquest treball ha estat possible gràcies a la gran implicació de la Dra. Anna Rigol i del Dr. Oriol Ramírez com a tutors del treball. Agraïxo també la col·laboració de la Dra. Laura Rodríguez, l'ajuda i suport dels companys del laboratori QUESTRAM R, Joel, Isabel, Ariadna, Roger, Eduard, Eugenia, Jordi i Raquel. Per últim i especialment agraïxo el suport moral de la Cristina, Lluïssa, Joaquím, i Marc.

REPORT

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1. SUMMARY

One of the techniques used for the remediation of contaminated water is the use of sorbents. In these techniques, the sorbents retain the contaminants from the water. One of the most common sorbents is the activated charcoal. It is an effective commercial sorbent. However, there are some greener, cheaper and equally effective alternatives that might be investigated. For this reason, this project evaluates the efficacy of some materials as sorbents for pollutants, concretely lanthanides. The materials studied include different biochars and a by-product that comes from the metallurgical industry.

A previous study¹ showed a high efficiency of the studied materials for the sorption of lanthanides (Sm, La, Lu) at a single concentration of 0.05 meq/L. The present study aims to keep going in that direction by doing more experiments to obtain additional information about these materials as sorbents.

In this work, it has been evaluated the sorption capacity (sorption percentage and solid-liquid distribution coefficient) of the target materials and of a commercial activated charcoal, all tested at different samarium concentrations in water. This test allows us to see until which contaminant concentration is the material efficient as a sorbent. It has also been tested the desorption of Sm from these materials at the different Sm concentrations, since a good sorbent needs to have a low desorption as well as a good retention of the contaminant. Finally, some information about the existing mechanisms in the sorption process were derived from the sorption-desorption experiments.

The obtained results show a very good efficacy of the materials for the sorption of Sm until arriving at high concentrations, and as well as, low desorption. Biochars are very good sorbents, as they only saturate at very high concentrations that are not common in environmental situations. An exception was the biochar obtained from sugarcane bagasse, that showed worse results. The coal fines material, which is a by-product of the metallurgical industry, showed a similar behaviour to a studied commercial activated charcoal. It showed a 100% of sorption in the hole

concentration range tested . This confirms that the materials studied can be an environmentally friendly, economical and equally effective alternative to the commercial activated charcoal.

Keywords: Biochars, coal fines, samarium, sorption, desorption, isotherms, Langmuir.

2. RESUM

Una de les tècniques per a la remediació d'aigües contaminades és l'ús de sorbents. En aquestes tècniques els sorbents retenen els contaminants de l'aigua. Un dels sorbents més comuns és el carbó actiu. El carbó actiu és un sorbent comercial eficaç, però es poden buscar alternatives a aquest sorbent que siguin més respectuoses amb el medi ambient, econòmiques i igualment eficaces. Per aquest motiu aquest treball avalua l'eficàcia de sorció d'uns materials que s'obtenen de subproductes de la indústria. Els materials estudiats són diferents biochars i un subproducte de d'indústria metal·lúrgica.

Un estudi¹ anterior va mostrar una gran eficàcia dels materials estudiats per a la sorció de lanthanids (Sm, La, Lu) a una única concentració de 0.05 meq/L. Aquest estudi pretén seguir aquesta línia de treball, fent més experiments per obtenir més informació sobre la capacitat d'aquests materials com a sorbents.

En aquest treball s'ha assajat la capacitat de sorció (percentatge de retenció i coeficient de distribució sòlid-líquid) per part dels materials estudiats i d'un carbó actiu comercial, a diferents concentracions de samari en aigua. Aquests assajos permeten veure fins a quina concentració de contaminant el material és eficaç com a sorbent. S'ha assajat també el grau de desorció d'aquests materials a diferents concentracions, ja que un bon sorbent a més a més de presentar una elevada sorció del contaminant ha de tenir una baixa desorció. Finalment, a partir dels assajos realitzats, s'ha pogut obtenir informació sobre els mecanismes involucrats en els processos de sorció.

Els resultats obtinguts en aquest treball mostren una molt bona eficàcia dels materials estudiats per la sorció de samari fins a arribar a altes concentracions, i una molt baixa desorció. Els biochars són molt bons sorbents i només saturen a concentracions molt elevades que ja no són representatives d'escenaris ambientals, amb excepció del biochar derivat del bagàs de canya de sucre (SB) que va mostrar pitjors resultats. El material de fins de carbó (CF), subproducte de la indústria metal·lúrgica, va mostrar un comportament molt similar al d'un carbó actiu comercial estudiat, amb gairebé un 100% de sorció en tot l'interval de concentracions assajat. Això

confirma tots els materials estudiats, excepte el SB, com a una possible alternativa més respectuosa amb el medi ambient, econòmica i igualment eficaç al carbó actiu comercial.

Paraules clau: Biochars, partícules de carbó, samari, sorció, desorció, isoterme, Langmuir.

3. INTRODUCTION

3.1 IMPORTANCE OF POLLUTION PREVENTION

Since many years ago there have been laws to control the pollution and preserve the environment, and consequently the health of people and animals. In England there have been laws since the thirteenth century that limited environmental emissions from the combustion of charcoal. But because of the increase of the world population since the seventeenth century and the increase in the quality of life, there has been an increase in the exploitation of the resources and consequently of waste and contaminants. For these reasons it is necessary to consider that since recent years the society is aware of the need to preserve the environment. Proof of this is the evolution of environmental conservation policies over the last hundreds of years.

While in the Rome treaties signed in 1957, which give rise to the European Economic Community, there were not references on the environmental problems, the Single European Act signed in Luxembourg in 1986 incorporated measures on protection of the environment (Title VII). But even though we are more aware of environmental management and prevention, as well as in the prevention of discharges to nature, there can be accidental contamination problems, or sometimes a bad management of the companies.

There are some examples of relevant pollution situations. One happened in the mines Gerais (Brazil) in 2015, where a broken dam caused the discharge of 34 million cubic meters of toxic sludge, which is the largest environmental disaster in Brazil caused by a company negligence. Another example is an institutional negligence in the village of Yongxing (China), where in 1991 they installed a 34-hectare of landfill. After that they installed two incinerators and a large waste-treatment plant that eventually polluted the wells and the agricultural fields. However, they had not stopped the agricultural activity, so at the end there has been an increase in cancer cases in the village. Other example happened in 1998 in Aznalcóllar (Spain), where a broken dam caused the discharge of toxic waste from the mines, contaminating the National and Natural Park of Doñana.

Therefore, efforts need to be focused on the environmental management and prevention, implementing environmental protection policies. But even with good environmental protection laws there can be situations of pollution that will be necessary to manage.

3.2 REMEDIATION OF POLLUTION EPISODES

In pollution episodes, the first thing to do is an analysis of the situation, collecting enough information about the discharge, and taking samples in different zones. So, we try to obtain enough information to evaluate the dangers and risks and to choose the most appropriate technique to solve the problem.

As Doménech and Peral explain², it must be taken into account that, once the contaminants are spilled or issued, they can reach different compartments. If the pollutant reaches the soil, it can be trapped, so it can be harmful to plants and even it can be incorporated into them. Moreover, it can be harmful to people by direct contact with the soil. The pollutant released into the soil can also be leached because of the rainwater. If it happens, it can reach the aquifers, then the rivers and finally the oceans. Besides, the contaminant can be discharged directly to rivers or can be emitted directly into the atmosphere.

Concerning the emissions to the atmosphere the efforts are mainly focused on the preventive control of emissions, as once released they expand easily. The rain is a natural resource to help cleaning the atmosphere by dragging some of the pollutants to the terrestrial surface. Several techniques can be used to solve soil and water contamination problems. These techniques can be classified in many ways.

Doménech X. and Peral J² suggest a classification of the types of techniques used to manage the soil, based on the process to remove or immobilize the contaminant, in the case of local contamination.

- Containment techniques: they consist on the use of barriers to prevent the mobilization of the contaminant to other places.
- Transfer methods: the transfer of soil contaminant to a liquid or gaseous medium is done to be treated somewhere else.
- Chemical and biological transformation methods: the contaminant is chemically degraded using either reagents or microorganisms.

Regarding the group of containment techniques, one possibility is the stabilization, which consists of reducing the mobility of the contaminant from the soil by the addition of materials to retain it. Regarding the remediation of groundwater, the authors explain that most of the techniques used are very similar to those used in soils and that they can be classified in the same mentioned groups above. Besides, there is another group of techniques consisting in building permeable barriers that eliminate the contaminants from the environment by letting the water pass through. One of that types of barriers are the reactive permeable, that are reactive walls made up of fillers and specific chemical components that let the water pass through but that react with contaminants. Other types of barriers are permeable sorbent barriers in which sorbent material is used to immobilize or stabilize the contaminant. As the authors say, the most used sorbent materials are iron oxides and ionic or highly functionalized organic compounds. Permeable stabilizing barriers are another alternative which tries to precipitate the contaminant with minerals containing phosphate. If the decontamination of the waters is done through a technique of treatment with sorbents, the function of the sorbents is to retain the contaminant and to remove it from the water.

3.3 USE OF SORBENTS FOR REMEDIATION OF CONTAMINATED WATER

Active charcoal is one of the most used sorbents for water remediation. Is a really effective commercial sorbent, but there are other materials that can be also effective and an alternative, more environmentally friendly and economical. Besides, if these materials are industrial by-products or non-hazardous waste, their reuse represents an added value. The searching possible materials need to be:

- Equally effective as sorbents for water remediation.
- Cheaper or easier to obtain.
- Obtained from non-polluting processes or reused.

As a result, sorbents obtained from by-products of industry or human activity are a clear alternative. They would be waste if they were reused, so humans would have to manage with that. As a proposal of materials with those characteristics we find the biochars and the charcoal residues of the metallurgical industry.

3.3.1 BIOCHARS

As pointed out in some works^{3,4,5,6}, a biochar is the solid product obtained from the biomass pyrolysis, that is, from heating the biomass in ovens at high temperatures without oxygen. Biomass is the organic waste generated in the nature or by some industries, such as leaf waste, algae, logs, nutshells, coconut husks, etc. A non-desirable method of treating biomass is the combustion, which generates CO₂ which is harmful for the atmosphere as it contributes to the global warming. There is an alternative to this treatment and is the valorization of the biomass by transforming it into biofuel and biochar using pyrolysis, which is shown in Figure 1. Furthermore, biomass is renewable and available in huge quantities.

The quality of the biochar and its chemical composition depends on the type of biomass used to generate it and as well on the conditions of the pyrolysis process. Depending on the pyrolysis conditions, it can happen that more biochar and less biofuel can be obtained, or it can happen the other way round. For example, if the pyrolysis is carried out at a low temperature (maximum 350°C) with the vapor staying quite a long time (70 min), the percentage of biochar obtained with regard to biofuel is increased. Regarding composition, biochars are rich in carbon (65-90%), and also contain functional groups with oxygen and aromatic compounds. Biochars contain labile components such as cations, and many other non-labiles. Another characteristic of biochar is that they are sorbents^{4,5,6,7} and good soil fertilizers⁴.

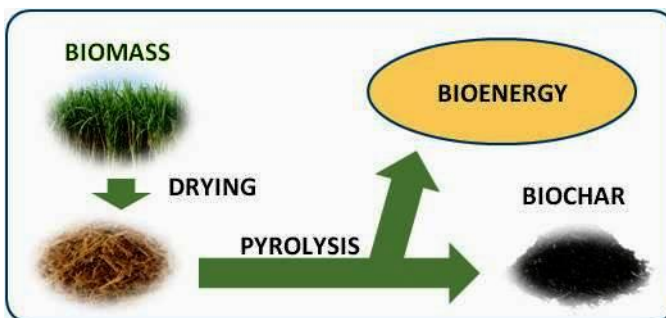


Figure 1: The process to obtain biochars.

3.3.2 CHARCOAL FINES

Another alternative material is a by-product that is obtained from the metallurgical industry. This by-product is obtained from the remains of charcoal with a small particle size, which must be

removed in order not to obstruct the gas tubes from the ovens, which can decrease their performance. Regarding its composition, an investigation⁸ shows that this material contains high quantities of C (35%), H (3.5%) Si, Fe, Ca, P, K, Mg and Mn, in which Ca^{2+} Mg^{2+} K^+ are labile cations. This material has been tested as a sorbent with some heavy metals, and showing satisfactory results⁸.

3.4 LANTHANIDES

3.4.1 CHEMISTRY OF LANTHANIDES

As Atkins and other authors⁹ explains, lanthanides (Ln) are the elements in the *f* block, that are those with electrons filling their orbitals *f*. Lanthanides are also known as "rare earth elements" and, within this group, there are 14 elements.

Many of the chemical properties of lanthanides are similar to other electropositive metals. Ln are white and soft metals with high density. They are bad conductors of heat and electricity. They oxidize very easily, that is, they are highly electropositive, although they can passivate. The most common oxidation state is Ln^{3+} . The Ln^{3+} ions are hard Lewis acids as indicated by their preference for the F^- and O^{2-} , as well as the fact that they are frequently found in phosphate-containing minerals. Ln^{3+} ions have lost their orbital electrons *s* and *p* but they do not lose their electrons *f*, which are internal and strongly attracted by the nucleus. For this reason, their electronic configuration is the same of the [Xe] plus the electrons of the orbitals *f*. As a consequence, they do not have orbital boundary with a directional preference, and the bonds established usually consist of electrostatic attraction between ions. Thus, Ln have a reduced chemical diversity. The only difference that often exists is in their magnetic behavior and size. This difference in size is due to the increase in the effective nuclear charge as the atomic number increases over the full period.

Regarding the formation of complexes, Ln usually has high coordination numbers (6, 7) and a wide variety of coordination environments. The stabilization of the ligand field does not influence the chemical properties of the Ln complexes, so the bonding of the complexes is best explained from an ionic point of view⁹. Regarding the organometallic formation, most Ln bind to ligands, which are good donors. There are similarities between organometallic Ln and early compounds of the *d* group.

3.4.2 ENVIRONMENTAL RELEVANCE OF LANTHANIDES

Lanthanides are found in nature (with the exception of promethium), but not uniformly. In China lanthanides are very abundant and there are some mining operations to extract and purify Sm and other lanthanides. They are usually found as mineral phosphates such as monacite or xenotime containing mixtures of lanthanides.

Lanthanide elements are gaining increasing importance due to high demand in the high-tech industry¹⁰. In particular, lanthanide elements possess good properties for high-tech devices such as plastic fiber optic lasers, ionic conducting oxides for fuel cells, liquid crystals and surfactants, reagents for organic synthesis and asymmetric catalysis. Ln are also used in the steel industry to eliminate impurities. Furthermore, europium Eu^{3+} and Sm^{3+} are valuable members of rare earth family elements and are used in the production of glass and ceramic, strong magnetic materials, as well in the metallurgical industry, electronics and agriculture and natural sciences¹⁰. The europium oxide is also used as a phosphorescent material in cathode ray tubes. Figure 2 shows their principal uses and how they are distributed.

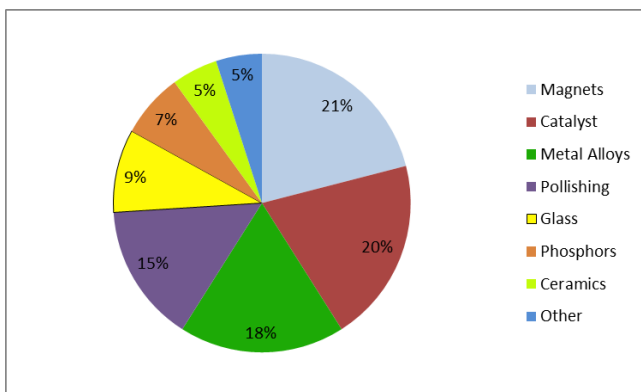


Figure 2. Rare earth elements uses (adapted from Kingsnorth¹³).

The accumulation of lanthanides in the soil can be produced by the pollution caused by their exploitation, and by the fertilizers containing lanthanides that are used in agriculture¹¹. This accumulation of lanthanides has a toxic effect on the soil, letting them enter to its nutrient net¹¹. For this reason, it can be harmful to plants and even it can be incorporated into them, for later contaminating the the food and causing toxic effects on people. Consequently, it has increased the concern about the potential harmful implications for non-human biota and human health derived from lanthanides contamination episodes¹².

3.5 INTERACTIONS BETWEEN SORBENTS AND SAMARIUM

The behaviour of Sm^{3+} and the others Ln^{3+} in terms of soil interaction is very similar, they can be considered as chemical analogs^{14,15}. Then, the results obtained for a study of Sm^{3+} can be valid for the other Ln^{3+} . Previous works^{5,6} that investigated the interaction of heavy metals with biochar found that when a solution with a heavy metal gets in contact with a biochar, the material acts as a sorbent retaining heavy metal ions. This is caused by the interactions of the heavy metal cations with the biochar. These investigations explain that these interactions can be based on a cation exchange, where the heavy metal occupy the sites of other labile cations of the biochar which are retained by negative charges such as functional groups. There is another mechanism that can happen. This refers to the complexation, where there exist chemical bonds between the metal and the oxygen atoms of the carboxylic and phenol groups. In that case, the retention will be stronger and less reversible. Other mechanisms that can exist are electrostatic attraction, physical adsorption or precipitation with anions.

However, there is only one work¹⁵ found that explains the interaction of Sm with one biochar. This investigation reports a 100% of affinity of Sm for that biochar at neutral pH solution and 20% of affinity at pH 2. At pH lower than 6, Sm^{3+} is basically present in the form of positively charged aqueous cation with a negatively charged surface of the sorbent, and the sorption of the metal ion is done by cation exchange reactions¹⁵. Moreover, the investigations for the increasing of initial concentration at pH 3 and 6, shows that above a certain concentration the relative sorption/removal increases dramatically, which suggests that there is a surface polymerization or a surface precipitation on the surface, respectively. Nevertheless, the sorption isotherms indicates sorption on specific surface sites with similar binding thermodynamics and hence the formation of inner-sphere surface complexes. The reaction is shown in Figure 3. The adsorption on the activated biochar is different on the two different pH regions, which indicates the formation of significantly different surface species on the biochar surface.

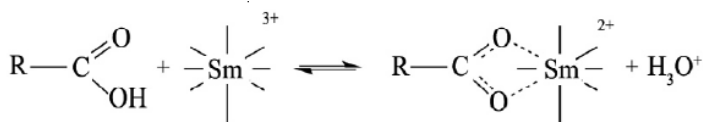


Figure 3: Formation of inner-sphere chelate complexes¹⁴.

It should be remembered that each biochar has different characteristics, and that there is only one investigation of one biochar which is pretended to be used to remediate contaminated waters with Sm. The reason why we wanted to investigate that process is that there is not too much information about that.

4. OBJECTIVES

The main objective of this work is to evaluate the viability of the use of various biochars and other by-product as sorbents for the remediation of water contaminated with lanthanides. To achieve this general goal, the following specific objectives will be addressed:

- To determine the sorption efficacy and its reversibility of the selected materials by varying contaminant concentrations. As well, to obtain sorption and desorption parameters.
- To identify the mathematical models that better explain the sorption isotherms.
- To obtain information about the interaction mechanisms of Sm with the different materials by interpreting the isotherms, characterizing the liquid phase of the materials and performing sequential extractions.

5. EXPERIMENTAL SECTION

5.1 MATERIALS AND METHODS

5.1.1 Materials tested

Four biochars were used in the present study. They were produced using the same method and conditions: the biomass was air-dried, then heated in a closed reactor, with little oxygen, from 20°C to 350°C at a rate of 5°C per minute and maintaining the temperature to reach a total of 70 minutes from the start. The vapors were collected in a water condenser to separate the condensable (bio-oil) and non-condensable gases³.

Biomass of different origins were used for the production of the biochars. Thus, each biochar will have different composition and properties^{4,5,6}. Here, we classify them according to the biomass from which they have been obtained^{8,16}:

CE: Eucalyptus forest residues, which consist of brushwood mixed with eucalyptus biomass.

CM: Castor meal, from the production of bio-oil from castor beans.

PC: Green coconut pericarp, accumulates in places where natural coconut water is consumed.

SB: Sugar cane bagasse, which is a waste material derived from the production of sugar.

Apart from these biochar samples, another material of organic origin is studied. This material is a byproduct of the metallurgical industry:

CF: charcoal fines particles.

Finally, a commercial activated carbon (**CA**) from Sigma Aldrich is also studied for comparison purposes.

5.1.2. Standards and reagents

Eight samarium solutions at concentrations of 0.6, 1, 3, 6, 10, 30, 60, and 100 meq/L were prepared from three stock solutions of 30, 60 and 100 meq/L of $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. This stock

solutions come from a 1000mg/L Sm standard solution of the salt. It has been used the same standard solution in the inductively coupled plasma (ICP) measures. The contact medium used in the test has been a double-deionised water, Mili-Q. For the sequential extractions, it has been used water Mili-Q, 0.01M CaCl_2 from the salt, and 0.43M acetic acid from the glacial acetic acid. Finally, it has been used hyper pure nitric acid in order to acidify the samples before the ICP measures.

5.1.3 Sorption tests

These tests show the sorption efficacy of each material at different concentrations of Sm. In the sorption test^{17,18}, all that is needed is to weigh 2g of the material to be studied, then add 45ml of deionised water in 80mL polypropylene centrifuge tubes and finally shake the suspensions during 24h using an end-over-end shaker at 60rpm. After 24 hours, the samples were spiked with 5mL of Sm to have an initial Sm concentration (C_i) which is between 0.06 and 10 meq/L. It has been tested eight concentrations of 0.06, 0.1, 0.3, 0.6, 1, 3, 6 and 10meq/L. Three of them have been replicated at 0.06, 0.6 and 6meq/L. Moreover, a blank is made by adding 5mL of water. The suspensions had been equilibrated again for 24h and centrifuged (10000rpm, 30min, 10°C) using a Beckman J2-HS centrifuge with a rotor JA14. After that, the supernatants were decanted off, then filtered using 0.45 μm nylon syringe filters, and finally transferred to 20mL polyethylene where the pH was measured. The supernatants obtained from sorption and blank tests were acidified with 1% HNO_3 and stored at 4°C until the analysis. The aliquots of the blank sorption supernatants were used to determine relevant solution parameters. Figure 4 show a scheme of the sorption test.

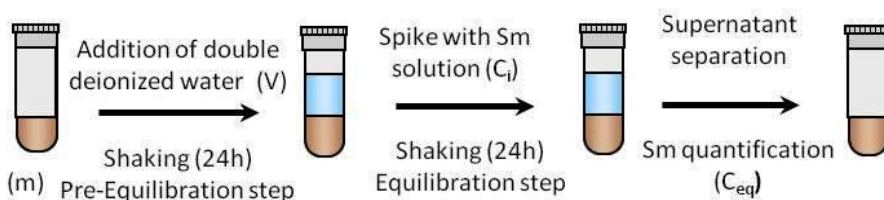


Figure 4: scheme of sorption test.

5.1.4 Desorption tests using sequential extractions

The reversibility of the Sm sorption in the target materials was evaluated using a desorption test¹⁷ for the 40°C-dried residues produced in the previous sorption experiments that were carried out at selected initial Sm concentrations of 0.06, 0.3, 1, 6, 10meq/L. 1g of material was weighed for the desorption. Then it has been done an extraction using 25mL of double-deionised water as contact solution in 50mL polypropylene centrifuge tubes and then shaking the suspensions for 24h. After that, the suspensions were centrifuged, then decanted-off, and finally filtered through 0.45µm, to transfer them to 20mL polyethylene vials. The collected supernatants were then acidified with 1% HNO₃ and stored at 4°C until analysis. Figure 5 shows a scheme of sorption test.

For sequential extraction test¹⁶, the extraction has been done following the same procedure and using the residue of the desorption test and adding 20mL 0.01M CaCl₂ as extractant solution in 50mL polypropylene centrifuge tubes. Finally, it has been done extractions with 20mL of 0.43M acetic acid.

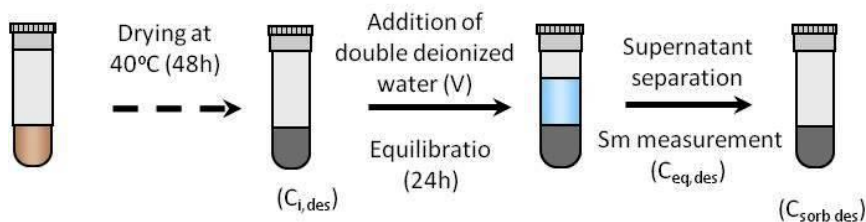


Figure 5. Scheme of desorption test.

5.1.5. Characterization of the liquid phase

5.1.5.1 Quantification of Sm and other cationic species

Representative aliquots of 10mL of samples, which had been previously homogenized by agitation, were taken. Then the samples were acidified with 0.1mL of hyper pure nitric acid and they were stored at 4°C to preserve it. Some samples have been diluted to satisfy the requirements of the analyzing instrument.

Once the samples have been prepared they have been analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES), on the *Centres Científics i Tecnològics de la UB*, CCIUB. The equipment used was a Perkin Elmer Optima 3200 RL. It has been studied at the wavelength of 359.3nm, and the quantification limit is 0.03 mg/L for Sm. The low concentration

samples have been measured with ICP-MS that reaches a quantification limit of 0.01 $\mu\text{g/L}$. In this case the equipment used has been the Perkin Elmer Elan-6000.

It has also been analyzed the composition of the major cations from the equilibration stage of the biochars with water and, from the equilibration of the biochars with water and Sm. The cations have also been determined by ICP-OES, and the preparation of the sample has been the same as it was for Sm. K^+ , Ca^{2+} , Mg^{2+} , Fe^{3+} , Al^{3+} cations have been analyzed at the wavelenghts of 766.49, 317.93, 279.08, 239.56 and 308.22nm respectively, and the quantification limit is 0.05 mg/L for all cations except for Al^{3+} with 0.01 mg/L.

5.1.5.2 Anionic chromatography

Cl^- and SO_4^{2-} were measured by anion chromatography in “Centres Científics i Tecnològics de la UB, CCIUTUB”. Then there were measured the blank and the samples for each material at an initial concentration of 0.06, 0.6 and 6 meq/L using an equipment KONTRON model 465.

5.1.5.3 DOC

DOC has been measured in the “Centres Científics i Tecnològics de la UB, CCIUTUB”, using the ANALYTIC JENA, model Multi N/C 3100, XYZ autosampler. The equipment measures the CO_2 to determine the carbon. The inorganic carbon in solution, DIC, is measured on the one hand using phosphoric acid, and on the other hand the total carbon in solution is measured by burning all the carbon present at elevated temperature in an oven. DOC is obtained by the difference between the two.

5.1.5.4 pH

The pH of the supernatant solutions from the sorption experiments was measured for each sample using EUTECH Cyberscan2500 equipment.

5.2 THEORETICAL FRAMEWORK

To study the sorption of Sm in the materials we will refer to some concepts that are described below.

5.2.1 Sorption parameters

The sorption capacity of each material at each concentration was quantified using two parameters^{17,18}, the solid-liquid distribution coefficient (K_d) and the sorption percentage (% sorb) obtained from the following expressions:

$$K_d \text{ (L/kg)} = \frac{C_{\text{sorb}}}{C_{\text{eq}}} = \frac{(C_i - C_{\text{eq}}) \frac{V}{m}}{C_{\text{eq}}} \quad (1)$$

$$\% \text{ sorb} = \frac{(C_i - C_{\text{eq}})}{C_i} \times 100 \quad (2)$$

Where:

K_d : is de solid-liquid distribution coefficient (L/kg)

C_{sorb} : is the concentration of Sm in the sorbent after equilibration (meq/kg)

C_{eq} : is the concentration of Sm in the supernatant after equilibration (meq/L)

C_i : is the initial concentration of Sm before equilibration (meq/L)

V : volume of water (L)

m : weigh of sorbent (kg)

5.2.2 Desorption parameters

The reversibility of the process is quantified with two parameters^{17,18} the solid-liquid distribution coefficient of the desorption process ($K_d \text{ des}$) and the desorption percentage (% des).

$$K_d \text{ des (L kg}^{-1}\text{)} = \frac{C_{\text{sorb des}}}{C_{\text{eq des}}} = \frac{C_i \text{ des} - C_{\text{eq des}} \times \frac{V}{m}}{C_{\text{eq des}}} \quad (3)$$

$$D \text{ (\%)} = \frac{C_{\text{eq des}} \times V}{C_i \text{ des} \times m} \times 100 \quad (4)$$

Where:

$K_d \text{ des}$: is de solid-liquid distribution coefficient of desorption (L/kg)

$C_{\text{sorb des}}$: is the concentration of Sm in the sorbent after desorption equilibration (meq/kg)

$C_{\text{eq des}}$: is the concentration of Sm in the supernatant after desorption equilibration (meq/L)

C_{eqs} : is the concentration of Sm of sorption equilibration

V : V: volume of extractant (L)

m: weigh of sorbent (kg)

$C_{i\ des}$: is the initial concentration of Sm in the sorbent before desorption equilibration. (meq/kg), calculated from:

$$C_{i\ des} = C_{sorb} + C_{eq} \times \frac{V_{res}}{m_s} \quad (5)$$

V_{res} : volume of residual extractant of the sorption test (L)

m_s : weigh of sorbent of the sorption test (kg)

C_{eq} : is the concentration of Sm in the supernatant after equilibration (meq/L)

C_{sorb} : is the concentration of Sm in the sorbent after equilibration (meq/kg)

5.2.3 Sorption isotherms

The sorption isotherms allows us to study the variation of the sorption of one or several species when varying their concentration. This also allows us to extract information from the sorption mechanisms involved in the experiment.

In order to build the sorption isotherms, sorption tests are carried out as explained above, and C_{eq} is determined to estimate C_{sorb} . After that, two representations were performed: C_{sorb} vs C_{eq} and K_d vs C_{sorb} .

5.2.3.1. Classification of sorption isotherms

The isotherms can be classified into different types¹⁹ depending on their shape. Here the main four types are explained, but it should be taken into account that sometimes experimental data does not fit to a single type, but to a combination of different types. The different types of isotherms are described below, and they are represented in Figures 6, 7, 8 and 9.

Langmuir (L):

C_{sorb} vs C_{eq} : C_{sorb} increases when increasing C_{eq} with good linearity at low concentrations until reaching a value of almost the constant C_{sorb} at high concentrations.

K_d vs C_{sorb} : K_d decreases constantly as C_{sorb} increases. This suggests a gradual saturation of the sorption surface until reaching the saturation.

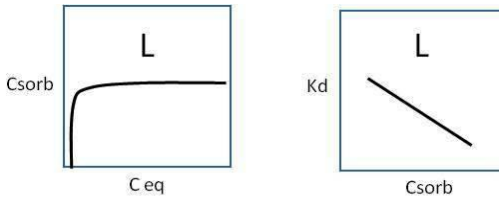


Figure 6: graphics of model L of isotherms

Linear (C):

C_{eq} vs C_{sorb} : The distribution of the solute between the liquid and solid phases remains constant within large concentration ranges.

K_d vs C under: there are constant K_d values seen when we increase C_{sorb} .

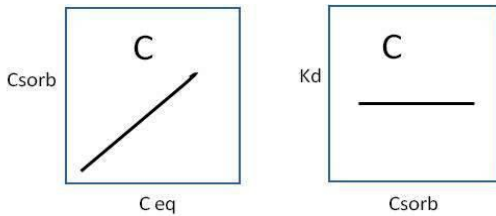


Figure 7: graphics of model C of isotherms.

High affinity (H):

C_{eq} vs C_{sorb} : They show an increase of C_{sorb} with high slope at low concentrations and less slope at high concentrations.

K_d vs C_{sorb} : The decrease of K_d vs C_{sorb} shows two zones. This process shows heterogeneity sorption sites commonly associated with the formation of internal spheres coordinate complexes that are recognized by a high affinity between sorbent and sorbate species.

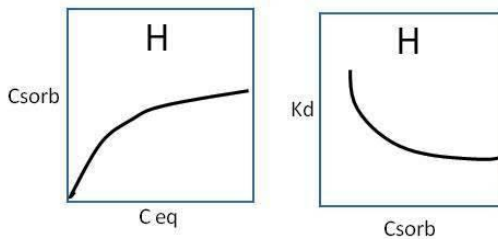


Figure 8: graphics of model H of isotherms

Sigmoidal (S):

C_{eq} vs C_{sorb} : the C_{sorb} goes low at low concentrations and increases when increasing analyte concentration which at the end means an increase of K_d with concentration. This type of isotherms can be explained by competition reactions within the solution when the analyte is a metal. In this situation the solution ligand competes with the metal at low concentrations, but at high concentrations the ligand gets saturated and the K_d increases. The most important fact in the curve reflects when the sorption of the surface metal exceeds the complexation produced by the ligand in solution.

K_d vs C_{sorb} : The slope decrease as C_{sorb} increase.

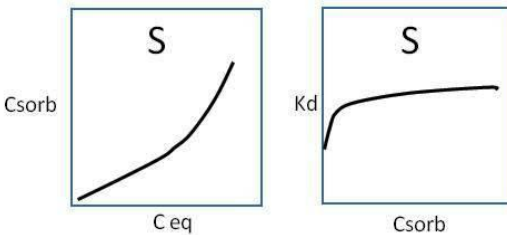


Figure 9: graphics of model S of isotherms.

5.2.3.2 Fitting of sorption isotherms.

Various models have been used to fit the sorption isotherms obtained.

5.2.3.2.1 Langmuir model

This model^{2,17,18} describes the isotherms of Langmuir type, and considers that sorption is a reversible process, which happens in a flat surface, with a finite number of identical sorption sites in which only one analyte can be bound. Once the analytes are absorbed they do not interact with each other on the surface and do not present lateral movements. As the sites are identical, the sorption's energy is the same for all sorts of sorption and does not depend on the saturation of the sites. The model follows the next expression:

$$C_{sorb} = \frac{b \times K \times C_{eq}}{1 + K \times C_{eq}} \quad (6)$$

Where:

K: (L/meq) estimate the bonding energy of the sites of sorption.

b: (meq/kg) estimate the maximum sorption capacity of the sorbent.

5.2.3.2.2 Freundlich model

This model^{2,17,18} refers to the possible heterogeneity of the sorbent's surface with different affinity to the element to be sorbed. In this model there is no maximum number of sorption sites. The model follows the next expression:

$$C_{\text{sorb}} = K_f \times C_{\text{eq}}^N \quad (7)$$

Where:

K_f: This is the Freundlich adsorption constant describing the distribution of the analyte into the different sites of the system.

N: This is a measure of the heterogeneity of sorption sites. If N < 1 indicates high affinity (H) at low concentrations. For N > 1, there are competition reactions at low concentrations and it show sigmoidal type isotherms (S). If N = 1 indicates that the sorption sites have the same affinity for the whole range of concentrations assayed and represents either a linear (C) sorption type where K_f is equal to K_d. Then the linear model follows the next expression:

$$C_{\text{sorb}} = K_d \times C_{\text{eq}} \quad (8)$$

6. RESULTS AND DISCUSSION

6.1 CHARACTERIZATION OF SUPERNATANTS IN SORPTION EXPERIMENTS

The supernatants obtained in the sorption experiments were characterized in terms of pH, dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and cationic and anionic composition. This characterization was done for each material without Sm and at three levels of Sm concentration, 0.06, 0.6 and 6 meq/L. The results obtained are shown in Table 1.

All the materials have pH values approximately between 6-8, except CA, that shows values close to 10. As well, when SB is in its highest concentration of Sm, it reaches values of 5.3. Regarding DOC, CM has clearly higher values than other materials. CA is the one that has less, followed by CF, while the other compounds have values between 100 and 200mg/L. DIC has one high value for SB at Ci of 6meq/L. It is also important to highlight high concentrations of K^+ from PC and CM, while CE and CM have the highest values of Ca^{2+} and Mg^{2+} . There was also analyzed Fe^{2+} and Al^{3+} ions, as these ones were not present in the medium. Regarding the anions we can highlight high concentrations of Cl^- from the PC, that strongly contrast with the values of the other materials, as well as high concentrations of SO_4^{2-} for CA, CM and CF.

The determined parameters of the supernatants varied when varying the material, so that suggests that as expected, each material has different composition because the biochars come from different biomass^{6,11} and CA and CF are different materials. There is observed a tendency to decrease the pH by increasing the initial concentration of Sm, probably due to the acidic hydrolysis of Sm in water and also perhaps to the displacement of H^+ by Sm^{3+} on the surface of the material. DOC in CE and CM, it slightly increased when increasing pH, due to the deprotonation of acidic functional groups, such as carboxylates, that they become anions when losing the H^+ . That allows some of the organic material to be solubilized. That existing tendency is not clear in PC. SB shows very high values of DOC and DIC at pH of 5.3, maybe due to the solubility of some of the phases of the material.

Material	Cl ⁻ (meq/L)	pH	DOC (mg/L)	DOC (mg/L)	DOC (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	K ⁺ (mg/L)	Ca ²⁺ +Mg ²⁺ +K ⁺ (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)
CM	0.00	6.91	1104-1245	<140	33	33	213	280	26	153	
	0.06	6.87	117- 1163	<147	34	36	224	293	30	118	
	0.60	6.92	863- 1007	<143	39	40	253	332	34	139	
	6.00	6.32	637- 780	<143	66	42	220	328	33	102	
PC	0.00	7.21	126-161	<35	1	5	397	403	358	<115	
	0.06	7.14	134-170	<35	1	5	413	419	415	<115	
	0.60	7.30	101	36	1	5	409	551	420	<115	
	6.00	6.34	92-127	<35	2	7	454	464	330	<115	
CE	0.00	6.73	196-231	<35	16	29	74	120	7	39	
	0.06	6.66	191-227	<36	16	30	77	123	7	31	
	0.60	6.74	126	42	20	34	86	308	9	<23	
	6.00	5.73	123-158	<35	30	32	96	159	<7	<46	
SB	0.00	6.41	88-124	<35	8	6	44	57	3	12	
	0.06	6.30	90-125	<35	8	6	45	59	<2	<12	
	0.60	6.14	89-124	<35	12	8	50	70	2	<12	
	6.00	5.31	374	226	19	7	52	678	<2	<46	
CF	0.00	7.80	42	27	15	9	150	244	11	86	
	0.06	7.67	11-15	<4	16	10	160	186	10	97	
	0.60	7.59	59	25	17	11	146	259	10	86	
	6.00	7.33	27	12	65	31	176	312	12	84	
CA	0.00	10.13	8	10	11	10	62	100	11	196	
	0.06	10.10	5	11	11	10	66	103	12	181	
	0.60	10.02	12	9	14	14	68	116	12	216	
	6.00	9.20	8-12	<4	54	28	61	143	12	192	

Table 1. Characterization of the supernatants in sorption experiments

In the case of the main cations, there exists a tendency from all the materials to increase the concentration of cations when the initial Sm concentration increases. That fact may be due to replacement of these cations by Sm. There is not a clear tendency seen with the anions, and taking into account the moderated concentrations of Cl^- and SO_4^{2-} and the solubility of SmCl_3 (95g/100g of water) and $\text{Sm}_2(\text{SO}_4)_3$ (3g/100g of water), precipitation of Sm might be disregarded.

It is important consider that pH is the most important factor to take into account, especially when the sorption is evaluated, as when there exists an acidic pH there are H^+ that compete with the Sm^{3+} for the negatively charged places of the material, whereas at basic pH there is no competition. Moreover, the functional groups such as carboxylates, are deprotonated and might interact with Sm^{3+} . Furthermore, if one material that has been equilibrated with water shows basic pH, it may indicate that it has negative charges in order to catch cations, which is the same that happens with the H^+ of the water.

6.2 SORPTION CAPACITY OF MATERIALS

The sorption can be influenced by different factors, such as the characteristics of each material, the concentration of contaminant, the pH, the temperature or other cations and anions present in the medium⁶. These results are obtained following the conditions studied, by controlling the initial concentration of Sm but not the pH or the final composition of ions in the medium. Results of sorption and desorption test are shown in Table 2.

All materials have sorption percentages above 95%, until initial concentrations of 1meq/L, except SB. Above these concentrations it is observed that some of the biochars are lowering the percentage of sorption before, while some of them are lowering the percentage of sorption later on. However, CF and CA maintain very high values until reaching 100%. The distribution coefficient is linked with the sorption percentage, but it must be taken into account that this is a much more sensitive parameter, as small variations in the sorption cause large variations in the K_d . This behavior of K_d is more affected when there are situations with a lot or very little sorption. This is our situation, and for this reason we will focus on the K_d 's order of magnitude. This K_d shows values of approximately 10^3 or even $10^4\text{L}/\text{kg}$ for all materials up to 1 meq/L, except SB.

Material	Sorption			Desorption		
	Ci (meq/L)	Kd (L/kg)	%sorb	Ci des (meq/kg)	Kd des (L/kg)	%des
CM	0.06	1800	98.6	1.4	3500	0.7
	0.30	40000	99.4	7.1	4900	0.5
	1.00	49000	99.9	23	11000	0.2
	6.00	1200	97.9	139	21000	0.1
	10.0	120	83.1	192	26000	0.1
PC	0.06	860	97.2	1.4	2700	0.9
	0.30	5700	99.6	7.1	3800	0.7
	1.00	75000	100.0	23	4000	0.6
	6.00	180	87.7	128	29000	0.1
	10.0	30	55.2	145	28000	0.1
CE	0.06	1300	98.2	1.4	5100	0.5
	0.30	9200	99.7	7.2	2600	1.0
	1.00	6600	99.6	24	3700	0.7
	6.00	41	62.6	103	2700	1.0
	10.0	16	39.0	131	690	3.7
SB	0.06	130	83.8	1.2	1700	1.4
	0.30	5100	99.5	7.1	1600	1.5
	1.00	2000	98.8	23	1400	1.8
	6.00	5	15.3	52	460	5.5
	10.0	2	8.3	72	110	23.6
CF	0.06	1600	98.5	1.4	15000	0.2
	0.30	3000	99.2	7.1	7300	0.3
	1.00	20000	99.9	23	10000	0.2
	6.00	85000	100.0	139	27000	0.1
	10.0	85000	100.0	238	100000	0.0
CA	0.06	40000	99.9	1.4	130000	0.0
	0.30	40000	99.9	7.2	290000	0.0
	1.00	35000	99.9	23	95000	0.0
	6.00	83000	100.0	141	210000	0.0
	10.0	65000	100.0	236	347319	0.0

Table 2. Sorption and desorption parameters of Sm in the tested sorbents.

Above this concentration, the biochar takes his values in a low magnitude, that is, Kd below 10^3 L/Kg, while CA and CF continue to show very high values, reaching 10^5 L/Kg. So in conclusion, these results show that the biochars CE, CM and PC have very good sorption capacity until arriving at initial concentrations of 1meq/L while SB shows worse sorption. On the other hand both the CA and the CF present excellent sorption capacities at any concentration.

The fact that the biochar have lower values for these parameters when increasing the concentration is due to a saturation of the material that no longer accepts more Sm. A saturation of the material means that do not exist situations where Sm sorption can be given, because the sites with affinity towards the Sm are already occupied, so the Sm remains in solution without being incorporated into the material. This is not observed in CA and CF, so that means that the material is not saturated even if we reach initial concentrations of 10meq/L.

Finally, we observe a tendency in the biochar to increase the concentration in the sorption until reaching first of all a maximum. After that, the values decrease. This is not seen in CA and CF, or it is not that clear.

If we compare the results obtained within the only study found about Sm sorption in a biochar, we see that it has been done at C_i of 0.03meq/L and a pH <6, a sorption between 80 and 100% was obtained with K_d value near 25000.

If we study the reversibility of the process we see that CA, CF, CM and PC do not show almost reversibility because they have desorption percentages of below 1%. CE shows a little more reversibility of the sorption reaching a desorption percentage of 4%. SB shows the highest reversibility reaching 24% in the test made with the material that comes from the highest initial concentration of Sm in the sorption experiment. K_d des values are agree with sorption percentages, it shows high values of 10^3 , 10^4 or 10^5 , except for SB. All these results, except for those of SB, show very little reversibility of the process at any of the concentrations studied. These are satisfactory results.

6.3 SORPTION ISOTHERMS

Sorption isotherms are useful to show information about the characteristics of a sorbent as well as the processes that allows sorption^{6,12}. These isotherms have been produced from the data obtained through sorption experiments, where the initial Sm concentration has been increased for each experiment. The sorption isotherms show two types of situation, depending on the sorbent used. The biochars CE, CM, PC and SB show the isotherms from the Figure 10.

By doing a qualitative analysis looking at the shape of the graphic, this behavior seems to correspond to isotherms type L or H, showing a fast increase of C_{orb} until reaching high concentrations without increasing much C_{eq} . However, at high concentrations the slope decreases (K_d). Therefore, C_{orb} increases or a lot or none, but the C_{eq} increases

considerably, which means that there is a saturation of sorption sites in the sorbent. CE, PC and CM seem to have a similar shape to L. SB shows a different behaviour as C_{sorb} at the end goes in declination, suggesting that some sites of sorption are lost from the material that was not expected. This may be due to that at high initial concentrations of S_m , the pH decreases. This can allow the carbonates phases to solubilise. All this facts are in relation with the high values of DIC and DOC, that appear in Table 1.

Another important parameter that can be obtained from Figure 10 is the maximum C_{sorb} for each material. This parameter indicates the maximum capacity of S_m that the sorbent can incorporate. So, high C_{sorb} indicate more sites are available to retain the S_m in the sorbent and more S_m can retain before the saturation. Like the K_d and $\%_{\text{sorb}}$ the value of $C_{\text{sorb max}}$ also depends on the conditions of the experiment like pH, temperature, etc. The material with the most available sites to retain S_m with a $C_{\text{sorb max}}$ of 189meq/kg is CM, followed by PC with 129, CE with 93 and SB with 33 meq/kg.

That values obtained are really similar to the ones obtained for cation exchange capacity (CEC), that appear in the literature³. The CEC of CM is 245meq/kg. For PC is 137meq/kg, for CE is 95 meq/kg and for SB is 67 meq/kg. This facts indicates that the sites where S_m is sorbed are the same that the ones that are implicated to determine the CEC, which would be carboxylates or other negative sites available on the surface.

The K_d versus C_{sorb} graphic shows how the biochars reach a maximum of sorption and then go down when increasing the C_{sorb} . This situation is different from that expected with the L or H model, in which it would only have to see a drop of K_d when increasing C_{sorb} . This decrease of K_d at low concentrations indicates that there are competitive effects at low concentrations. These competitive effects might involve the sorbent and DOC in solution. When there are low initial concentrations of S_m , then small sorptions of S_m from the DOC involve an important percentage of S_m that remains in solution with DOC. However, with huge concentrations of S_m , the amount of DOC is the same and the amount of S_m sorbed by DOC is nearly nothing respecting the amount of total S_m . For this reason, as the initial concentration of S_m in each experiment increases, we can observe that these competitive effects in the sorption are becoming less important. In this situation, these effects are overcome and a maximum

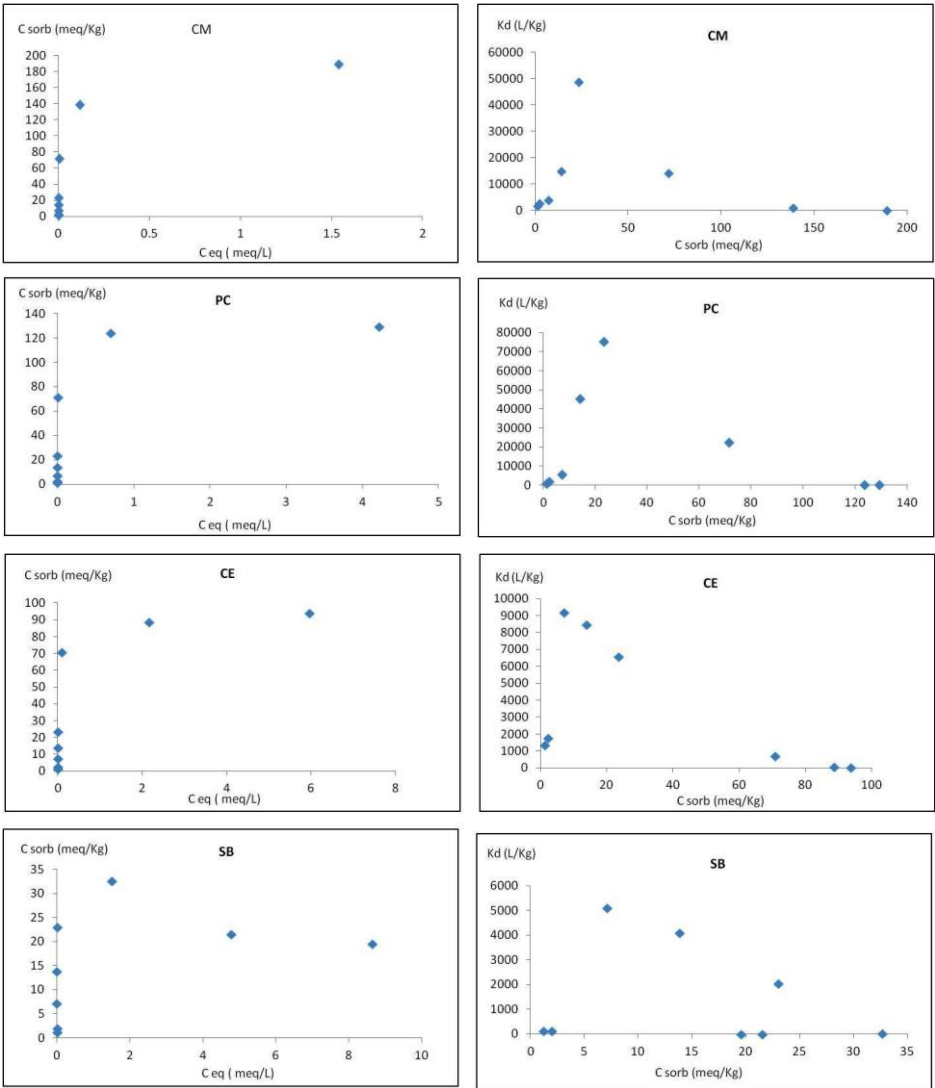


Figure 10. Sorption isotherms of biochars.

of sorption is reached. Finally, the K_d descend due to the saturation of the sorption sites as predicted by the L or H model.

On the other hand, the isotherms are shown by CA and CF in the Figure11.

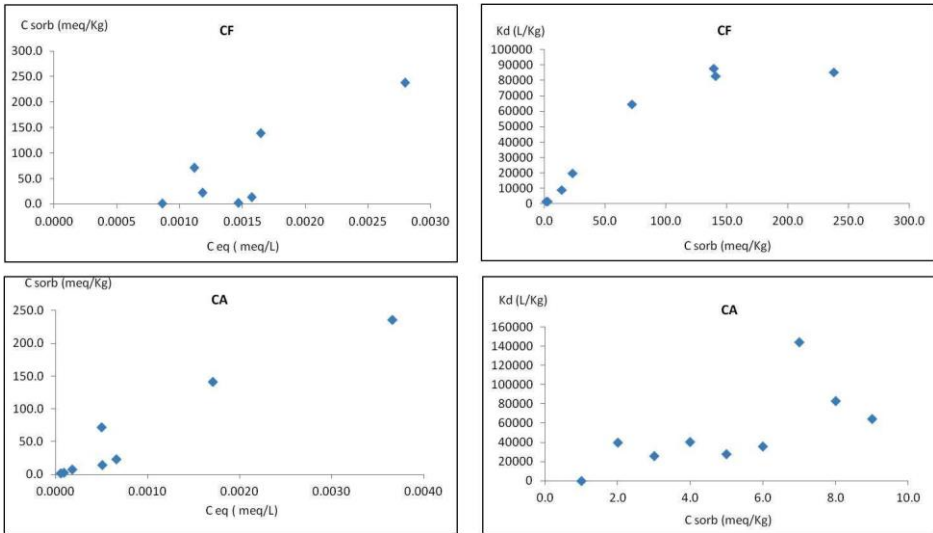


Figure 11. Sorption isotherms of CF and CA.

By doing a qualitative analysis of the shape of the graph C_{sorb} vs C_{eq} of CA, we can observe that it shows a form with a C type as it is shown a slope (that is the K_d) for all the studied concentrations. CF shows a similar behaviour to CA, although is different to one for the biochars. This fact suggest that different mechanisms seems to be involved in the sorption process of the biochars by one hand, and CA and CF by the other hand. However, it does not have to be forgotten that in its lower part, CF shows some points that are separate from linearity, which shows higher C_{eq} values than expected. This fact could be due to competitive effects at low initial concentrations of Sm. Also the linearity of the slope moves away from zero with disagreement to the C type isotherms. There is not observed any saturation of these sorbents at high concentrations.

If we look at the maximum C_{sorb} we see that the two materials show the largest values of all with 238meq/kg for CF and 236meq/kg for CA. This value obtained for CF is different to the one obtained for CEC that appears in the literature⁸. CEC of CF is 30meq/kg. This fact indicates that the sites where Sm is mostly sorbed are not the same sites implicated to determine the CEC, suggesting one more time that other mechanisms are involved in the sorption process of CF. The same type of shape for the CA and CF suggest that two materials follow the same sorption mechanism. Apart from that, CA and CF have not yet saturated, so these values of C_{sorb} max will be even bigger if we increase the initial concentration of Sm.

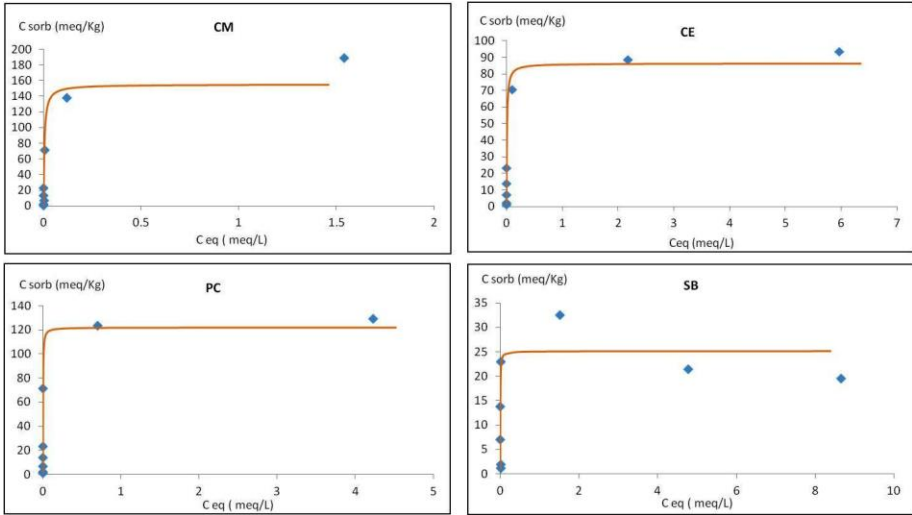
The plot involving K_d vs C_{sorb} in CA shows values of K_d from 10^4 for all the points except one. In CF, values are observed of 10^4 and although they are not seen the lowest are of 10^3 . As it was said before, low values of the sorption at low concentrations could be due to competitive effects with DOC. Despite this, K_d shows a great sorption during all the experiments made with these two materials that do not fall below 10^3 . It should not be forgotten that these values of K_d correspond to percentages of sorption higher than 97% and that K_d is very sensitive in conditions of high sorption, Although we see large variations of K_d , the sorption capacity does not change much in these cases.

6.4 FITTING OF THE ISOTHERMS TO MATHEMATICAL MODELS

Although there has been made a qualitative analysis of the isotherms, it is better to adjust them to mathematical models in order to be able to compare quantitatively the isotherms¹², to be able to predict for any C_{sorb} the C_{eq} that will be given, and to see the nature of the sorption sites.

As well, the isotherms of the biochars have been adjusted to two models, that are Langmuir and Freundlich. However, it has been seen that they adjust better to a Langmuir model. The isotherms and the Langmuir models are shown in Figure 12.

Looking at the shapes of the graphs, we can predict that the adjustment is good enough. The error parameter and the parameter R^2 indicate that there is a no good fit for all the biochars. High values error of K could be due to low reproducibility caused by competitive effects at low concentrations. Looking at this figure, the values of the Langmuir constant, that is K , which is associated with the bond energies, and therefore show the affinity between the S_m and the sorbent, we see that PC shows the highest affinity for S_m with K value of 500 kg/meq. It follows SB with 300, CM with 220 and CE with 130 kg/meq. The other important parameter is the maximum concentration of S_m sorbed on the surface of the sorbent, b , which shows that CM is the sorbent that retains the highest quantity of S_m , with a value of 155meq/kg, followed by PC with 121, CE with 86 and SB with 25meq/kg. The Langmuir models obtained for the different materials also allows predicting the behavior of the sorbent at other concentrations that are different from those studied. Finally, the fact that this process get well to a Langmuir isotherm suggest that there are high affinity sorption sites that are rather homogeneous¹² and that there is a finite number of this sorption sites.

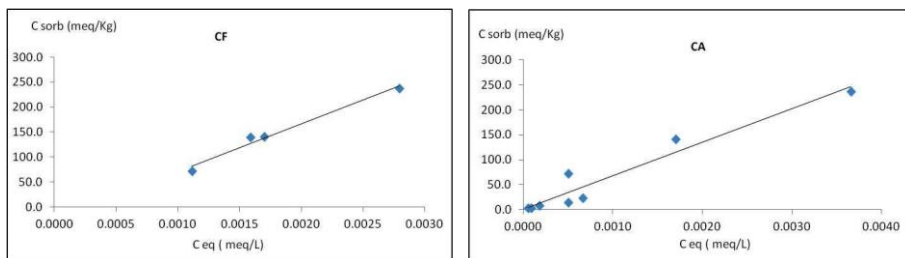


Parameter	CM	PC	CE	SB
b (meq/Kg)	160 (14)	120 (19)	86 (4)	25 (5)
K (L/meq)	230 (85)	500 (300)	130 (32)	300 (328)
R ²	0.88	0.67	0.96	0.36

Figure 12. Sm sorption isotherms of biochars fitting to Langmuir model and their parameters (+/- error).

The other materials fit better with a linear model. The Figure 13 shows the fit to the model.

As it is seen, CF show only the higher points which are the points that agree with the linear model, because the other points could be influenced by competitive effects. The adjustment is good for CA and CF. This model suggests a constant K_d and does not show saturation. Also it has been demonstrated that the line crosses through zero by regression analysis. The parameters of the equations allow us to predict strange situations within this concentration range.



Parameter	CF	CA
K _d (Kg/L)	83000 (3000)	67000 (7000)
R ²	0.99	0.94

Figure 13. Sm sorption isotherms of CF and CA fitting to linear model and their parameters (standard deviation).

6.5 SEQUENTIAL EXTRACTIONS

In order to obtain more information about the processes that occur during the sorption, there have been made some sequential desorptions, which are shown in Figure 14.

PC and CM shows little desorption and only significant for acetic acid extractant. The acetic acid extractions suggest that the protons occupy sites where the Sm was attached. These sites may be functional groups such as carboxylates which when pH decrease they are protonated and release Sm or may be other places with negative charges on the surface of the sorbent that are protonated or have electrostatic interaction and release Sm. We can see also little values of desorption, suggesting that Sm is bound to sites that are not affected by these extracts either because of their nature or because it is very strongly bound.

CE and SB, that are the biochars that became saturated at lower concentrations, clearly shows more desorption by increasing Sm concentration. This fact may be because the first places to be occupied are those with more affinity to the Sm, and the less affinity places will be occupied by increasing the concentration of Sm. The extraction with water caught the Sm bonded more weakly with the sorbent. Extraction with CaCl₂ could be attributed to cation exchange where Ca²⁺ displaces a little portion of Sm that has been sorbed.

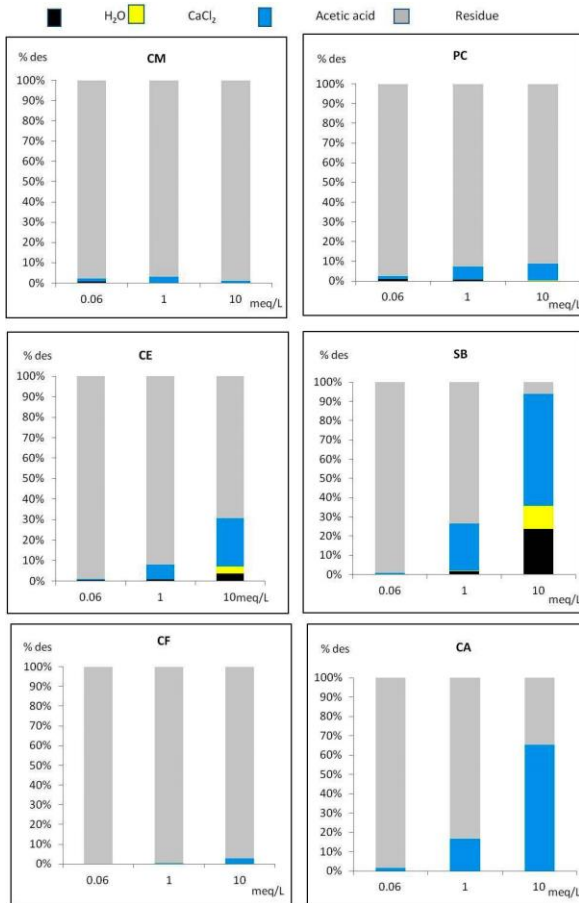


Figure 14. Fractionation of Sm sorbed in sorbent residues originated from sorption

tests with 0.06 meq/L, 1 meq/L and 10 meq/L of initial concentrations of Sm.

CF shows almost no desorption for any of the extractants in any of their concentrations. Only a little desorption is seen with acetic acid at 10 meq/L. This could indicate that the binding of the sorption sites with the Sm is strong or they are not affected by these extracts because of their nature. Although CA have excellent sorption in all the range studied, at acidic conditions it can be desorbed. That contrasts with the CF, that has no reversibility even at high concentrations.

6.6 EVALUATION OF THE MATERIALS AS SORBENTS OF LANTHANIDES

To evaluate the capacity of the materials studied as sorbents we will study it based on three characteristics, which are the sorption capacity, the degree of reversibility and the capacity to incorporate as much contamination as possible and compare them with the commercial material CA. These three parameters clearly indicate the capacity of the materials to act as sorbents, so they will be very important in the evaluation. The other studies have as objective to understand the processes that take place during the sorption. For a more visual comparison, these characteristics are summarized in Table 3.

Parameter	Ci (meq/L)	CM	PC	CE	SB	CF	CA
%sorb	0.06	98.6	97.2	98.2	83.8	98.5	99.9
	0.30	99.4	99.6	99.7	99.5	-	99.9
	1.00	99.9	100	99.6	98.8	99.9	99.9
	6.00	97.9	87.7	62.6	15.3	100	100
	10.0	83.1	55.2	39.0	8.3	100	100
% des	0.06	0.7	0.9	0.5	0.0	0.2	0.0
	0.30	0.5	0.7	1.0	1.5	-	0.0
	1.00	0.2	0.6	0.7	1.8	0.2	0.0
	6.00	0.1	0.1	1.0	5.5	0.1	0.0
	10.0	0.1	0.1	3.7	23.6	0.0	0.0
b (meq/Kg)	-	160 (14)	120 (19)	86 (4)	25 (5)	-	-

Table 3 Global evaluation of suitability of materials to remove lanthanides present in water. Green: high suitability; yellow: medium suitability; red: non suitable.

The commercial material, CA, is a good sorbent that shows excellent sorption throughout the concentration range studied without showing reversibility in the process. CA has not saturation, and moreover, it has a high capacity to incorporate the Sm in the sorbent.

Non-viable material as sorbent:

SB is the biochar with lower sorption capacity, at concentrations that are under 0.1 meq/L, the results indicate low sorption. As well as that, when the concentration is more than 1 meq/L, it happen the same situation. There is no reversibility in the range of concentrations where there are shown good sorption. When there is more than 1 meq/L, it saturates quickly, and it clearly shows less capacity to incorporate Sm into the material. SB has a small range of concentrations in where it shows a good sorption capacity.

Useful materials as sorbents:

The CM, PC and CE biochars have excellent values of sorption (>95%) for concentrations until 1meq/L without reversibility in the sorption process. They show saturation when reaching high concentrations because they have limited amount of available sites of sorption. They can also incorporate Sm into the sorbent. For that reason, these materials can be used as sorbents showing excellent results until concentrations of 1meq/L. CM has better results than the other biochars, reporting no saturation until 6meq/L and maximum sorbed concentration, b , of 155meq/kg.

CF is a good sorbent that also shows excellent sorption for all concentrations studied without showing reversibility in the process of sorption. Moreover, like CA it also does not show saturation, and what's more, it has a great capacity to incorporate the Sm in the sorbent with a value equal to the CA. Then, CF has the same capacity as a sorbent that has CA so it can be used as sorbent even with higher concentrations than 10meq/L. CF shows lower reversibility than CA when is exposed to acid condition.

7. CONCLUSIONS

At moderate concentrations of Sm, four of the five materials, CF, CM, PC and CE, showed near a 100% of sorption capacity for this element, as well as an extremely low reversibility (< 4%). SB reported good sorption only in a short range of concentrations and it is considered not useful as sorbent for lanthanides.

When talking about higher concentrations than 6 meq/L the biochars become saturated with Sm and a decrease of the sorption capacity is observed. CF shows an excellent sorption (> 98%) at all the concentrations studied also highly irreversible. For that reason this material is an excellent sorbent with a sorption capacity equivalent to that of the commercial activated charcoal studied.

The sorption isotherms of the biochars show that there exist some competitive effects at low concentrations of Sm due to the presence of dissolved organic matter. The sorption isotherms fit to the Langmuir model in the case of biochars. Besides, the value of the maximum sorbed concentration derived from the Langmuir model was very similar to the CEC value of the material. Thus the sites where Sm is sorbed seem to be the same that the ones that are implicated to determine the CEC, which would be carboxylates or other negative sites available on the surface. In contrast, CF fit a linear model with a sorbed Sm concentration much higher than the CEC, suggesting other mechanisms different from interaction with negatively charged sites.

Some characterization of the materials based on scanning electron microscopy or porosity determination might help in elucidating the mechanisms involved in the sorption process. To study the pH influence on sorption of Sm in the materials would be also interesting to complete this work, as well the study of the influence of the ionic strength.

The use of by-products like CF, CM, PC, CE can be an economical and environmentally friendly alternative to commercial sorbents currently used such as active charcoal for the remediation of contaminated water with samarium or other lanthanides. CF is a clear alternative because even at very high concentrations, reports the same sorption capacity than CA.

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