# SCREENING OF NATURAL MATERIALS FOR POLLUTANT REDUCTION OF METALS AND ORGANICS

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### Abstract

In this work, a screening using different natural materials has been carried out in order to show their efficiency in the removal of inorganic (mercury, chromium) and organic (the antibiotic flumequine) contaminants from aqueous solutions. Among the biomaterials tested, the ubiquitous bracken fern (Ptheridium aquilinum) shows a high efficiency either for mercury and chromium (about 100% of elimination from solution) or flumequine (60%).

## Introduction

Adsorption is a process that meets many of the criteria for removal of metals and other pollutants from water (M. Cox, 2006) and is cited by the EU as an example of a Best Available Technology (BAT). Activated carbon is one of the most well-known adsorbents employed but the high costs of either activated carbon, the most well-known adsorbent, or the synthetic ion-exchangers have led to investigation of materials of biological origin as potential low cost adsorbents/ion exchangers. This work reports some results about the ability of some biomaterials for sorbing metals (Hg, Cr) and organics (flumequine) following previous contributions of the research group "Fisicoquímica de Aguas Naturales" from the University of A Coruña, see for example: (Rey-Castro et al., 2003), (Lodeiro et al., 2006), (Carro et al., 2009)

## Materials and methods

All the adsorbent materials were collected in Galicia (NW Spain). They were washed with tap and deionised water and then they were oven dried at 60 °C for 24 h, crushed with an analytical mill, sieved (size fraction of 0.5-1 mm) and stored in polyethylene bottles until use. Removal studies were done placing 0.1 g of sorbent material with 40 mL of solution containing the pollutant. Suspension was stirred at room temperature in a rotary shaker (at 175 rpm). An aliquot of the supernatant solution was analysed in order to determine the pollutant removal after sorption took place. Chromium (VI) concentration was analysed by forming a complex with 1,5- diphenilcarbazide in acid solution. The complex was measured in a Cary 100 Bio UV-visible spectrophotometer. Mercury (II) concentration was then analysed by Michler`s thioketone method. Flumequine concentration was determined by HPLC coupled with mass spectrometry detection. In the case of chromium, pH of the solution was maintained at pH 1 by addition of NaOH or $HNO_3$ solutions as required. Mercury studies were done at a pH close to 5. For flumequine, pH was not controlled and experiments were done at natural pH.

## Results and discussion

In this study several materials were tested to determine their capacity for chromium reduction. As it can be seen in Figure 1 many materials present high metal reduction values. Brown alga *Sargassum muticum*, bracken fern, banana skin and vegetable *Carpobrotus edulis* remove 100% of chromium (VI) from the solution. Other materials such as orange peel, pine cone, pine leaf or vegetable *Ulex europaeus* have also high chromium reduction capacities. On the other hand, materials such as chitin or red alga *Chondrus crispus* show negligible reduction capacity.

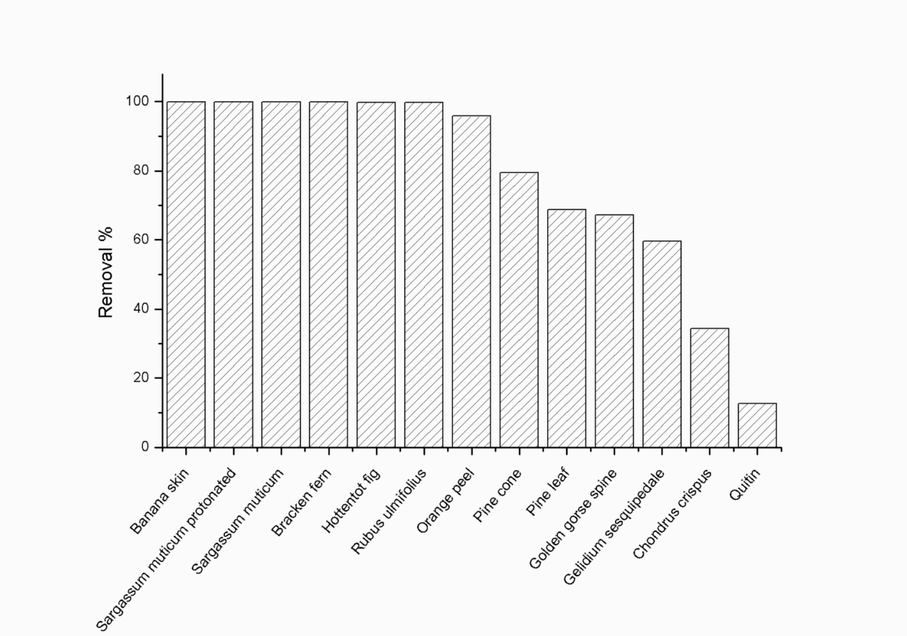


Figure 1.- *Screening of biomaterials (sorbent dose 2.5 g $L^{-1}$) for aqueous suspensions of chromium (VI) with an initial metal concentration of 1.92 mmol $L^{-1}$, pH = 1*

In the case of mercury, most of the materials present metal removal capacities higher than 80%, see Figure 2. It is remarkable the results obtained with brown algae, specially *Sargassum muticum* but many other material of vegetable origin show also very good results. Mercury sorption studies have been completed with some of these materials in order to determine equilibrium optimum conditions, biosorption kinetics and influences of different parameters in mercury elimination. Not only batch experiments were performed, but also continuous flow processes.

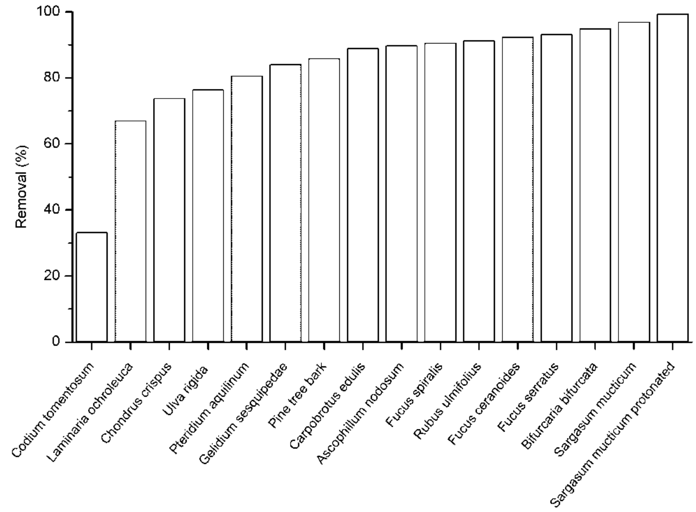


*Figure 2. Screening of mercury sorption onto different natural materials. Initial mercury concentration of 0.5 mmol/L. pH interval 4.5-5. Sorbent dose 2.5 g/L. Mercury removal values after 24 h of equilibrium.*

Figure 3 shows the results obtained for flumequine removal. In this case, a much lower initial concentration was used (50 µg/L). Many materials show an important removal percentage, surpassing 40%. Some of them have values above 60%. In the case of flumequine, the reproducibility of the sorption experiments is not very high; this is possibly due to the fact of the low concentrations used, which can introduce minor modifications in the experiments themselves, originating relative large variations in the removal percentages obtained.

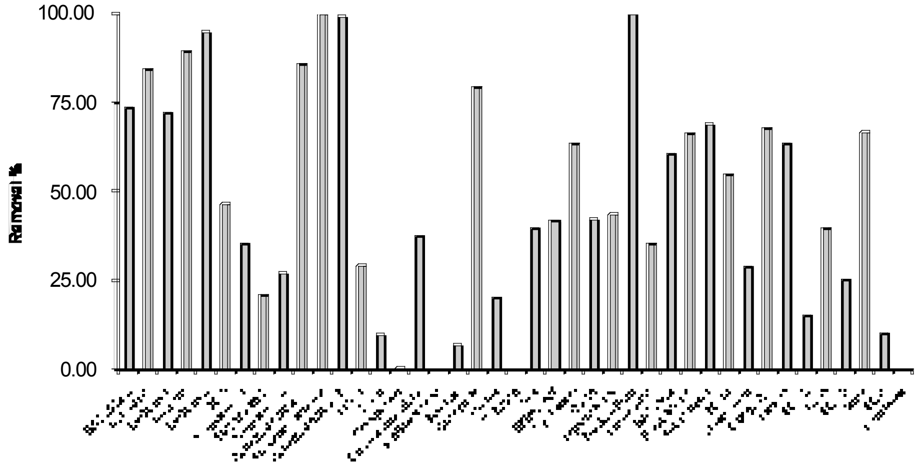


*Figure 3. Screening of flumequine sorption onto different natural materials. Initial flumequine concentration 50 µg/L. Sorbent dose 2.5 g/L. Natural pH.*

## Conclusions

From the results obtained it can be concluded that there are some sorbent biomaterials more specific for Hg or Cr while one of them (bracken fern) show an acceptable relatively high ability for removing either metals (Hg/Cr) or the organic compound flumequine. The behaviour observed in the screenings preformed is both related to the physico-chemical characteristics of the pollutant, but also to the biopolymeric nature of the sorbents used. In the case of algae the alginates contained in the wall cell structure are supposed to be responsible of the sequestration process, meanwhile the lignocellulosic structure of bracken fern is thought to determine its chemical behaviour towards pollutant removal.

## References

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